Analysis of volatiles in flavor-scored vegetable oils and detection of flower petal essences by unconventional instrumental means

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The use of gas chromatography (GC) for detecting and quantitating volatile materials has traditionally been associated with pretreatment or enrichment techniques to concentrate the volatiles for analysis. Such methods are difficult, tedious, and time consuming.[1,2] Further, these practices sometimes result in the formation of products that are not present in the original sample.[3] High-vacuum distillations[4-6] minimize this effect because of the low heat requirements; however, such procedures are inherently complex.

In 1971, a direct, unconventional GC procedure was described for the detection of volatiles in vegetable oils.[7] This method requires no prior enrichment procedures. The technique was further refined to include salad oils and shortenings of varying quality[8] and raw and roasted peanuts,[9] and to correlate the flavor scores of taste panels with instrumental data for such items as peanut butter, vegetable oils, soy protein products, and other foods.[10-18] The method is simple, rapid, sensitive, and versatile.

This paper describes the direct, unconventional GC procedure as applied to flavor-scored soybean oils and its potential utility for detecting the delicate volatile essences in flower petals.

Materials

Materials included Tenax GC,[a] 60-80 mesh (a thermostable polymer, 2,6-diphenyl-*p*-phenylene oxide), and Poly MPE[a] (poly-*m*-phenoxylene). Teflon O-rings,[b] sandwich-type silicone septums,[c] and Pyrex glass wool[d] were purchased. (The O-rings, septums, and glass wool were conditioned at 200°C for 16 hr prior to use.) Inlet liners, 10 x 84 mm, were cut from borosilicate glass tubing. The soybean oil samples[e] were experimental oils specially treated to provide a wide range of flavor variance. The oils were flavor-scored by 12 taste panels from industry, academia, and government laboratories on a 1 to 10 scale. The number of judges in an individual panel varied from 3 to 24, and in all, totaled 156. The flower petal samples were obtained from a locally grown camellia plant and from a white orchid plant produced in a local greenhouse.

A Tracor MT-220 gas chromatograph with dual independent hydrogen flame detectors was used with a Westronics MT22 recorder and a Hewlett-Packard integrator, model 3380 A. The columns were stainless-steel U-tubes, ⅛ in. o.d., 3 m long, packed with Tenax GC that had been coated with 8% Poly MPE. Nitrogen carrier gas was 60 ml/min in each column. Hydrogen was 60 ml/min to each flame, and air was 566 ml/min (fuel and scavenger gas for both flames).

Operating conditions for oils and flower petals

The inlet temperature was 170°C. The detector was at 250°C. The column oven was maintained at 30°C during the initial 40 min hold period. After removal of the inlet liner, the column was heated to 100°C within 5 min, then programmed to rise 3°C/min for 30 min. The final hold was at 190°C for 30 min at which time the column was clear. A Teflon O-ring was positioned at the bottom of the inlet of the GC to provide a leakproof seal. Electrometer attenuation was 10 x 4.

The GC conditions for analysis of the flower petals were similar to those used for analysis of the oils with the following exceptions: The inlet temperature was 120°C. The column oven was maintained at 30°C during the initial 10 min

[a] Obtained from Applied Science Laboratories, State College, PA
[b] Alltek Associates, Arlington Heights, IL
[c] Hamilton Company, Reno, NV
[d] Corning Glass Works, Corning, NY
[e] Provided by AOCS Flavor and Nomenclature Committee

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hold period. After removal of the inlet liner, the column was heated to 70°C within 5 min, then programmed to rise 5°C/min for 29 min. The final hold was at 215°C for 30 min until the column was clear.

Sample preparation for GC analysis

A 3⅜ in. length of ⅜ in. o.d. borosilicate glass tubing was packed with volatile-free glass wool, loose enough to permit diffusion of oil throughout the packing, yet tight enough to prevent seepage of the sample from the liner onto the GC column. Clearance of ¼ in. was allowed at the bottom of the liner and ½ in. at the top. The septum nut, septum, and retainer nut of the GC were removed, and the liner containing the sample was inserted into the inlet of the GC and placed on top of the Teflon O-ring. When the retainer nut was tightened above the upper rim of the liner, a seal was formed between the base of the inlet and the lower rim. When the inlet system was closed with the septum and septum nut, the carrier gas was forced to flow upward and down through the sample. This procedure has been described previously.[12]

For flower petal analysis, the borosilicate tube was lightly packed at one end with a small plug of glass wool. The intact flower petals were introduced and covered with another small plug of glass wool. The inlet liner containing the flower specimens was inserted into the GC inlet as described above.

Results

The three chromatograms shown in figure 1 were obtained by applying the direct, unconventional GC procedure to three soybean oils with a known flavor score. Chromatogram 1 represents a high-quality oil having a flavor score of 8. It reveals the smallest number of volatiles, present in relatively low intensities. These data confirm the flavor panelists' high ranking of the oil for its blandness and absence of off-flavors. Chromatogram 2, however, was derived from an oil of lower quality, designated with a flavor score of 5.5. In this instance both the number and intensity of volatile peaks have increased significantly. In particular, the peak eluting at about 75 minutes (subsequently identified as *trans, trans*-2,4-decadienal) has increased from a recorder response of 20 in the high quality oil to an off-chart intensity in the 5.5 flavor-scored oil. Evidently this compound and others were accurately detected by the flavor panels. The poorest quality oil, shown in chromatogram 3, was rated at 4 on the flavor scale. This indicates a highly unsuitable rise in essentially all of the volatile compounds, five of which have achieved off-scale intensities. It is evident from the three chromatograms that the number and intensity of volatile peaks reflect a progressive rise that corresponds with deteriorating flavor quality. A regression analysis of the oil flavor scores with the log of the total volatiles in these oils reveals a correlation coefficient of −0.994 with an F-value of 157.1, significant at the 99% confidence level. The standard error for these calculations was 0.23. Thus, the volatile organoleptic components in vegetable oils can be effectively detected by the instrumental means of direct, unconventional GC.

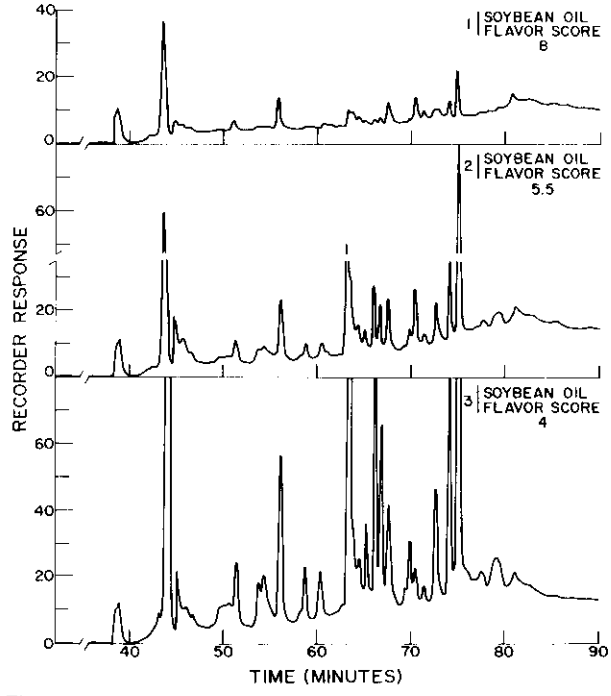

Figure 1. Profiles of volatiles obtained for three flavor-scored soybean oils by the direct, unconventional GC procedure.

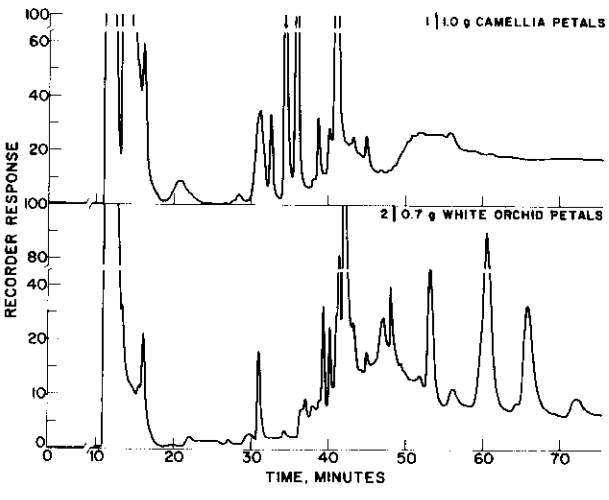

Figure 2. Profile of volatiles obtained from two types of flower petals by the direct, unconventional GC procedure.

Figure 2 shows the profiles of volatiles obtained directly from flower petals by the direct, unconventional GC method employed for the vegetable oils analysis. This technique is capable of detecting volatile materials present in the

flower samples. Chromatogram 1, for example, reflects approximately nine major volatile components present in camellia flower petals. These volatiles have been resolved along with a number of other minor peaks. The pattern obtained constitutes a "print" or profile of camellia volatiles. Similarly, chromatogram 2 shows approximately twelve major volatile peaks and numerous smaller ones obtained from white orchid petals. The types of peaks, their intensities, patterns, and retention times differ markedly in both chromatograms, indicating a pronounced difference in the number and composition of volatiles present in each flower. By interfacing a mass spectrometer in conjunction with the GC used for these experiments, it should be possible to characterize many of the individual peaks detected.

Conclusions

The direct, unconventional GC method of analysis is a simple and rapid means for effectively assessing the quality of many volatile-based materials. By providing a tangible record of volatiles profiles, it offers a potential for establishing demonstrable and reproducible standards in the areas of essential oils, flavors, and essences. Both the producer and the formulator of such products are afforded a practical method for monitoring their raw materials or products, by reliable, objective, instrumental means.

References

1. D. E. Smith and J. R. Coffman, Anal. Chem. **32,** 1733 (1960)
2. J. P. Waldrat, R. C. Lindsay, and L. M. Libbey, J. Agric. Food Chem., **18,** 926 (1970)
3. P. H. Todd, Jr., Food Technol., **14,** 301 (1960)
4. S. S. Chang, J. Am. Oil Chem. Soc., **38,** 669 (1961)
5. C. H. Lee and P. A. T. Swoboda, J. Sci. Food Agric. **13,** 148 (1962)
6. E. Selka, H. A. Moser, and W. K. Rohwedder, J. Am. Oil Chem. Soc., **47,** 393 (1970)
7. H. P. Dupuy, S. P. Fore, and L. A. Goldblatt, Ibid., **48,** 876 (1971)
8. H. P. Dupuy, S. P. Fore, and L. A. Goldblatt, Ibid., **50,** 340 (1973)
9. D. F. Brown, F. G. Dollear, and H. P. Dupuy, Ibid., **49,** 81 (1972)
10. S. P. Fore, L. A. Goldblatt, and H. P. Dupuy, J. Am. Peanut Res. Educ. Assoc., **4,** 177 (1972)
11. S. P. Fore, H. P. Dupuy, J. I. Wadsworth, and L. A. Goldblatt, Ibid., **5,** 59 (1973)
12. S. P. Fore, H. P. Dupuy, and J. I. Wadsworth, Peanut Sci., **3,** 86 (1976)
13. H. P. Dupuy, E. T. Rayner, and J. I. Wadsworth, J. Am. Oil Chem. Soc., **53,** 628 (1976)
14. H. P. Dupuy, E. T. Rayner, and J. I. Wadsworth, Ibid., **54,** 445 (1977)
15. J. L. Williams and T. H. Applewhite, Ibid., **54,** 461 (1977)
16. H. W. Jackson and D. J. Giacherio, Ibid., **54,** 458 (1977)
17. E. T. Rayner, J. I. Wadsworth, M. G. Legendre, and H. P. Dupuy, Ibid., **55,** 454 (1978)
18. G. S. Fisher, M. G. Legendre, N. V. Lovegren, W. H. Schuller, and J. A. Wells, J. Agric. Food Chem., **27,** 7 (1979)