Gas Chromatography as a Tool for the Perfumer

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Perfumers and flavorists deal largely with volatile substances, many of which occur as components of natural mixtures, while others are synthetic organic chemicals. The interests of these workers range from analysis to the creation of new blends and mixtures (with a view to consumer acceptance), to establishing the degree of correlation between specific components and the overall sensory attributes of those mixtures.

The attainment of these goals, whether they are primarily qualitative or quantitative, may require and is almost always facilitated by resolution of the individual components in the mixture under investigation. "Chromatography," defined as the science of separation, has become an indispensable tool to both perfumers and flavorists. Gas chromatography is by far the most powerful of the chromatographic techniques; indeed, it is so powerful that untrained analysts can misuse poorly designed equipment and still generate useful data. As a result, only a fraction of the vast numbers of practicing chromatographers possess an understanding of the fundamental chromatographic concepts sufficient to its most efficient utilization.

Recognition of the tremendous utility of this process was slow in coming. Following its conception in 1948 by James and Martin, it lay largely fallow until 1954 when Ray combined gas chromatography with thermal conductivity detection, and published the first "chromatogram." That action seduced many workers, including me and probably some of you, into this field.

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The first problem facing the Neanderthal chromatographer was instrumentation; there wasn't any. We built crude ovens, usually oil baths, to house incredibly primitive columns drenched with ill-defined stationary phases that eluted to do-it-yourself catherometers with needlessly massive internal volumes.

Developments in this field have occurred as a series of short bursts of progress sporadically in-

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terrupted by switchbacks. Logically, most of our attention was directed to whatever problem was most limiting at any given point in time; the solution to that problem was rarely complete, but limited progress usually resulted in a partial solution, so that some other problem became more limiting, and attention shifted. In time, the second problem would be partially resolved, and the first problem area again became limiting, and our research emphasis was again re-directed.

The first crude commercial instruments were usually designed by engineers rather than chemists, and we learned to improve these by radical surgery; indeed, the saber saw was often brought into play before the salesman got the instrument off his shoulder. With the improvement of instrumentation, we began to worry about columns . . . their separation efficiencies were lamentably low. Golay's invention of the open tubular column and Desty's invention of a machine for drawing glass capillary tubing combined to help us make more efficient columns—but now we had to go back to the instrument, redesigning inlets, and inventing new modes of detection.

About this time inertness became the watchword; we noted that not everything entering the column left the column; the flavor chemist could inject neral and watch the column change a goodly portion of it to geranial. A number of probes and test mixtures were proposed to evaluate column "inertness." One of the more demanding of these was the Grob mixture, and when it was first proposed in 1978, it was used essentially to establish what compounds should be avoided with a particular column because no column could pass the entire mixture. A better understanding of the siliceous glasses led to more inert columns, and eventually to better methods of deactivation. The Grob test is no problem today, and we use even more demanding probes, such as the substitution of the more acidic chlorophenols in place of the alkyl phenols used here. With more inert columns, we returned to the removal of active sites in the instrument. Now, the intermediate column efficiencies that we had achieved in the mid seventies were no longer adequate, and we turned again to improving column efficiency.

Today, we have some good instrumentation, and some superb columns, but we have not achieved perfection in either area. Indeed, the ball is back in the court of the instrument supplier, and in our lifetimes, we'll see these cycles repeated yet again.

Today we are capable of performing some reasonable separations, but we usually find there are still areas for improvement. Because some of these solutes are relatively unstable to the analytical conditions, we have to subject every column to still another test for "inertness."

About this time, I like to bring in a note of caution—gas chromatography cannot establish what something is, it can only establish what it is not. It is not any number of other solutes whose retentions are demonstrably different on that column under those conditions. Possible identifications should be confirmed by a non-redundant means of analysis such as mass spectrometry or infrared spectroscopy.

In 1956, when I was a very junior assistant professor, I was given the benefit of a senior professor's advice, to wit: "find another field of research; gas chromatography is now a fully developed science." Fortunately, I didn't agree with him then, and even if he were still alive, I wouldn't agree with him today. This technology that we've been discussing—gas chromatography—is at present based on an incompletely developed science. Only after we have the science in place can we bring the technology to fruition.

And will this success then solve the problems of those in perfumery and flavor? Not necessarily:

—Many of these compounds are relatively fragile, and we haven't even touched the subject of sample preparation.

—We also have to realize that gas chromatography is (we hope) an objective means of analysis, while aroma and flavor result from stimulation of receptor organs; they are highly subjective phenomena.

—In addition, it is doubtful that we will ever match the sensitivity of the biological sensory receptor, the nose and/or the palate, for some compounds.

—Nor can we forget that gas chromatography differentiates, while the nose and the palate yield integrated responses.

More than in any other field, we must use reason, intelligence, and restraint in interpretation of analytical results. But used wisely, gas chromatography can be a very useful tool for the modern perfumer and flavorist.

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