

Analysis of Volatiles

Methods · Applications

**Editor
Peter Schreier**



de Gruyter

Analysis of Volatiles

Methods and Applications

Proceedings

International Workshop

Würzburg, Federal Republic of Germany

September 28 – 30, 1983

Editor

Peter Schreier



Walter de Gruyter · Berlin · New York 1984

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D-8700 Würzburg
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CIP-Kurztitelaufnahme der Deutschen Bibliothek

Analysis of volatiles: methods and applications;
proceedings, Internat. workshop, Würzburg, Fed. Republic of Germany,
September 28 - 30, 1983 / ed. Peter Schreier. –
Berlin; New York: de Gruyter, 1984.
ISBN 3-11-009805-9
NE: Schreier, Peter [Hrsg.]

Library of Congress Cataloging in Publication Data

Main entry under title:
Analysis of volatiles.
Includes bibliographies and indexes.
1. Food--Analysis--Congresses. 2. Flavor--Congresses.
3. Food--Odor--Congresses. I. Schreier, Peter,
1942- . II. Title: Volatiles.
TX511.A53 1984 664'.07 84-1721
ISBN 3-11-009805-9

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PREFACE

The progress in the area of analysis of volatiles is closely related to the development of instrumental measurement techniques, and nowadays we are being inundated with new information about analytical techniques. Today's analyst must make many decisions that influence chromatographic and analytical results. He has to select the appropriate sample preparation, and with regard to the separation of volatiles - carried out generally by the most powerful process, gas chromatography - choices must be made as to length, diameter, stationary phase, film thickness of the column, selection of glass or fused silica etc. The analyst makes decisions concerning the separating parameters, and others relating to sample injection and detection that are essentially sample- and aim-dependent. Of course, the analyst can benefit from all new developments in the field of analysis of volatiles, but that requires exchange of information and experience, and basic understanding of the interrelationships involved.

Therefore, an International Workshop was held at the Chemistry Department of the University of Würzburg from September 28-30, 1983, to bring together analysts working in different fields of analysis of volatiles, e.g. in analytical, food, environmental, and biological chemistry, but who all use very similar chromatographic and analytical techniques. The possibilities and limits of different methods were discussed, and new trends and perspectives of various analytical and chromatographic techniques demonstrated. This book contains the lectures presented during the Workshop, covering the following main topics: sample preparation, analytical techniques, and applications.

Many individuals and authorities contributed to the success of the Workshop. In particular, the Editor is grateful to the members of his staff who acted as registrators, operators, technicians, and in many other functions, and who helped to create a friendly working atmosphere.

The Editor also thanks all contributors for their ready collaboration in the preparation of this book. Special thanks go to the Publisher's staff for their expert guidance given at all stages of publication, and to Mrs. S. Grimm for her secretarial assistance.

December 1983

P. Schreier
University of Würzburg
Food Chemistry

ACKNOWLEDGEMENTS

For economic support received to accomplish the workshop we want to express our gratitude to the following companies,

BRUKER GmbH, Karlsruhe
CARLO ERBA Instruments, Hofheim
CHROMPACK GmbH, Mülheim
DANI GmbH, Mainz
DIGILAB GmbH, München
FINNIGAN-MAT GmbH, München
FRITZ GmbH, Hofheim
ICT GmbH, Frankfurt
NICOLET GmbH, Offenbach
ORION Corp. (Seekamp GmbH), Achim
PERKIN-ELMER GmbH, Überlingen
SIEMENS AG, Karlsruhe
WGA Analysentechnik, Düsseldorf

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SAMPLE PREPARATION

PREREQUISITES FOR SAMPLE PREPARATION IN FLAVOUR ANALYSIS

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Introduction

In flavour analysis, the first step is to obtain, from the food of interest, a sufficient quantity of the volatiles in order to permit a meaningful analysis. Consequently, sample preparation is an important aspect in flavour analysis. Too often, emphasis is placed on the fractionation and identification steps, while selection of a representative sample and isolation of the volatile compounds from the food are not always stressed. The latter two aspects receive less attention, because fractionation and identification are more interesting, especially in view of the sophisticated instruments such as gas chromatograph, mass spectrometer and nuclear magnetic resonance spectrometer available to the researcher.

Several isolation techniques have been developed for volatiles representative of the true characteristic flavour of a food. The method used depends on the structure of the food, e.g. an oil, an aqueous solution, or a solid mass.

Distillation, extraction, adsorption and other procedures are frequently used for the isolation of flavour constituents from specific food materials. Because the method used to isolate the flavour compounds can have profound effects on the resultant "aromagram", our knowledge of flavour is influenced by the procedure used in sample preparation and isolation. Therefore, volatiles should be taken when the sample of inte-

rest is at its optimum flavour development. Recently, the important and critical aspects of sample preparation have been discussed briefly by Sugisawa (1), but improvement in sample selection and volatile isolation is still needed.

Sample Selection

Identification and quantitation of the volatiles that constitute the characteristic aroma of a particular food product, require that the product possesses the characteristic flavour and has no objectionable off-flavour.

1. Sample selection of fresh fruits and vegetables

Sample selection in the case of some fruits, vegetables or other plant products should be determined by the stage of maturation or ripeness, or by some other appropriate index. Problems arise when amounts of the material have to be processed and often the desired commodity is available only for a few days or weeks each year.

It is generally known that green odorous compounds such as C_6 aldehydes and C_6 alcohols are produced by enzymatic reaction, which catalyzes the oxidative splitting of linolenic acid and linoleic acid. This enzyme reaction usually proceeds fairly quickly and is complete within a few minutes in the presence of oxygen (2).

a) Enzymatic reactions. During the disintegration of green tea leaves, variable amounts of trans-2-hexenal and cis-3-hexenol are produced (Fig. 1). The level of these compounds reached a maximum in 3 min during disintegration of tea leaves (2).

Dirinck et al. (3) showed that the evaluation of strawberry flavour quality is possible by measuring the total amounts of

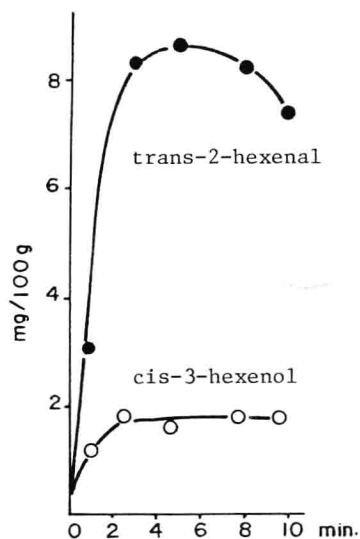


Fig. 1. Variation of C_6 compounds in homogenates of fresh tea leaves (2).

volatiles through specific analysis of sulfur compounds. They also found that the sulfur containing compounds such as dimethyl disulfide, methylthiol butyrate and methylthiol acetate are important constituents in strawberry flavour. During maceration of some varieties in a blender and sniffing the headspace, they detected a rotten odour, which after only a few minutes more resumed its fruity odor. The rotten odor is caused by methanethiol, formed enzymatically from the thiol esters during the maceration procedure of strawberries.

These studies demonstrated that the enzymatic reactions in the macerated fruits or vegetables are rapid and can lead to noticeable changes in flavour quality. Precautions such as working at low temperatures, in an inert gas atmosphere or in the absence of sunlight, may be required to avoid enzymatic reaction and other chemical oxidation during the sample preparation.

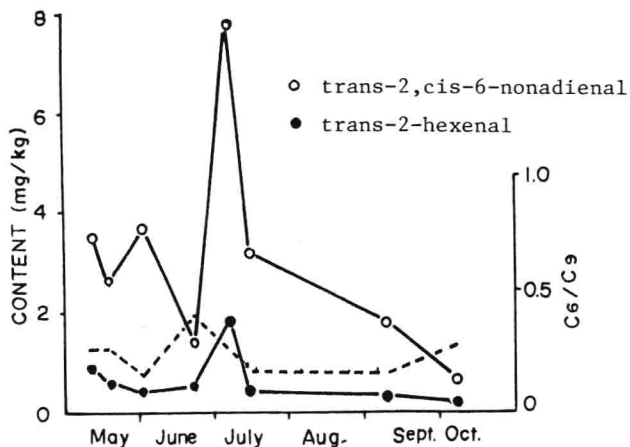


Fig. 2. Seasonal variation of a C₉ aldehyde and C₆ aldehyde in cucumber (2).

b) Seasonal variation. Hatanaka (2) reported on the seasonal changes of character impact flavours of fresh cucumber. The amounts of trans-2, cis-6-nonadienal and trans-2-hexenal reached a maximum between June and July, but little change was noted during the rest of year (Fig. 2).

Ripening fruits are in a dynamic metabolic state, and short term variation and wide fluctuation in the formation of individual volatiles are not uncommon.

Tressel and Jennings (4) investigated the changes in volatile compounds of ripening bananas kept at 25°C. They observed that acetate and butyrate ester formations were cyclical. The cycle observed for the acetates was apparently out of phase with that observed for the butyrates. Ethanol began to appear in the postclimacteric ripening phase and increased thereafter. These three compounds, acetates, butyrates and ethanol were relatively minor components in the period of maximum desirable flavour, but became major components 10-12 days later, a point where the banana was over-ripe with an undesirable flavour. Their result suggest that the most suitable period for desir-

able flavour may be lost after only a few days (3-4 days with bananas).

The changes of fresh green odorous compounds, C_6 and C_9 aldehydes, in the bananas kept at room temperature were investigated by Hatanaka (2). Green bananas contained large quantities of C_9 aldehyde (trans-2, cis-6-nonadienal), but the C_6 aldehyde (trans-2-hexenal) increased when the bananas turned yellow. These results agree with the volatiles from unpeeled banana reported by Tressl and Jennings (4).

The influence of maturity on the volatiles in Hamlin and Valencia orange peel was discussed by Lund and Dinsmore (5). A remarkable variation was observed in the amounts of C_6 compounds such as hexanol, hexenal and hexenal in the Hamlin orange (Fig. 3). Valencia orange peel aroma did not change as much and the amounts of the C_6 compounds were also much lower.

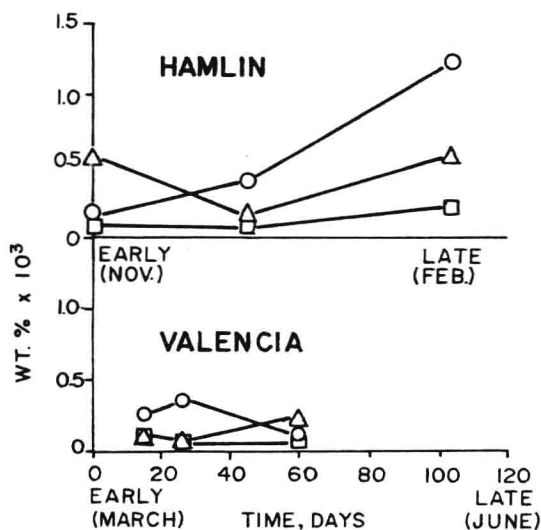


Fig. 3. Seasonal variation in the concentrations of cis-3-hexen-1-ol (O), 1-hexanol (Δ), n-hexanal (□) in orange peel aroma (5). Copyright by Academic Press, Inc. (1978).

Another interesting observation was the variation of acetaldehyde in the juice. Acetaldehyde increased significantly in juice held at room temperature for 4 hrs, but not in juice that was pasteurized or kept at low temperature (4°C) (5).

2. Sample selection in processed foods

Sample selection in processed foods that have been boiled, roasted, fried, or baked, becomes very difficult, especially if uniformity is to be realized. Some information on the sample before process is desirable.

a) Complexity of samples. The volatiles in eggs and egg products as well as the influence of storage, feed source, and extraneous odors on these volatiles have been presented by Maga (6). Generally, feed and other feed additives have been thought to be the cause for off-flavours, but off-flavours were not found in all of the eggs. These kinds of results make sample selection all the more confusing and difficult.

The off-flavour described as fishy egg is caused by trimethylamine precursors in feeds made from fish meal, rapeseed meal and other soybean gums. With feeding herring meal, it was found that 2-7% of the resulting eggs smelled "fishy" and 17% had a "crabby" odor. Analysis of the off-flavoured eggs showed levels of trimethylamine greater than 10 times of that in normal eggs. Feed contaminated with wood chip or sawdust resulted in off-flavoured eggs that contained anisoles and other phenolic compounds (6).

b) Influence of roasting time. Many products such as peanuts, almonds, coffee, and cocoa are roasted to achieve flavour changes acceptable for the products. A knowledge of the effect of roasting on the sensory attributes would therefore not only be desirable, but also necessary if quality control and flavour acceptance are to be maintained.