The Significance and Use of Trace Components in Flavors

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Flavor creativity has been the most significant part of my professional career. From the very beginning and through the many years of my becoming an experienced flavorist I have found it difficult to discuss the subjective intricacies of a flavorist's theme, the underlying or essential artistic representation, which is factual in practice yet nebulous and indefinite in expression and considered by the layperson as mystical.

Personal zeal and patience over many years of training and practice are primary and indispensable to a flavorist's fulfillment and acquisition of a vast knowledge of scientific and artistic materials.

Fifty or sixty years ago there weren't more than 75-100 chemicals that were satisfactory for flavor compositions. There was a much wider range of natural products, resins, solids and liquid extracts, and essential oils. The problem, therefore, in creating flavors can only be appreciated when we consider today's immense number of materials available to the flavorist.

It is interesting to reflect upon the composition of old type flavors in which the ingredients were used in bold, and by today's standards, random quantities. In contrast to perfumery, flavor creations at that time lacked refinement, harmony, subtlety—all traits of artistic work. Whereas the creation of an exclusive and luxurious perfume was the perfumer's supreme artistry, the creation of a flavor was skeletal, unrefined and significantly governed by commercial rewards without any thoughts of artistry. G. N. Revie, a flavorist with Fries & Fries in England, said in a recent speech "The most popular hard-boiled sweets in the early 1900s were pear drops in which the flavor was amyl acetate." I am sure that all we flavorists today have seen old flavor formulations in our companies' archives in which only two and perhaps three chemicals constituted the basic ingredients. The need for more satisfactory flavors became rather obvious.

The innate desire to know, the curiosity to discover together with the ambition to simulate nature have all contributed to the designing and manufacturing of highly sophisticated instruments that have enabled us to delve into nature's recesses. Flavor creativity has been strongly supported within the last 25-30 years by the advent of such instruments and by the resultant teamwork of the research and flavor chemists. Research chemists have done sensational work in this area by making available to the flavorist a vast number of synthetics.

The flavorist in attempting to simulate nature continually seeks to blend the diversified tastes

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into one balanced and single rendition. Yet, in so doing he or she also has the sacrilegious effrontery of wanting to improve upon nature by adding ingredients other than those already identified. I've asked myself often if this was really effrontery or was it the manifestation of a despondent attitude for not being able to identify all the "small ingredients," the trace components. Nature seems to delight in combining basic and obvious ingredients that we find common to all products, and then intentionally adding in a discriminate fashion very small quantities of other ingredients, contributing to the individual characteristics and identity of the vast panorama of creations with which we are familiar.

Only too recently, as I mentioned earlier, have we delved into and realized the complexities and learned the value of the trace items that now enable us to convert basic formulations into many different and characteristic flavors. The artistry that goes into formulating a flavor today depends largely upon the research chemist's techniques in identifying the trace element and upon the skill of the flavorist in using those minute quantities that contribute to the uniqueness of a flavor!

I am sure that all we flavorists, at one time or other, have gone through the simple exercise of formulating a flavor by using the exact quantitations of ingredients as found through instrumental research. I am also sure that we have all experienced the fact that the exclusive reliance upon such findings does not necessarily recreate the original flavor rendition. This becomes very frustrating and disillusioning. Flavorists then resort to their artistic talents to make up for the lack of accurate identification of trace ingredients using their own trace elements.

A trace element by definition is anything that is barely perceivable; it's a minute quantity, it's a constituent that is present in quantities less than a standard limit, micrograms or milligrams that cannot be measured easily by scientists and that elude the most zealous researcher. Arbitrarily, we may set the values of trace components as those present in a complex mixture of active ingredients at not more than 1%.

One single trace element may not necessarily contribute to the character, or to the uniqueness of a flavor; the harmonious contribution of several trace elements with their aroma impacts give a flavor its individual personality, its very character.

The pursuit of isolating and then identifying trace components by mass spectrometry and other complex instruments seemingly makes the cost of research prohibitive beyond all commercial value and perhaps practicality. Most often trace elements are artifacts that tend to mislead the flavorist. How far should we conduct our meticulous research and creation of flavors? We know that the more trace elements we discover the more demands we place upon ourselves to achieve closer fidelity to the natural product.

Portrait artists may use bold strokes of the paint brush to achieve the desired effects when painting a portrait. They then add barely perceptible lines or strokes, apply delicate shadings of color and texture to produce effects that change the portrait's expression significantly and achieve more realistic results. The flavor artist, in a similar way, will use bold quantities of ingredients to build the skeleton or shell of a flavor and subsequently embellish it by painstaking and meticulous addition and combination of trace components identified in natural products.

Painters often step back from the canvas to study and evaluate the effects of the strokes of the brush or application of pigments. Flavorists smell and taste their developing creations after each addition of ingredients, especially when starting to combine the trace components, and eagerly evaluate the effects produced by those additions.

Are all these efforts justified by the commercial returns? Are we pursuing the ultimate realistic rendition when, perhaps, an impressionistic rendition of flavor may be all that is required? Dr. Gunther Ohloff of Firmenich Research Laboratories stated in his talk in 1977 at the VII International Congress of Essential Oils in Kyoto, Japan: "The vigorous development (of research methods) is particularly impressive in the field of flavors if the number of products discovered in one year is taken as a measure of

progress. While in 1967 not more than 750 aroma components were known, today there are around 3,000 . . . At this stage of accumulation of information the natural products chemist has to ask what value trace components actually have in flavors. The most important feature of an aroma compound is its sensory contribution to the odor pattern of a complex mixture of natural substances."

In the early days of flavor creation the name "aldehyde" was given to many aromatics, irrespective of their chemical structure, only because of their potent odors and tastes. We still use these names today: aldehyde C-14 (peach aldehyde, a lactone), aldehyde C-16 (strawberry aldehyde, an epoxide), aldehyde C-18 (coconut aldehyde, a lactone). We can imagine, for instance, what diacetyl did for a butter flavor in which the preponderant ingredient was then ethyl butyrate or what gamma undecalactone did for a peach flavor in which the main ingredients were ethyl acetate, ethyl valerate, and amyl butyrate.

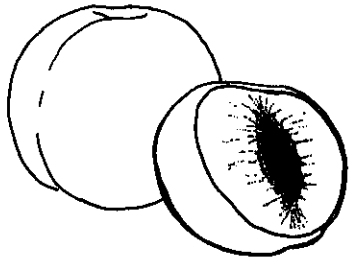
The use of those ingredients, however, once they were made available, required no great skill or imagination by the flavorist in creating flavors because of their self-descriptive profile, nor did they require special manipulation in the composition of a flavor. Artistry, however, prevailed when those same items were used to achieve specific effects in other flavors, and at quantities much less than commonly used. The absence of modern instruments had given the early flavorists many advantages. It challenged their imagination by supplying them with a thorough and intrinsic knowledge of aromatics by extensive use of and reliance upon their own senses, and by stimulating their sense of creativity.

Flavor research has advanced dramatically and has been the great contributor to the flavorist's ability to create products no longer skeletal, no longer cold, no longer stereotyped. The identification of trace items makes it possible for the flavorist to create subtle, harmonizing and softer effects, emulating in a modest way those that were only reserved for nature.

The flavorist's excitement becomes dynamic when a new flavor ingredient, a trace component, is detected and identified. The excitement is further enhanced by the subsequent synthesis and availability of the trace constituents. The imagination is given the proper support leading to experiments with the new discoveries in all types of flavors. How well we all remember the deep feeling of expectancy when we were first provided with the pyrazines, the pyridines, and

sulfur chemicals, just to mention a few. The flavorist, so armed and equipped, wishes then to be as exact as a scientist and, more importantly, as flexible as an artist. The flavorist's shelves, like a painter's palette, are continually supplied with more "pigments." Insatiably the flavorist seeks out new discoveries blending the trace items into one harmonious effect that will make this creation different and outstanding from all others.

Flavor manufacturers have basically the same assortment of flavors; each, perhaps, has one particular flavor that stands out among its competitors. In all cases those outstanding flavors have one thing in common: the application of trace components discovered by the researcher and the skillful evaluation and use of them by the flavorist. Such creations are classical and suggest long, laborious and fastidious creativity, which, unfortunately, is a luxury that is curtailed by commercial demands.



I cannot emphasize strongly enough the importance of trace items in flavor work and I must quote Mr. E. F. K. Denny of Denny McKenzie Associates, Ltd., Tasmania, who comments "Our first lesson from Nature is that she never makes a well-rounded attractive (product) without backing up the main components with a small quantity of mixed trace constituents. These traces are the most important part of a formula. The difference between otto of rose and the simple mixture of citronellol and geraniol that comprise most of the oil is quite obvious. It is arguable that users of the otto are paying over thirty thousand dollars per kilo for those trace components and are getting value for the money."

Don't we find this comment applicable to many modern flavors? We could as well reflect upon the immense quantities of flavor manufacturing that necessitates large equipment and storage space; yet, the production quantities of the trace elements are literally in terms of small bottles or jars, rather than drums and tanks!

Every flavor chemist has felt the frustration of knowing that there are many ingredients in a natural product left to be identified. Through the elution port of the gas chromatograph they usually smell quite powerful and diffusive, yet at quantities so small not to be graphically manifested by the instrument or identified by the researcher. Often we encounter aromatics of very low vapor pressure that tempt us to think they have weak odor and taste. Such may not be the case—phenyl ethyl methyl carbinol and other carbinols, for example, come to mind. Their power in the finished products at trace quantities of 1-2 ppm is quite perceptible.

Trace components collectively may amount to less than 1% in the natural product, yet they contribute so much! The flavorist incessantly seeks their identification by the researcher since they are decisive for the development of a flavor. The flavorist always tastes newly discovered ingredients, evaluates them and determines which are fundamental and which are redundant.

Trace constituents are used in such small amounts that one would doubt their practical value. Their removal from a formula, however, is invariably detectable. We flavorists have, at one time or another, used in our basic creations one or several compounded flavors that contain numerous basic chemicals the total of which would be above the trace quantity value. The expansion and quantitation of those compounded ingredients into single components would produce amounts that, in all practicality, would be beyond the detection of our modern sophisticated instruments. I am reminded of a formulation which contained among many basically structured chemicals three compounded flavors the sum of which totaled a little over 2% of the formula and collectively contained 97 ingredients. A computer percentage calculation printed out 76 of those ingredients having a value of 10^{-7}! Removing some of those ingredients gave measurable differences in the taste of the flavor.

We are tempted now and then to remove some ingredients for either economic reasons, manufacturing convenience, or we may just believe them to be ineffective. The results can be detrimental!

In all practicality, we have come to realize the importance of trace constituents and how significant the knowledge of the chemistry of their precursors can be. Most are quite expensive, yet the judicious use by the flavorist and the minimal quantities needed for the effects desired

make them reasonably economical. The demand for flavors that were nonexistent 15-20 years ago has engendered them today and at an increasing rate. The availability of nitrogen and sulfur containing chemicals and the continuing discovery of valuable trace constituents have given the flavorist delicate and refined tools to reproduce flavors for the dairy, meat, vegetable and fruit industries of higher quality and similarity to natural products.

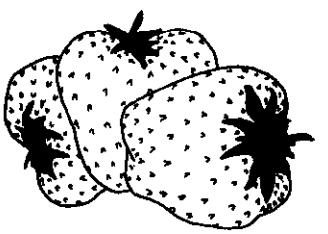
The flavorist will add the newly discovered trace ingredients to pre-existent flavor formulations for improvement, of course, but often to achieve something different. Using one single trace ingredient may not necessarily achieve the desired effect. The flavorist will combine it with other extraneous components, yet preserve the fidelity of the natural product. This is a very painstaking and time consuming job, but the results when successfully achieved are quite rewarding.

What is a trace ingredient for one flavor may not be so for another. Ionones, ionols, for example, are used in quantities beyond trace levels in berry type flavors. In other types of flavors they are used at trace quantities or they may be combined separately into one single well balanced rendition which the flavorist would use as a specialty to achieve certain effects. Lactones that are used at higher than trace levels in peach, apricot, coconut flavors may play very critical roles in berry, citrus, nut, dairy, and some vegetable type flavors when used at trace levels.

Citrus type aldehydes, likewise, are used at above trace levels in citrus flavors, but at trace quantities they are quite effective for desired results in berry, meat, nut and some vegetable type flavors. Pyrazines, pyridines, and/or sulfur containing chemicals are knowingly associated with flavors such as roasted nut, coffee, cocoa/chocolate and some vegetable flavors, yet at levels that defy instrumental detection they convey very interesting notes in cheese and fruit flavors.

Many more examples could be mentioned, all of which point to the ever expanding area of meticulous flavor research and to the flavorist's utilization of trace constituents to meet the ever changing and demanding standards in the food industry. The identification and the study of traces of sulfur and nitrogen compounds in natural food products has unquestionably opened the doors to dramatic improvements in many flavors.

Experienced flavorists have a thorough knowledge of trace constituents used in making both artificial and natural flavors. Although, as I mentioned earlier, they may use aromatics not found to occur naturally, it is more likely that the identity of many times the number of aromatics produced synthetically for flavors, specifically the nitrogen and sulfur compounds is still hidden. Unfortunately, such trace constituents are often unstable and it has been rather impossible to retain the odor and taste of fresh natural products containing them.



The flavorist makes compromises to approximate the unknown or unstable components: they may improve but do not exactly reproduce. It is necessary, and practically impossible, to preserve the flavor rendition of those constituents by combining them with other ingredients to obtain stable characteristics and by continually trying to unravel nature's "opus operandi" in components of fruits, spices, and vegetables. The research chemist unfortunately does not reproduce by synthesis the purity of those components that have been identified.

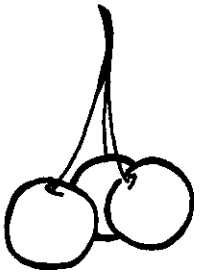
Nearly every flavorist and food technologist who has worked on formulations or applications has realized that the flavor of cherry, for example, was due in large part to benzaldehyde and tried the obvious step—using synthetic benzaldehyde. The results were not gratifying. The flavorist, consequently, included in the flavor formula modifiers, which from an artistic interpretation only, were items such as tolyaldehyde, geraniol, a few benzyl esters and few other alcohols. Today, a formula for an acceptable cherry flavor might contain 30-50 ingredients each of which the flavorist has evaluated, smelled and tasted individually. Still, there is no cherry flavor that is quite close to the natural fruit. Research has not been able to isolate and identify the many, many trace constituents in a cherry.

The difficulty compounds itself when we realize that a large number of constituents undergo chemical changes during the process of extraction and concentration, and subsequently, by the more drastic treatments of isolation and identification by instruments. How small can the

trace items be when we also consider that a little less than 3 mg of benzaldehyde are derived from approximately 25 gallons of cherry juice! The research chemist and flavorist team will exuberantly pride itself, justifiably, for identifying up to 95-98% of the constituents in an essence removed from the natural product, later to realize that the unknown 5-2% of the constituents make the difference!

Klas Anjou and Erik Von Sydow in their research paper published in 1967 on the aroma of cranberries report that 89 constituents amounting to 83% of the essential oil have been conclusively identified. Of these, 19 are aliphatic alcohols, 20 are aliphatic aldehydes and ketones, 19 are terpene derivatives and the rest are other aromatic compounds, of which alpha-terpineol dominates. However, 2-methyl butyric acid is the most important aroma chemical and is in a very negligible amount! Furthermore, 28 kg of the berries delivered, after extraction and distillation procedures, an essence of a volume of 125 microliters! The cranberries studied contained 1.1 ppm essential oils of the fresh weight!

Unlike cranberries or strawberries for which there are no constituents characteristic of their odor and/or flavor, raspberry, citrus, and vanilla products have components such as ionones, citral and other citrus aldehydes and vanillin, respectively, that offer the flavorist a sound foundation for structuring the corresponding flavors.



The discovery and use of trace constituents enable the flavorist to develop outstanding flavors of greater quality than previously created. The trace constituents are becoming more and more indispensable for modern flavor creations but in the final analysis the fidelity of the flavor depends on the skill of its creator and the principles of application.

Vanilla is still among the most popular if not the most popular flavor today. It has been so for hundreds of years and the original research on its flavor principles was done over the past 120-130 years. Vanillin is the most characteristic constituent. It was synthesized in 1874 and other ingredients later found to occur in the vanilla extract were actually synthesized and used years before they had been discovered in nature.

I remember during my early years at Givaudan how Jim Broderick had so intensely delved into the composition of vanilla and had written extensively about it. In later years research on vanilla was further pursued by Dick Potter, but, unfortunately, today there is still no satisfactory reproduction of the natural product. Since the compilation of the literature on vanilla is still deficient, painstaking research attempts are being made to approach the true vanilla bean flavor. Unknown aromatics—all in the trace quantities area—are missing. The flavorist, however, continues to try to compensate for the missing elements with most frustrating and disappointing results.

Extensive research has been done on strawberries and their varieties. The technique of combined mass spectrometry and gas chromatography has been applied to the analysis of the complex oil of strawberry volatiles. Over 200 components have been indicated to occur. Most of the major components have been identified, all in the areas of alcohols, esters, acetals, aldehydes, ketones, a few terpenes and a few hydrocarbons. Attempts at reconstituting the flavor from the research findings were rather disillusioning and frustrating!

Many trace constituents, though olfactorily detected through the elution port of the GLC and determined by the flavorist as being very important have continually and enervatingly eluded identification. The work in investigation of volatiles from fruits, vegetables, dairy products, and others continues, however, in the hope that someday the ultimate reproduction of natural flavors will be captured. It is of no consolation to reflect, at this writing, upon the overwhelming threat that governmental agencies and consumerists are posing upon flavor manufacturers to disclose their trade secrets!

Research instruments today can detect, at very expensive costs, constituents at levels of one part per trillion (1 ppt)!! How far can the flavor manufacturer carry out its research program before it becomes economically impractical and unrealistic? This may be discouraging to the romanticist flavorist but sensible to the pragmatic sales/marketing and research executives.

I do not intend to end with with an indication of an uncertain future. These are just new problems for the young and clever flavorist to meet. I am confident that challenges will be accepted and resolved.