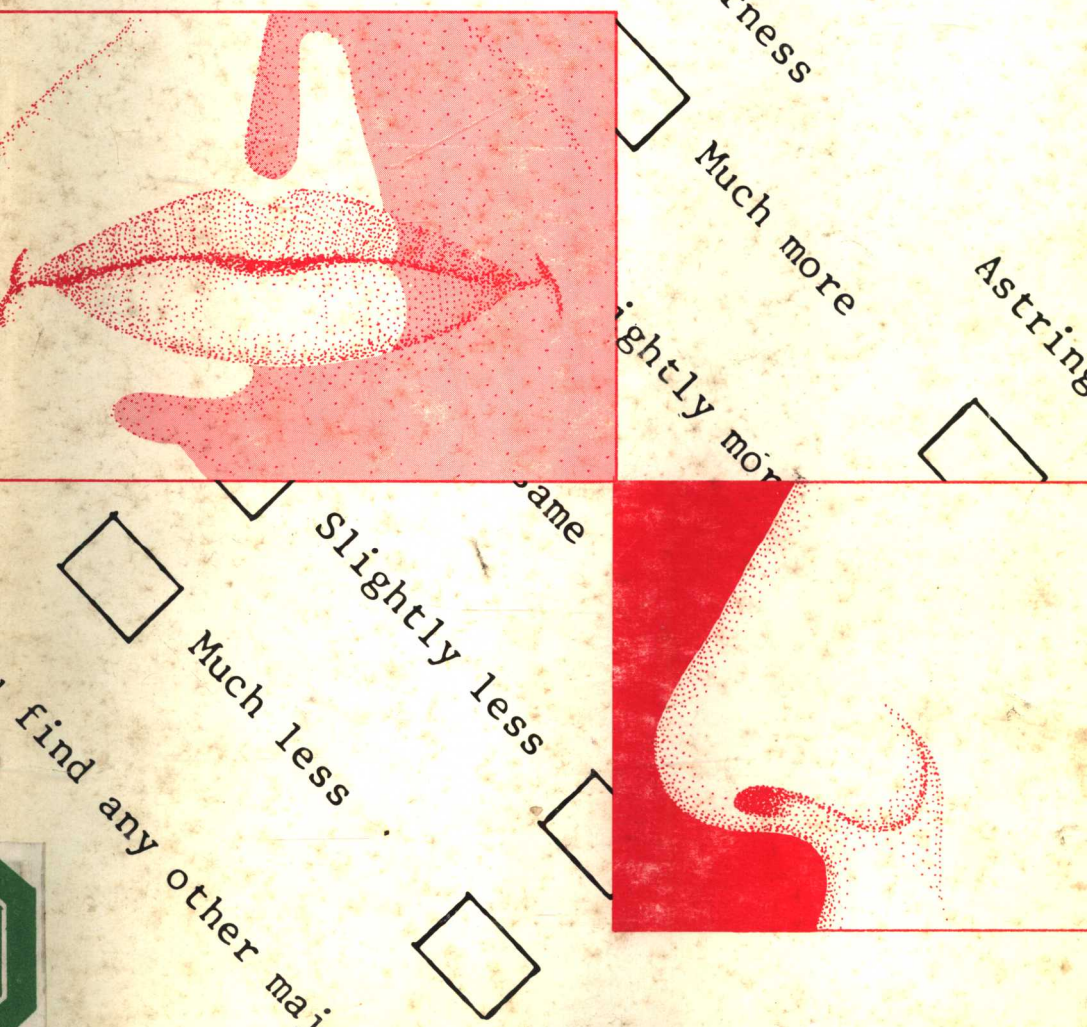
Flavor Quality: Objective Measurement

Richard A. Scanlan



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Robert F. Gould, *Editor*

FOREWORD

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the SERIES parallels that of its predecessor, ADVANCES IN CHEMISTRY SERIES, except that in order to save time the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. As a further means of saving time, the papers are not edited or reviewed except by the symposium chairman, who becomes editor of the book. Papers published in the ACS SYMPOSIUM SERIES are original contributions not published elsewhere in whole or major part and include reports of research as well as reviews since symposia may embrace both types of presentation.

PREFACE

Over the past 15 years we have witnessed remarkable advancements in areas relating to objective measurement of flavor quality. A look at several of the analytical techniques used today in flavor research provides examples of this. The common use of glass capillary gas chromatographic columns and high pressure liquid chromatographic systems allows separation of labile compounds which were virtually impossible to separate several years ago. Improvements in vacuum systems and in carrier gas separators has made gas chromatographic–mass spectrometric analysis much more efficient. Use of computers with mass spectrometers and other instruments has increased our ability to make correct structural assignments.

These advances have been extremely helpful, and undoubtedly we could also point to similar advances in sensory evaluation, in statistical applications, and in other areas relating to measurement of flavor quality. Perhaps at this point we should remind ourselves that flavor is the sensation perceived when one takes food or beverage into the mouth. Ultimately it is this sensation which we attempt to define and measure, and we usually try to do so by measuring those things in the food which effect, or are responsible for, the flavor sensation. How successful are we? What type of problems do we encounter, and what type of research will be necessary to solve these problems? The papers in this symposium on objective measurement of flavor quality provide information helpful to the solution of these questions.

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Flavor Quality: Objective Measurement

A symposium sponsored by the Division of Agricultural and Food Chemistry of the American Chemical Society

During the past 15 years, many advancements have been made in the area of objective measurement of flavor quality. Sophisticated chromatographic systems, computers with mass spectroscopy, and other instruments have made possible many compound separations and flavor–structure correlations that were impossible several years ago. Advances have also been made in the techniques of sensory evaluation and statistical applications.

These recent improvements in techniques and instrumentation are discussed in eight chapters covering general approaches; odor intensities and vapor pressures; flavor chemical mixtures; structural and mechanical indicators; and objective flavor quality of green beans, apples and ciders, beer, and processed orange juice.

TITLES COMING

Bioinorganic Chemistry—II

Cellulose and Fiber Science Developments

Chemometrics: Theory and Applications

Coordination Chemistry—II

Evaporation–Combustion of Fuels

Paper Preservation

Solid State Chemistry of Energy Conversion and Storage

Sulfur Utilization

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Objective Measurements of Flavor Quality: General Approaches, Problems, Pitfalls, and Accomplishments

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After I had accepted the invitation to prepare an opening paper for this series, I was filled with a sense of foreboding, and for very good reasons. First, I can think of a number of individuals who beyond any doubt are better qualified to discuss this multi-disciplinary area than I am, and second, the title itself is enough to flash a warning light. While the complexity of this attribute we call "flavor" has been stressed by several workers (e.g. 1), Moncrief (2) argued that taste and odor are the major components. Certainly it is generally agreed that flavor requires the participation of sensory receptors, which makes it an individual, and at least within certain limits, a variable characteristic. Because of this, flavor is necessarily a highly subjective trait. Rereading my title, I find that I'm committed to discussing objective measurements of a subjective characteristic and my first thought is, "I'm in trouble." But as long as we recognize this contradiction and are willing to accept a degree of compromise, hopefully we can make some progress.

An early quest for an objective measurement of quality has been cited from the 13th and 14th centuries, when "ale conners" or "ale tasters" in England were assigned the task of setting the price on batches of brew based on their individual flavor judgments. In an effort to achieve a greater degree of objectivity, this was combined with a test of the ale strength: some of the ale was poured on a bench, and the ale conner sat in it. After a predetermined interval, "he made to stand up"; if his leather breeches stuck to the bench, the ale was of the right quality (3).

To most of us, an "objective measurement of flavor quality" means establishing a chemical or physical method for measuring the amount of a substance responsible for a particular flavor attribute. This requires first establishing which compound or compounds are responsible for a particular attribute, which has been done in relatively few instances, at least in complex mixtures. The problem is further complicated by the fact that synergism and antagonism can exist between compounds that elicit flavor responses. In many cases, flavor is due to an integrated

response to at least several compounds, and as we change the relative ratios and/or absolute amounts of these compounds, the flavor responses change in a manner that is usually unpredictable. Moskowitz (4) argued that the activities of the flavor chemist, who is usually concerned with establishing the contribution of individual components to flavor, diverge from but are complementary to psychometric efforts concerned with the quality of flavor mixtures.

Two general approaches have been utilized in attempts to obtain objective measurements of flavor quality. One has been concerned with the measurement or recording of the minute electrical response of olfactory or taste cells elicited by odor or taste stimuli (e.g. 5, 6), but a great deal of work remains to be done in this area. Another widely used approach has involved sniffing the outlet of a gas chromatograph (e.g. 7). Certain problems are immediately obvious: flavor is an integrated response to a mixture of compounds, and the gas chromatograph provides a differential rather than an integrated response to those compounds. Secondly, it can be most disturbing when the panel reports that interesting odors exist between the peaks (e.g. 8, 9) which emphasizes the fact that for some substances, the gas chromatograph has not yet matched the sensitivity of the human nose.

Even so, useful results can be obtained by this route. Barylko-Pikielna et al. (10) split the effluent from a gas chromatographic column to assign qualitative odor assessments to the individual peaks of a sugar-amino acid reaction mixture. McLeod and Coppock (11) used a similar technique to assign odor evaluations to fractions from boiling beef. A number of workers interested in correlating their analytical results with sensory response have also used the odors of individual peaks, sometimes to good advantage (vide infra).

Tucknott and Williams (12) pointed out that sniffing the effluent from a gas chromatograph suffers from a number of other shortcomings, and suggested that the effluent gas containing peaks of interest be trapped in individual disposable syringes for subsequent odor assessment. Clark and Cronin (13) utilized a novel method; peaks were trapped in short sections of support coated open tubular (SCOT) glass columns, which were then crushed under water to produce a solution for sensory analysis. Parliment (14) bubbled the gas chromatographic effluent into water to prepare solutions for taste-testing, which he reported was in some cases more satisfactory than sniff-testing.

When we resort to gas chromatography, we have of course restricted our objective measurements to volatile compounds; it is all too easy to forget that taste is also a major contributor to flavor (1). Weiss and Schaller (15, 16) studied the influence of several variables--e.g. titratable acidity, pH, dissolved gases--on the sensory properties of apple juice; a number of such studies

on other products have been published. Recently, Noble (17) used gel chromatography to fractionate flavor components of tomato.

Another major problem is obtaining gas chromatographic results that reflect with high qualitative and quantitative fidelity the volatile composition of the material in question. Compositional changes are frequently caused in the preparation of a sample suitable for gas chromatography, and additional errors may be introduced by the gas chromatographic analysis itself.

Many materials require some type of treatment to free the compounds of interest from materials that would otherwise interfere with the analysis (e.g. water and non-volatile components) before the sample can be injected into the gas chromatograph. Also, some type of concentration is frequently required so that the limited amount of sample that can be injected contains detectable quantities of the compounds to be studied. Most of the procedures that are used to achieve these ends involve distillation, extraction and/or evaporation, or adsorption, all of which cause quantitative changes and some of which may engender qualitative changes in the concentrated sample, so that it no longer reflects the composition of the starting material. In efforts to surmount these difficulties, many investigators prefer to use direct injections of headspace gas for analysis, but the chromatogram is then restricted to those components whose partial pressures are relatively high. A great deal of attention has been given to the use of porous polymers in concentrating headspace volatiles by less strenuous means (e.g. 18, 19, 20). Sample preparation remains a critically important area, and forms the subject of another symposium at this meeting.

Another source of problems lies in the gas chromatographic analysis itself; not all compounds are stable to the conditions of the analysis, and the chromatogram may not accurately reflect the composition of the material injected. Additionally, minor components that are not well resolved from larger constituents may be of critical importance to a given flavor attribute, but unless these are unambiguously separated from the other components, we are frequently not even aware of their existence in the sample. Recent developments in wall-coated open tubular glass capillary columns (WCOT: 21, 22, 23) make it possible to resolve many of these previously poorly separated components. Additionally, the more inert character of the glass columns has permitted analysis of some constituents (notably sulfur-containing compounds) that are almost surely of great importance to some flavors and which have resisted packed-column or metal-capillary analysis (e.g. 24, 25, 26). Glass inlet splitters of much higher linearity (27, 28), when combined with the open tubular glass capillary column, are capable of producing chromatograms that reflect much more accurately the composition of the injected sample.

Unfortunately, column efficiency--i.e. the inherent power to separate the components of a mixture--is inversely proportional to column capacity. The maximum theoretical efficiency of WCOT columns, expressed in theoretical plates per meter, is approximately 1000/r, where r is the inner column radius in mm (29). A compromise is also usually necessary in the thickness of the film of liquid phase, as columns with thinner films have higher efficiencies but impose severe limitations on sample capacity, and columns with thicker films possess higher capacities at the expense of column efficiency (e.g. 29, 30). While the lower capacities of small diameter (e.g. 0.25 mm) WCOT columns are still sufficient for applications such as gas chromatography-mass spectrometry, their use for the sensory analysis of individual fractions poses very difficult problems. Some investigators have compromised on larger diameter WCOT columns (e.g. 31, 32), or columns whose roughened or extended inner surfaces (PLOT or SCOT columns) increase the surface area of the liquid phase (e.g. 33, 34). Because of this capacity requirement, there remains a use and a need for packed columns. It is, however, critically important to duplicate the analysis on a high resolution system, so the investigator is not misled by peaks that may play a crucial role in the sensory qualities and that are not well resolved on the lower resolution high capacity system. The investigator must also frequently compromise in selecting gas chromatographic parameters, balancing the degree of separation desired against the length of time required for the analysis, and, for thermally labile materials, the amount of heat to which the samples are exposed (35). Attention must also be given to the suitability of the system for the separation of the components of a given mixture.

Once the problems of sample preparation and sample analysis are overcome, one has at best a well-resolved chromatogram, without overlapping or co-chromatographing components, which may qualitatively and quantitatively reflect the composition of the original material. It cannot be overemphasized that even this is rarely achieved. Still to be reckoned with are the myriad problems and sources of error inherent in the sensory testing procedures. Most of us would now agree that it is not sufficient for the chemist, untrained in sensory analysis, to casually sniff the outlet of his gas chromatograph and record his impressions. Sensory analysis, too, has come a long way, and a meaningful study should use selected panels of trained personnel utilizing quantitative procedures amenable to statistical evaluation. Martin (36) described procedures used in the selection and training of panelists for various types of sensory evaluations. Larmond (37) emphasized the importance of controlling physical stimuli to which the panelists are subjected. Best (38) described the analysis of taste-test data, and Harries (39) reviewed the complexities of sensory assessment. Stone et al.

(40) described a sensory evaluation technique termed "quantitative descriptive analysis" which uses an interval scale and a panel of at least six trained panelists, and Moskowitz (41) has argued for a method he terms "magnitude estimation", in which numbers are assigned to stimuli so that the ratios of judgments reflect sensory ratios.

Taking all of these factors into account--changes engendered by sample preparation; poor separation, artifacts and errors in the gas chromatographic analysis; sins of omission and sins of commission in the sensory analysis--the investigator may finally be in a position to try and relate variations in the sensory properties to variations in the chromatographic pattern. Here again, however, results can be over-interpreted. Szczesniak (42) and Persson et al. (43, 44) both emphasize that even a significant correlation between a physical measurement and a sensory rating establishes only a predictive relationship, not a causal one.

Two general approaches, which are not necessarily mutually exclusive, have been used in attempts to correlate the analytical data with sensory attributes. One has involved attempts to establish the qualitative and/or quantitative flavor properties of individual compounds, sometimes with attention to the synergism or antagonism that they exhibit in mixtures with other compounds, or in one solvent as opposed to another. Meilgaard (45, 46) and Clapperton et al. (47) have accumulated a large amount of information on the flavor characterisitics and threshold values of aroma volatiles in beer. As emphasized by these workers, the odor purity of the compounds tested is critically important to this type of study. They point out, as one example, that Murahashi (48) reported 1-octen-3-ol as possessing a mushroom aroma, while Hoffmann (49) ascribed the odor to 1,3-dioxalans formed on decomposition of the alcohol. Later Meilgaard (46) found that the odor in question was due to contamination by 1-octen-3-one, which had a metallic aroma in fat solutions, and a mushroom aroma in aqueous medium; the purified alcohol had an odor he reported as "spicy, perfumed and grass-like." Similarly, Boelens et al. (50), who identified a large number of compounds in onion oil, suggested that 2,4-dimethylthiophene and 3,4-dimenthythiophene possessed an odor of fried onions. Recently, Galetto and Hoffman (51) synthesized these compounds, and reported that alone or in combination with other compounds they did not make a significant contribution to the fried onion aroma.

The other major approach has involved attempts to correlate flavor with gas chromatographic patterns. Guadagni et al. worked on such correlations for apple (7); these and other efforts have been reviewed by Powers (52), ASTM (53, 54) and von Sydow (55); additional efforts include those of Salo et al. (56) and Salo (57).

Bednarczyk and Kramer (58) reported that four gas chromatographic peaks accounted for 85% of a sensory panel's flavor response to ginger essential oil. Cited as prime contributors to the characteristic ginger attribute were β-sesquiphellandrene and ar-curcumene; α terpineol and citrals contributed a lemony attribute, and an undesirable woody or soapy note was caused by nerolidol.

Using linear regression analysis, Fore et al. (59) found a high correlation between the flavor score of stored peanut butter and the ratio between 2-methyl propanal and hexanal as determined gas chromatographically. Dravnieks et al. (60) used stepwise discriminate analysis to classify, by gas chromatographic techniques, the odor of corn. Galetto and Bednarczyk (61) used multiple regression techniques in establishing that the amount of methyl propyl disulfide, methyl propyl trisulfide and dipropyl trisulfide as determined gas chromatographically showed a high degree of correlation with overall onion flavor. Tassan and Russell (62) used a micro olfactometer to evaluate the odors of individual cumin constituents trapped from a gas chromatograph, and reported that variations in four aldehydes influenced the main odor character; 3-p-menthen-7-al was shown to be necessary for the characteristic odor of heated cumin.

Karlsson-Ekström and von Sydow (63) using a psychophysical-statistical approach, found that the sensory changes that occur when black currants are heated could be well correlated with a decrease in monoterpene hydrocarbons and an increase in dimethyl sulfide and aliphatic aldehydes.

Persson and von Sydow (64) examined the sum, differences, ratios, geometric means and vectorial sums of peaks from gas chromatographic analyses for their correlation with flavor scores of frozen and refrigerated cooked sliced beef. A number of different models involving both sensory response and gas chromatographic data exhibited high coefficients of correlation. Studies on canned beef (43) established that a high degree of correlation existed between 15 odor properties and four gas chromatographic peak combinations. In later work the methods were extended to a variety of meat products and found to hold true (44).

Åkesson et al. (65) used headspace sampling techniques and open tubular gas chromatography combined with a flavor profile technique to see if sensory properties and preference values for a variety of food materials could be predicted by gas chromatographic data. Testing a large number of models that used gas chromatographic peak areas in various combinations and in several types of functions, they found that the assessment of sensory qualities was related monotonicly to gas chromatographic data, while estimated preference values were in most cases related in a more complex non-mototonic way. Using the proper models, very accurate predictions could be made. Von Sydow (66)

generalized that all compounds present above threshold levels contribute to the aroma of foods, and that the number of important aroma contributors is variable, but is usually high in thermally processed foods or foods of animal origin. He emphasized that the instrumental technique must be gentle, so that the sample investigated represents the true situation in the food, and that the sensory technique must be detailed and sensitive. The development of numerical and psychophysical models capable of relating the physicochemical data with the sensory data is crucial.

It would appear that we may finally have arrived at a point where we have the opportunity to combine improved methods of sample preparation, gas chromatographic separation, sensory analysis and computerized data analysis to achieve some realistic results in the search for objective measurements of flavor quality in at least some products. Success in these efforts will depend to a large degree on how well we combine advances in sample preparation with high resolution gas chromatography, valid sensory procedures and advanced methods of data analysis. This requires judgments and evaluations on the part of the investigator. No single sample preparation procedure can be accepted as uniformly satisfactory; one or another may be superior depending on the sample composition and the compounds of interest. Gas chromatographic parameters must be selected carefully, with attention to the sample composition, its stability under the conditions of analysis and whether one's immediate goal is resolution or capacity. Neither are all procedures for sensory or data analysis--including those cited in this paper--equally valid under all circumstances, nor are all of them acceptable to experts in this field (e.g. 40, 41, 58). And no degree of sophisticated computer analysis can compensate for careless sensory procedures, or for an incompletely resolved chromatogram in which peaks of sensory importance have failed to separate. But we do now have increased capability in all of these areas, and the next few years should see some exciting results.

I would like to conclude by thanking several close friends, especially Erik von Sydow, Morten Meilgaard, Rose Marie Pangborn and Gerry Russell for their help in preparing this information. There are of course many other investigations which could and perhaps should have been included in this presentation. I can only apologize for such omissions, but in a very short time the data I have presented will be largely obsolete, as the papers that follow this brief introduction extend our efforts and knowledge in this very important area.

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