Topics in Flavour Research

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TOPICS IN FLAVOUR RESEARCH

PROCEEDINGS of the
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PREFACE

The international conference on TOPICS IN FLAVOUR RESEARCH took place in Freising-Weihenstephan,April 1-2,1985,in honour of one of the pioneers in this field,Prof.Dr.F.Drawert who,in these days,celebrated his 60th birthday.
Friedrich Drawert started his academic career in the group of nobel prize winner Richard Kuhn at Heidelberg,where he obtained his Ph.D. working on biochemical and physiological effects of cardiac active substances.In the early fifties he focused his interests on the biochemistry of plants and on the promising and quickly developing technique of gas chromatography - both together leading him directly to flavour research.When he took over the Department of Biochemistry and Physiology of the Federal Research Station for Viticulture at Geilweilerhof in 1958,he sucessfully applied the new chromatographic tools to investigate the complex flavours of grapes,wines ,and - later on - of a number of other fruits and beverages.
The developments of radio- and reaction gas chromatography enabled him to elucidate the structures of numerous flavour compounds and the metabolic pathways involved in their biosyntheses.Since 1968 he is the director of the Institute of Analytical Chemistry and Food Technology at the Technical University of Munich,where he continued to turn out a series of thought-provoking papers.Some topics within the broad scope of his research activities can be emphasized: Biogenesis of major and minor food constituents,enzymatic analysis and use of technical enzymes,recovery of proteins from waste materials,continuous fermentation process,use of microorganisms and plant tissues for aroma production,irradiation of food,removal of undesirable emissions,and,last not least,development of methods for detection and enrichment of sensori-

ally active trace compounds.
Friends,collegues and former collaborators of F.Drawert,well knowing that he would not enjoy long-winded anniversary addresses,had the idea to express their high esteem by organizing a symposium.
The contributions presented on this occasicn are collected in this book and cover the following main topics: Analytical techniques,chemical formation and technology,biogenesis,biotechnology and physiology.Scientists from both industrial and academic research were urged to select representative aspects of their own work to give with this book a synopsis about the different approaches and disciplines in modern flavour research.
The close connection between progress and development of instrumental techniques was stressed by the speakers of the first session (W.Jennings,N.Christoph,W.Postel) and the advantages of combined GC-HPLC (P.Sandra),GC-GC (S.Nitz),and GC-FTIR (L.Nykänen) were clearly demonstrated.Contributions on reaction-type flavours and technology-related aspects (R.Tressl,P.Schieberle,H.Nursten),fruit flavours (H.J.Bielig), off-flavours (H.Maarse),and chiral flavour compounds (R.Emberger,G.Heusinger) followed.
New modifications and variations of well known metabolic pathways were found to yield new flavour compounds in essential oil containing plants (L.Jaenicke,D.Lamparsky),fruit tissue slices (R.Berger),and plant cell cultures (C.Ambid). Biocatalysis (P.Schreier) and biotechnology (U.Faust) were the keywords in reviews on principal methods for the production of natural substances,leading over to papers on microbial biosyntheses (E.Sprecher),biotransformations (K.Kieslich),and the application of immobilized microorganisms (J.Crouzet) for the production of natural flavours.The symposium was closed with contributions on the physiology of odour perception (J.Boeckh) and on the effect of flavours on animal behaviour (R.Teranishi).

The papers of G.Reineccius on trapping and microwave desorption of headspace volatiles,of K.Knobloch on the essential oil of Ocimum basilicum,and of P.Williams on the origins of volatiles in wines and grapes were submitted in absentia.

The Editors wish to thank all who attended and participated in the conference,and especially the speakers for taking pains with their manuscripts.We are grateful to Dr.W.Pickenhagen for his help in last minute,and to Dr.R.Emberger,Prof. W.Jennings,Prof.H.Nursten,Dr.R.Teranishi,and Prof.R.Tressl for their active assistance before and during the conference. Special thanks are due to all members of our staff which acted inside and outside the lecture hall to create an atmosphere appropriate to the occasion of the meeting,and to the Technical University of Munich whose guests we were privileged to be.

We hope that the book will not only be informative,but - quite in the sense of F.Drawert - will stimulate thinking on many topics in flavour research which are still unresolved,bringing about new activity in this fascinating field of work.

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and Würzburg , June 1985

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ANALYTICAL TECHNIQUES

Developments in Analytical Gas Chromatography

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Summary

Gas chromatography has enjoyed a long enduring popularity, and market surveys (e.g. [1]) indicate that it still remains the world's most widely used analytical technique. Gas chromatography maintains this dominant position because it gives reliable results in a short time, it is generally convenient (i.e. reasonably good instruments are readily available and generally affordable), and probably most important, the technique has such immense powers of separation that untrained people can misuse even poorly designed equipment and still generate some useful data. Recent developments in this field offer the knowledgeable chromatographer many opportunities for improvement, but can serve as pitfalls to the unwary.

Introduction

Golay's invention of the open tubular column [2] , followed by that of Desty's machine for drawing glass capillary tubing [3] , encouraged a significant number of investigators to move from packed columns into the field of capillary chromatography. The majority of these were in academia and governmental laboratories, and were largely involved with research

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into gas chromatographic phenomena and development of the gas chromatographic process per se. Most of the applications performed by these researchers had as their primary purpose the demonstration of a point, such as improved separation of a difficult sample, or the increased inertness of this improved system. But the glass capillary column of that day was not only easily overloaded, but it was fragile and placed additional demands on the operator, not only in terms of chromatographic skills, but in the manual dexterity required for flame straightening column ends, and in column installation. It also exhibited considerable column-to-column variation, which resulted in unpredictable and usually unacceptable levels of activity. Some industrial use of these very labor-intensive columns did occur, largely in the petrochemical and fragrance areas, where analysts were primarily concerned with the separation of complex mixtures of relatively inert compounds. With the advent of the fused silica column [4] , the picture changed rapidly. These were strong and flexible, and analysts with no special skills could easily install them in almost any configuration; in addition, they were much more inert. However, they remained labor-intensive and were also materials-intensive: these higher quality columns were no longer do-it-yourself projects.

With the commercial availability of high quality columns, a larger percentage of industrial analysts became capillary chromatographers, but most of them continued to employ, then and now, packed columns. Because it operates at higher gas flow volumes, the packed column offers a "more forgiving system", and requires no instrumental modifications; it is often capable of producing the required results simply and quickly. Conventional capillary columns can tolerate only limited carrier gas flow volumes, and usually necessitate

minor changes to the inlet and detector; as a result, packed columns have retained their popularity with the average analyst. Another reason that many users continue with packed columns is based on the fact that most regulatory agencies (e.g. FDA, USDA, EPA) developed their analytical procedures during the infancy of capillaries; packed columns offered the advantages of being generally available and simple to use. This resulted in the analyst being locked into methods that specified packed columns, a serious limitation that is still the subject of much controversy.

But capillary chromatographers had learned to use these columns that usually ranged from 200 to 320 µm I.D., and which required the fitting of special inlets and the addition of make-up gas to detectors. Their strong, flexible, fused silica columns possessed high levels of inertness, and highly efficient columns containing a variety of cross-linked chemically bonded stationary phases became available.

Microcapillary Columns

A small segment of the dedicated capillary community has been re-exploring the advantages offered by micro capillary columns, i.e. columns of I.D. 150 µm and smaller (e.g. [5-7]). These can be employed either as longer columns delivering extremely high numbers of theoretical plates, or as shorter columns, producing "equivalent separation" in much shorter times. Figure 1 indicates that a 50 µm I.D. column would, under the conditions shown, exhibit an h_{min} of 0.05 mm, generating ca. 20,000 theoretical plates per meter of column length for a solute k = 5.0, with hydrogen carrier gas.

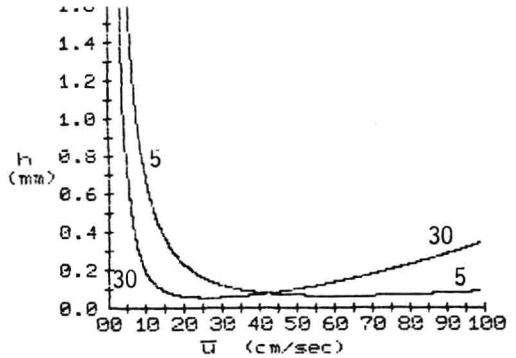

Figure 1. Computer generated van Deemter plots for 50 um diameter columns, in 5 and 30 m lengths; hydrogen carrier (D_M = 0.561 cm^2sec^{-1}); D_S taken as 1.5 x 10^{-6} cm^2sec^{-1}; d_f 0.2 um; k = 5.

In theory, thirty meters of such a column would generate 600,000 theoretical plates, and the analysis time for the solute k = 5 would be ca. 10.3 min at the optimum carrier gas velocity (μ_{opt}) of 29 cm/sec. The five meter length would generate ca. 100,000 theoretical plates, and at the optimum velocity of 71 cm/sec, the analysis time would drop to ca. seven sec, or 0.11 min.

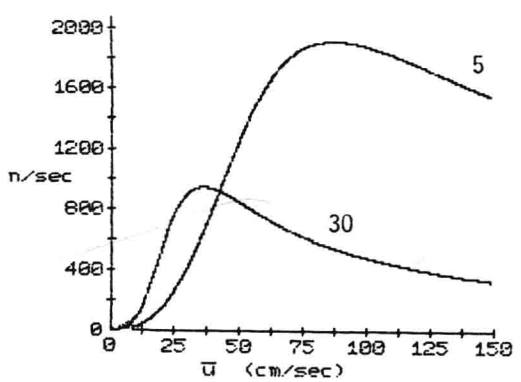

Figure 2. Optimum practical gas velocity curves generated for the two columns shown in Figure 1; all conditions as shown in Figure 1.