Semiquantitative Determination of Off-Notes in Mint Oils by Solid-Phase Microextraction

W.M. Coleman, III*, B.M. Lawrence, and **S.K. Cole**
R.J. Reynolds Tobacco Company, P.O. Box 1487, Winston-Salem, NC 27102-1487

Abstract

Mint essential oils are produced by the steam distillation of dried or partially dried harvested plant material. In the United States, harvesting is done mechanically so that any weeds found in the field are concomitantly harvested. Steam distillation of contaminated plant material leads to off-notes in the oil, which are currently determined by a sensory panel. Furthermore, nonoptimized distillation conditions can lead to the thermal degradation of carbohydrates and proteins resulting also in the formation of very volatile off top-notes. As a result, the use of a nonequilibrated solid-phase microextraction (SPME) procedure to determine the off-notes is evaluated. The results of this evaluation include a combination of semiquantitative data, odor threshold data, and mathematical data manipulation to ascertain the capabilities of a SPME approach. The results are correlated with sensory panel data to yield a relatively rapid analytical methodology that can be used either in place of or in support of sensory analyses. The main advantage of the technique described is to provide some semiquantitative data in support of the odor-panel screening of mint oils for off-notes. Based on the data presented in this report, it is believed that this has been successfully demonstrated.

Introduction

Three of the four commercially important mint oils have been produced in the United States for many years. Peppermint (*Mentha piperita* L.) was introduced into the United States around 1810 (1), and for the past hundred or more years it has been the leading producer of peppermint oil. Prior to 1900, all spearmint grown in the United States for oil production originated from *Mentha spicata* L. (known as Native spearmint). In 1910, a second spearmint known as Scotch spearmint (*Mentha gracilis* Sole) was introduced into the United States. Since then the United States has been the leading producer of both spearmint oils.

There is only experimental cultivation of cornmint (*Mentha arvensis* L. var. *piperascens* Malinv. ex Holmes) oil, which is the fourth most commercially important mint oil. This latter oil, which is grown in large quantities in India and China, is the source of natural L-menthol. Peppermint and Native and Scotch spearmint are cultivated in the Midwest (Indiana, Michigan, and Wisconsin), western (South Dakota), and Farwest (Oregon, Montana, Idaho, and Washington) of the United States. A moderate amount of Scotch spearmint is also grown for oil production in Southern Alberta, Canada.

In all of the mint farming areas in the United States, the three mints are harvested by windrowing them to allow the plant material to wilt. Windrowing, which is practiced to reduce the moisture content of the plant material prior to distillation, has two major benefits: (*a*) to reduce the distillation time and (*b*) reduce oil decomposition such as hydrolysis that could take place during distillation. Depending upon the climate at harvest time, the harvested plant material is left in a windrow for as little as 12–24 h or as long as 48–72 h. The best time to harvest peppermint is at the onset of flowering. Oil produced at this stage of development is of higher quality even though the yield is slightly lower than oil produced from the plant material harvested at full flowering. During peppermint maturation, chemical changes in the oil take place fairly rapidly, thus the ideal harvesting time to produce oil of a high quality is limited to a certain extent.

This harvesting window is not as critical for either Scotch or Native spearmint as it is with peppermint because during the development stages of the spearmint plant from the onset of flowering to full flowering, the chemical composition of the oil is considerably more stable.

The three mints are cut and windrowed using a piece of farm equipment known as a swather (or more commonly known as a reel or rotary windrower). The rotary windrower is mounted either on the front or back of a tractor. The mint, which is cut close to the ground, is left in the windrows in the field for 12–72 h to allow the herbage to partially dry. It is then picked up and chopped into approximately $^1/_2$- to $^3/_4$-inch (approximately 0.6–1.9 cm) pieces

* Author to whom correspondence should be addressed.

using a silage chopper. The chopped herbage is blown into a prefabricated distilling tub of approximately 2–8 metric tons (approximately 2.2–8.8 tons) capacity.

Each tub is fitted with an evenly distributed series of perforated pipes that run lengthwise along the bottom. These are connected to a steam inlet manifold that is usually mounted on the outside of the back-end of the tub. The condenser is either a continuous series of pipes of decreasing diameter of the horizontal tank type or a vertical tank type containing a spiral condensing tube. Water is fed in and out of the tank that contains the condenser pipes to maintain an optimum temperature for economic oil condensation. An oil separator (often known as a receiver) is placed at the end of the condenser to collect the condensed water and oil. Because the mint oils are all lighter than water, the separator, which has a narrow top and wide base, is designed so that the condensate is channeled to the bottom of the receiver past some baffle plates, which allows the oil particles to coalesce and rise to the surface into the narrow neck of the receiver. The oil, which is found in the narrow neck of the receiver, can be tapped off into a tarred drum above the water level.

Condensers and separators are usually constructed of aluminum because of its heat transfer properties and resistance to corrosion. Once the "throat" doors of a tub that is full of chopped mint herbage are closed and the flexible pipe is connected to the condenser, the steam inlet from the satellite boiler is connected and the stem is turned on. Once the first drops of condensate appear in the receiver, the steam pressure is reduced depending upon the wetness of the chopped herbage and the size of the distillation charge.

For optimum oil production the condenser water is maintained between 33°C and 36°C for spearmint (both Native and Scotch) and 42°C and 46°C for peppermint. Distillation takes anywhere from 1.5–2.5 h depending mainly upon the size and wetness of the charge. Oils are tapped off the receiving cans into clean epoxy-lined mild steel or reusable stainless steel drums. The distiller seals the drum after it is filled to the brim and transports it to a storage area. Before the drums are shipped to a mint oil blender, the distiller reopens the drums and removes any water from the oil that has separated upon standing. Mint oil blenders receive the oils from the farmer/distiller, and a sample is sent to a quality control laboratory of the mint oil blender where the chemical and physicochemical properties are determined and GC analysis is performed. A second sample of the same drum is further examined by a trained odor panel (also at the facility of the mint oil blender) to determine the existence of any off-notes and their magnitude and to make any recommendations for oil disposition (including redistillation).

We have used nonequilibrated SPME in the past to examine the most volatile constituents of a mixture. It is well-known that the principle behind SPME is the equilibrium partition process of the analyte between the fiber coating and the surrounding media. In our earlier study, this partition process was between a 100-µm polydimethylsiloxane (PDMS) fiber and the surrounding atmosphere above a Virginia cedarwood oil sample inside a sealed glass container (21). We varied the amount of time that the fiber was in contact with the vapor above the oil and found that a difference of a few seconds resulted in markedly different vapor distributions of the most volatile compound (α-pinene) that was found. This led us to the conclusion that this nonequilibrated SPME method had potential as a novel semiquantitative technique.

To address a more complex problem we initially screened some U.S.-produced cornmint oils (the source of natural L-menthol) to see if we could determine whether the oil had off-notes. Because the technique still looked promising, the method of nonequilibrated SPME was used to screen a variety of natural L-menthol samples produced by freeze crystallization from cornmint oils of different geographical origins. (2,3). In this example, weighed and crushed samples of natural menthol were exposed to a 100-µm PDMS fiber for 10 s in a sealed vial. Thermal desorption of the fiber yielded analyses in which the > 99.6% pure menthol was determined to be only 55–74% of the headspace profile. The other 26–45% of the profile comprised of the lower boiling cornmint oil constituents that remained as a coating on the crushed menthol crystals. Replicate analyses revealed that the relative standard deviation (RSD) was ±10%.

As a result of the aforementioned successes, we decided to use the technique to examine the off-notes in peppermint and both Native and Scotch spearmint oils. We explored the use of various fiber coatings and concurred with the findings of Shirey (22) that carboxen was more efficient in absorbing low-molecular weight analytes than PDMS, which partitions them. Consequently, because the mix of compounds in the mint oils were both highly and moderately volatile, we settled on a 50:30 divinylbenzene (DVB)–Carboxen–PDMS fiber, which gave us the most reproducible results for all components absorbed or partitioned on the fiber.

Because the odor screening by a trained panel is very subjective, we felt that a more robust screening process was needed to differentiate "good quality" oils with those that have off-notes. A technique that has been used in the past is nonequilibrated SPME. In this paper we would like to describe the use of this semiquantitative nonequilibrated SPME technique to differentiate between oils that were determined by a trained odor-panel to be of good quality with oils determined by the same panel to possess off-notes.

A significant portion of the compounds responsible for the off-aroma notes in essential oils are of relatively low molecular weight with accompanying relatively high volatility. Compounds such as acetaldehyde, dimethylsulfide, 2-methylbutanal, and 3-methylbutanal are representative of the types of compounds identified as contributing to the off-aroma notes in essential oils. Often these low-molecular-weight compounds will not be sufficiently chromatographically resolved from a solvent front in typical analyses of essential oils. Thus, their presence most likely would not have been detected. SPME presents an excellent alternative opportunity to examine essential oils for the presence of these compounds because no solvent is involved. Selection of the proper type of fiber affords the additional potential for extracting the off-aromas from the headspace of essential oils. Analysis of essential oils and flavors by SPME has been applied in a variety of cases (2–9) but as yet SPME in a nonequilibrium mode has not yet been used to

establish a link between the presence of low-molecular-weight off-note producing components of essential oils and the resultant quality of the oils (10,11).

In a further treatment of the data, a novel "quality scale" for the oils was developed that incorporated the raw integrated ion count areas (total-ion chromatograms, TIC) from the AUTOSPME–GC–MS experiments. The TIC area from approximately ten selected compounds in the three oils and an aroma impact parameter were employed to generate a scaled cumulative intensity for each sample.

Experimental

Thirty-six samples of crude peppermint oil, 13 samples of crude Native spearmint oil, and 18 samples of crude Scotch Spearmint oil were all produced in the United States in 2000 (I.P. Callison, Chehalis, WA). All of the samples were initially screened organoleptically by one of the authors to determine which oils had low levels of off-notes and which did not. The same oils were also screened by a trained mint oil evaluation panel, and the so-called "good oils" along with the oils with increased amounts of off-notes were subjected to the non-equilibrated SPME analysis.

Instrumental settings

The AUTOSPME–GC–MS analyses were performed using a Varian Instruments (Walnut Creek, CA) 8200 vibrating SPME III autosampler fitted with a 50:30 DVB–Carboxen–PDMS Stable Flex SPME fiber (Supelco, Bellefonte, PA) mounted atop a Hewlett-Packard (Palo Alto, CA) 5890 GC equipped with a Hewlett Packard 5972 MSD. The GC was fitted with a DBWAXETR fused-silica column (30-m × 0.25-mm i.d., 0.25-µm film thickness) (J&W Scientific, Folsom, CA). The back pressure on the column was 15 psi, and the AUTOSPME injections were made in the split mode with a split ratio of approximately 10 to 1. The fiber was exposed to the headspace above the sample for 0.1 min with vibration prior to injection. The GC oven was held at an initial value of 35°C for 1 min and then programmed to 160°C at 2°C/min. The oven was held at 160°C for 3 min. The GC injection port and MSD interface were held at 230°C. The MSD was operated in the electron-impact mode at 70 eV. The scan range was 33 to 250 *m/z*. The SPME fiber was activated, stored, and handled strictly following manufacturer's instructions. Compound identifications were facilitated by using the Wiley and National Bureau of Standards mass spectral libraries as well as retention time databases of authentic compounds.

Sample preparation

A 2-µL amount of the oil of interest was added to a 2-mL screw-top clear vial with a hole cap and polytetrafluoroethylene/Silicon septum (Supelco) using a 10-µL Auto Pipet (Rainin Instruments, Emeryville, CA). The vial was sealed and placed in the autosampler "puck" for analysis. Six separate vials were prepared for each sample. Single injections of each of the six vials were made for each individual essential oil sample. The RSD percentage for six injections ranged from 5% to 10%.

Results and Discussion

It is well-known that an essential oil is a mixture of many constituents whose relative amounts cover many orders of magnitude. The amounts and ratios of the constituents give the oil its characteristic odor. For the oils under study, the compositions (constituents identified and their amounts) for peppermint, Native spearmint, and Scotch spearmint are well-known (12–14). Also, it is obvious that the mint oils con-

Table I. Influential Constituents on the Odor Profile of the Mint Oils

		Aroma impact components of the oils			
Component	Threshold (ppb)	Peppermint	Scotch spearmint	Native spearmint	Threshold reference
Dimethyl sulphide	0.3	4*	6	7	reference 16
2-Methyl propanal	1.0	6	–	–	reference 17
2-Methyl butanal	0.2	2	3	3	reference 20
2-Ethylfuran	1.0	5	10	8	estimate
Methyl 2-methyl butyrate	0.25	–	4	6	reference 11
α-Pinene	6.0	3	5	5	reference 15
β-Pinene	140.0	9	–	–	reference 15
Sabinene	75.0	10	–	–	reference 10
Myrcene	15.0	7	8	4	reference 15
(–)-Limonene	300.0	–	9	10	reference 19
1,8-Cineole	1.3	1	1	1	reference 15
3-Octanol	14.0	–	7	9	estimate
(–)-Menthone	350.0	8	–	–	reference 18
(–)-Carvone	10.0	–	2	2	reference 18

* Order of importance to the odor profile.

tain individual constituents that appear to be totally unrelated to the composite odor profile of the oil. Nevertheless, the odor quality of mint oils is judged by the extrinsically fixed quantitative interrelationships found in the oils produced from these clonally reproduced plants.

As noted, the odor quality is judged by the interrelationship of all constituents; however, in our situation we wanted to differentiate the oils based on the volatile off-note influence on them. In order to do this, we developed the nonequilibrated top note screening process using AUTOSPME as described in the Procedure section.

The results of the nonequilibrated AUTOSPME analyses revealed that the identified components could be used to differentiate between good and off-note samples of the Scotch and Native spearmint oils, respectively, as well as for peppermint oil. Examination of the mean quantitative data of the "good oils" with those obtained from the oils with off-notes was useful, although somewhat cumbersome.

In order to determine the relative importance of the individual constituents in the mint oils, we have used the hypothesis that the odor intensity/top note quality of the oils is influenced by their relative amounts and odor thresholds. From the organoleptic evaluations of peppermint, Native spearmint, and Scotch spearmint oils, five samples of each oil were judged to be of good quality (free from unacceptable off-notes). As a result, the quantitative range data (in parts per billion) for each of the individual constituents obtained from these good oils were divided by their odor threshold (in parts per billion). Using these data manipulations, the ten most influential constituents on the odor profile of each oil were realized. A list of the selected influential constituents in peppermint and two spearmint oils and their odor thresholds (10,11,13–20) appears in Table I.

The acquisition of the data using a nonequilibrium condition for the SPME fiber is of note. The robustness and accuracy of the data under these nonequilibrium conditions was made possible by maintaining strict regulation over three parameters: headspace volume above the essential oil, sampling time, and sample quantity. Therefore, by controlling crucial experimental parameters, meaningful data can be attained using SPME under nonequilibrium conditions.

Table II. Integrated Ion Count Area Percent Ranges for High-Quality Oils*

	Peppermint		Scotch spearmint		Native spearmint	
Compound	Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
Acetaldehyde	0.005	0.005	0.005	0.005	0.005	0.005
Dimethyl sulphide†,‡,§	0.069	0.254	0.067	0.164	0.054	0.100
2-methylpropanal†	0.103	0.128	0.005	0.069	0.041	0.087
2-methylbutanal†,‡,§	0.958	1.132	0.142	0.433	0.340	0.517
2-ethylfuran†,‡,§	0.168	0.421	0.061	0.135	0.096	0.195
Pentanal	0.005	0.045	0.005	0.005	0.005	0.005
Methyl 2-methylbutyrate‡,§	0.005	0.005	0.005	0.227	0.108	0.167
α-Pinene†,‡,§	3.213	3.923	3.672	4.003	3.746	4.035
α-Thujene	0.339	0.380	0.005	0.207	0.376	0.451
cis-2,6-Diethyltetrahydrofuran	0.092	0.178	0.005	1.012	0.224	0.600
β-Pinene†	4.110	4.806	3.064	3.325	2.961	3.238
Sabinene†	2.196	2.598	1.775	2.242	2.017	2.397
Myrcene†,‡,§	0.877	1.122	3.367	3.640	8.517	9.572
α-Terpinene	1.188	1.817	0.107	0.228	1.097	1.296
Limonene‡,§	4.732	6.568	42.196	48.943	31.627	35.089
1,8-Cineole†,‡,§	14.477	16.449	4.850	6.272	7.293	8.868
(*E*)-2-Hexenal	0.161	0.389	0.005	0.469	0.219	0.456
(*Z*)-β-Ocimene	0.729	1.626	0.029	0.051	0.401	0.578
γ-Terpinene	1.612	2.494	0.120	0.315	1.499	1.702
(*E*)-β-Ocimene	0.193	0.420	0.005	0.121	0.230	0.327
π-Cymene	0.491	0.664	0.005	0.057	0.250	0.333
3-Octanol‡,§	0.193	0.354	3.515	4.436	1.498	1.769
Menthone†	26.056	30.418	1.208	1.424	0.005	0.005
trans-Sabinene hydrate	0.451	1.381	0.005	0.195	1.001	1.862
Menthofuran	1.008	5.263	0.005	0.005	0.005	0.005
Isomenthone	4.124	4.614	0.173	0.222	0.005	0.005
Menthyl acetate	2.225	3.416	0.005	0.048	0.005	0.005
Neomenthol	2.695	3.216	0.246	0.341	0.422	0.886
Terpinen-4-ol	0.005	0.005	0.005	0.169	0.724	0.887
Pulegone	0.232	1.957	0.005	0.005	0.005	0.005
Menthol	14.726	15.981	0.005	0.005	0.005	0.005
Carvone‡,§	0.005	0.005	23.512	30.632	26.664	33.500

* The range is set by the maximum and minimum values for the high-quality rated samples for each compound. The detection limit for the SPME–GC–MS procedure is 0.005%. Entries of this magnitude should be considered equal to zero.
† Compound used to determine the scaled excess aroma intensity for the peppermint oils.
‡ Compound used to determine the scaled excess aroma intensity for the Scotch spearmint oils.
§ Compound used to determine the scaled excess aroma intensity for the Native spearmint oils.

SPME GC–MS data analysis

In order to facilitate the analysis of mint oil quality in the future, a quality scale was developed that incorporates integrated ion-count area fractions from the SPME GC–MS analysis with an aroma impact parameter for ten selected compounds in the three types of oils (shown in Table I). The quality scale is essentially a semiquantitative measure of the extent the ten selected compounds in a particular oil deviate from that of a rated high-quality oil. The aroma impact parameter serves as a weighting function of the relative importance of each compound in the oil samples. This simple scaling is based upon the following notions: (*a*) the integrated ion count area fractions are linearly related to their mass fraction in the sample, (*b*) the most important factor determining the comparison of quality between oils is the variation of individual compound concentration between oil samples and not the relative concentrations between compounds within a single sample, and (*c*) the contributions of the individual compounds included in the model to oil quality are orthogonal (i.e., there is no odor interaction involved in

the quality assessment).

Assuming that these factors are applicable to these types of oils, a simple scaled excess aroma intensity for each sample can be defined:

$$I_j = \sum_{i=1}^{n} d_i S_i, \qquad \text{Eq. 1}$$

where I_j is the scaled excess aroma intensity for sample j, n is the number of compounds included in the analysis, d_i is the integrated ion count area excess, and S_i is the aroma impact scalar for compound i.

The integrated ion count area excess is simply the difference in the recorded area and either the maximum or minimum area count defined by the high quality oils.

$$d_i = F_{i,\min} - F_{ij} \qquad (F_{ij} < F_{i,\min}) \qquad \text{Eq. 2}$$

$$d_i = 0 \qquad (F_{i,\min} < F_{ij} < F_{i,\max}) \qquad \text{Eq. 3}$$

$$d_i = F_{ij} - F_{i,\max} \qquad (F_{ij} > F_{i,\max}) \qquad \text{Eq. 4}$$

where $F_{i,\min}$ is the minimum integrated ion count area for compound i in a good quality oil, $F_{i,\max}$ is the maximum integrated ion count area for compound i in a good quality oil, and F_{ij} is the integrated ion count area fraction for compound i in sample j.

$$d_i = \frac{A_{ij}}{\sum_{k=1}^{N_j} A_{kj}} \qquad \text{Eq. 5}$$

where A_{ij} is the integrated ion count area for compound i and sample j and N_j is the total number of compounds analyzed in sample j.

If the integrated ion count area lies within the range defined by the maximum and minimum values for the high quality oils, the area excess will have zero value. Thus, an oil that has an integrated ion count area for each of the ten compounds that lies within the defined "good" range will have a scaled excess aroma intensity of zero. Deviations from zero indicate that one or more compounds have integrated ion count areas outside the defined limits for high-quality oils. These maximum and minimum values for selected compounds appear in Table II.

The aroma impact scalar (S_i) is a linear function of the aroma impact parameter (Table I). An impact parameter of one is assigned a scalar value of ten, and an impact parameter value of ten has a scalar value of one. The linear function is:

$$S_i = P_{\max} + 1 - P_i \qquad \text{Eq. 6}$$

where P_i is the aroma impact parameter rating for compound i and P_{max} is the maximum impact parameter rating.

In this case, the aroma impact ratings are simply the rankings of the ten compounds deemed to have the greatest impact on quality. This linear scaling proved to be sufficient for this data set. Other functions such as:

$$S_i = e^{\left(\frac{1}{P_i}\right)} \qquad \text{Eq. 7}$$

and e^{-P_i}, which yield values of the aroma impact scalar that vary significantly less and more from first (P_i = 1) to last (P_i = 10)

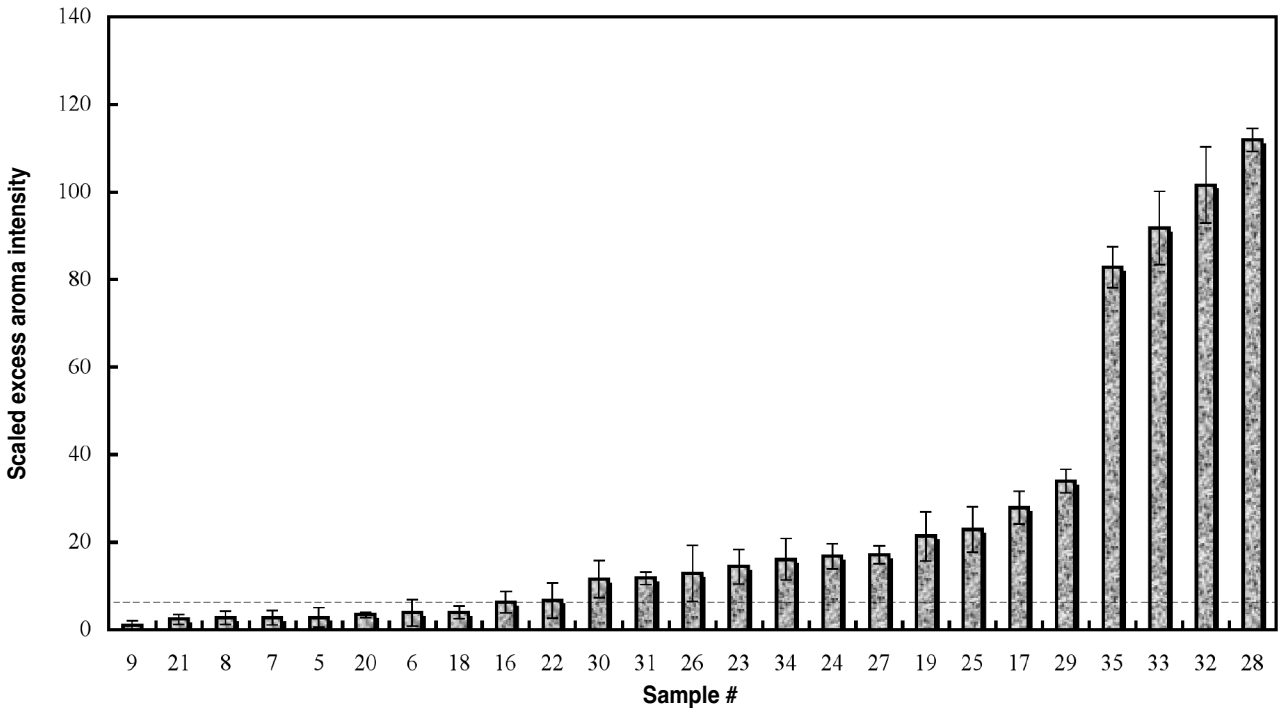

Figure 1. Plot of scaled excess aroma intensity (arbitrary units) versus sample number for peppermint oils. The dashed line indicates the maximum intensity for a high-quality oil. The error bars are ± one standard deviation. Oil samples 5–9 were rated high-quality organoleptically.

than the previous linear function, were tried and found to minimally affect I_j.

The summation in equation 1 is over all compounds included in the analysis for each type of oil. In this work, ten compounds were chosen for each of the three oils. Results were also determined using all 32 compounds identified in the SPME–GC–MS experiment. These results were identical to those that included only ten compounds.

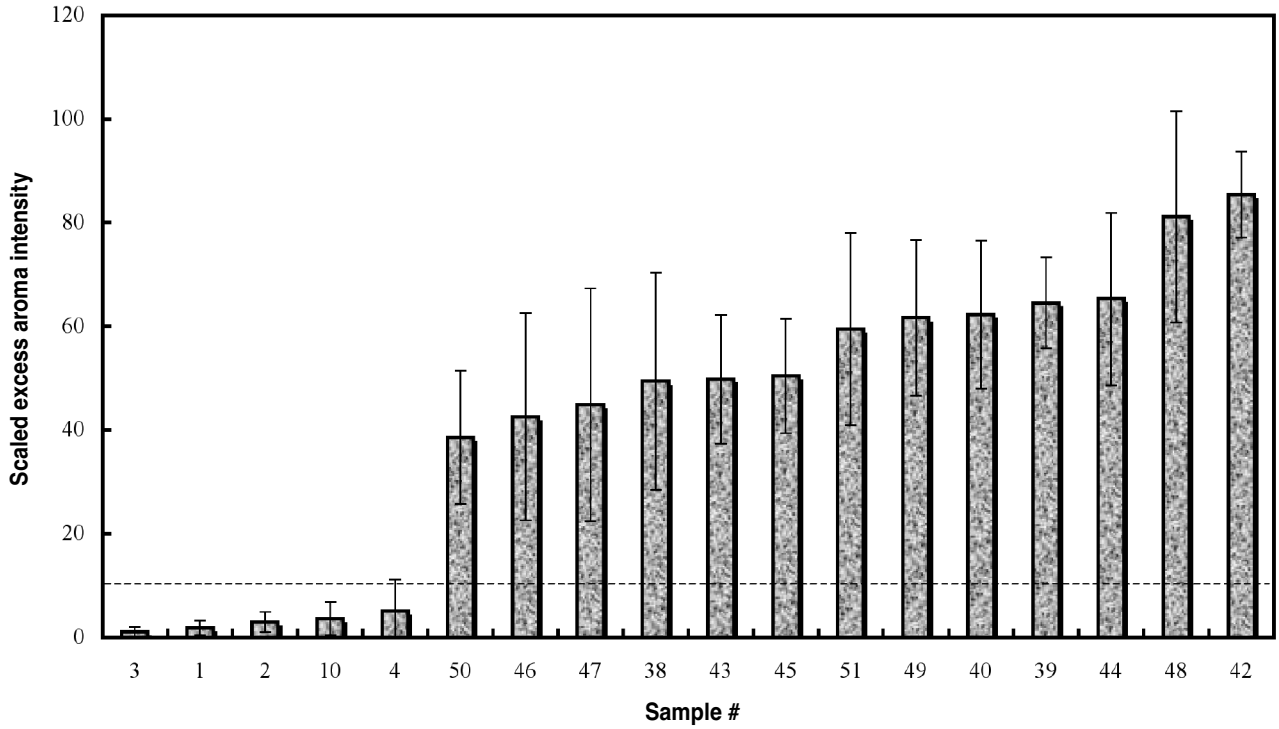

Figure 2. Plot of scaled excess aroma intensity (arbitrary units) versus sample number for Scotch spearmint oils. The dashed line indicates the maximum intensity for a high-quality oil. The error bars are ± one standard deviation. Oil samples 1–4 and 10 were rated high-quality organoleptically.

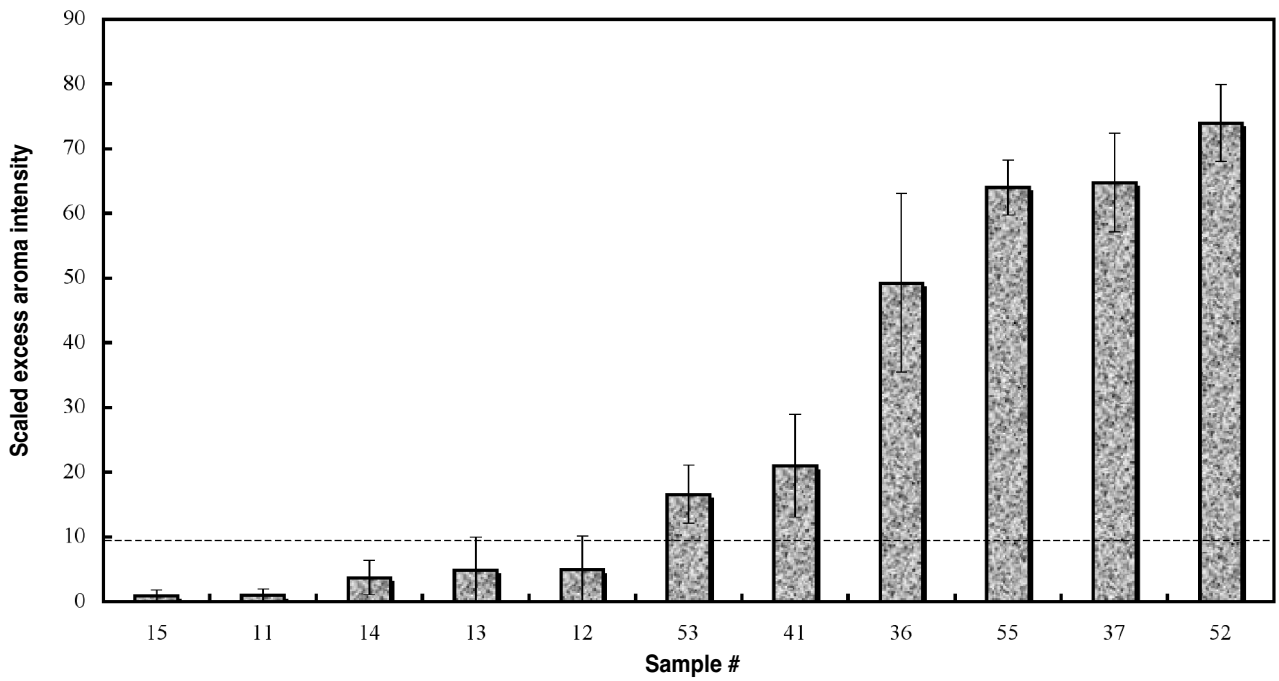

Figure 3. Plot of scaled excess aroma intensity (arbitrary units) versus sample number for Native spearmint oils. The dashed line indicates the maximum intensity for a high-quality oil. The error bars are ± one standard deviation. Oil samples 11–15 were rated high-quality organoleptically.

The calculated scaled excess aroma intensities for the samples are shown in Figures 1–3. The samples in each plot were ordered from lowest to highest intensity. Five samples from each type of oil were organoleptically determined to be of high quality. The dashed line in each figure indicates the maximum value of the scaled excess aroma intensity for a high-quality oil. This maximum was merely the highest value observed for the high-quality-rated oils for each type of oil. Oils with intensities above the maximum were predicted to be of lower quality. For the peppermint oils, samples 5 through 9 were given a high-quality rating. However, samples 16, 18, and 20–22 also have excess aroma intensities within the high-quality range. In particular, sample 21 had a very low intensity but was not rated a high-quality oil. An inspection of the integrated ion count area fractions for this oil relative to other high-quality oils over all 32 compounds would indicate it should be a high-quality oil. This result was potentially because of the compounds in the oil headspace that were not detected by the SPME–GC–MS analysis or simply because of the fact that the assumptions discussed previously are not universally true. Therefore, there may be subtle interactions of the various compounds in the oil headspace that can and probably do affect perceived oil quality. The results for the spearmint oils showed considerable differences between the high- and low-quality oils.

Although reasonable discrimination between high- and low-quality oils was seen in these oil samples, the true test of the technique and model will be its application to larger sample sets that contain a greater concentration variance of the compounds in the oil headspace. This test is currently underway.

Conclusion

We believe that a combination of the organoleptic data and the semiquantitative data from nonequilibrium AUTOSPME on the mint oils in question yields a more robust differentiation of good quality oils versus oils with off-notes than merely screening them organoleptically.

Furthermore, AUTOSPME operated under the nonequilibrated conditions described in this report is a rapid analytical technique. It presents the crude mint oil user with a potentially very useful rapid analytical substantiation of why an oil is considered to be of good quality or not. The main advantage of the technique described is to provide some semiquantitative data in support of the odor-panel screening of mint oils for off-notes. From the data presented in this report we believe that this has been successfully demonstrated.

References

1. J.E. Landing. *American Essence, A History of the Peppermint and Spearmint Industry in the United States*. A.M. Todd Foundation, Kalamazoo Public Museum, Kalamazoo, MI, 1969.
2. W.M. Coleman, III, and B.M. Lawrence. Examination of the enantiomeric distribution of certain monoterpene hydrocarbons in selected essential oils by automated solid-phase microextraction–chiral gas chromatography–mass selective detection. *J. Chromatogr. Sci.* **38:** 95–99 (2000).
3. W.M. Coleman, III, T.A. Perfetti, and B.M. Lawrence. Automatic injection solid-phase microextraction–chiral-gas chromatography–mass selective detection analysis of essential oils. *J. Chromatogr. Sci.* **36:** 575–78 (1998).
4. D. Harmon. Solid-phase microextraction for the analysis of flavors. *Food Sci. Technol.* **79:** 81 (1997).
5. W.M. Coleman, III, and B.M. Lawrence. A comparison of selected approaches to the analysis of an essential oil. *Flav. Fragr. J.* **12:** 1 (1997).
6. M. Keszler, T. Kriska, and A. Nemeth. Mechanism of volatile production during storage of sunflower oil. *J. Agric. Food Chem.* **48:** 5981 (2000).
7. J. Rohloff, E.B. Skagen, A.H. Steen, and T.-H. Iversen. Production of yarrow (*Achillea millefolium* L.) in Norway: essential oil content and quality. *J. Agric. Food Chem.* **48:** 6205 (2000).
8. X. Yang and T. Peppard. Solid-phase microextraction for flavor analysis. *J. Agric. Food Chem.* **42:** 1925 (1994).
9. *Applications of Solid Phase Microextraction*. J. Pawliszyn, Ed. Royal Society of Chemistry Chromatography Monographs, Royal Society of Chemistry, Cambridge, U.K., 1999.
10. R.G. Buttery, R.M. Seifert, D.G. Guadagni, D.R. Black, and L.C. Ling. Characterization of some volatile constituents of carrots. *J. Agric. Food Chem.* **16:** 1005–1009 (1968).
11. G. Takeoka, R.G. Buttery, R.A. Flath, R. Teranishi, E.L. Wheeler, R.L. Wieczorek, and M. Guentert. "Volatile Constituents of Pineapple (*Ananas cosmos* (L.) Merr.)". In *Flavors Chemistry, Trends and Developments*. ACS Symposium Series 338, American Chemical Society, Washington, DC, 1989, pp. 223–34.
12. B.M. Lawrence. Progress in essential oils. *Perfum. Flavor.* **18(2):** 43–57 (1993).
13. B.M. Lawrence. Progress in essential oils. *Perfum. Flavor.* **18(3):** 61–62 (1993).
14. B.M. Lawrence. Progress in essential oils. *Perfum. Flavor.* **18(4):** 59–72 (1993).
15. G. Ohloff. *Scent and Fragrances*. Springer-Verlag, Heidelberg, Germany, 1994, p 62.
16. R.G. Buttery, D.J. Stern, and L.C. Ling. Studies on flavor volatiles of some sweet corn products. *J. Agric. Food Chem.* **42:** 791–95 (1994).
17. R.G. Buttery, L.C. Ling, and D.J. Stern. Studies on popcorn aroma and flavor volatiles. *J. Agric. Food Chem.* **45:** 837–43 (1997).
18. A. Padrayuttawat, T. Yoshizawa, H. Tamara, and T. Tokunaga, Optical isomers and odor thresholds of volatile constituents in *Citrus sudachi*. *Food. Sci. Technol. Int. (Tokyo)* **3:** 402–408 (1997).
19. R.G. Buttery and L.C. Ling. Additional studies on flavor components of corn tortilla chips. *J. Agric. Food Chem.* **46:** 2764–69 (1998).
20. R.G. Buttery, W.J. Orts, G.R. Takeoka, and Y. Nam. Volatile flavor components of rice cakes. *J. Agric. Food Chem.* **47:** 4353–56 (1999).
21. B.M. Lawrence. "Mint Oils of Commerce". In *4th Colloque Produits Natureles d'Origine Vegetale*. G. Collin and F.-X. Garneau, Eds. University of Chicoutimi, Quebec, Canada, 1999, pp. 101–31.
22. R.E. Shirey. Optimization of extraction conditions for low-molecular-weight analytes using solid-phase microextraction. *J. Chromatogr. Sci.* **38:** 109–16 (2000).

Manuscript accepted November 6, 2001.