Application Note

Instrument: Pegasus® BT

Pairing Olfactory Detection with GC-MS to Clarify Identification of Isomers

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Key Words: Olfactory Detection, Stereoisomer Differentiation, GC, TOFMS, Phaser Pro

Introduction

Uncovering information about individual analytes in complex samples is an important part of food, flavor, and fragrance work. This type of information can help with product development, method optimization, and quality control, and it can lead to a better general understanding of samples, processes, or systems. Accurate identification of the individual analytes is an important part of these objectives and gas chromatography with mass spectrometry (GC-MS) is a powerful tool for uncovering this type of information. GC provides separation of the components so that individual analytes within a complex mixture can be determined. Pairing this separation with MS detection often yields tentative identification of these separated analytes. Mass spectral patterns can be matched to library databases, and retention order information can be used to support the identifications through retention index (RI) calculation and subsequent matching of those values to library databases. In many cases, these tentative identifications are reliable and sufficient for answering the analytical questions that are related to the samples. In some cases, though, RI information and MS information may be too similar or vague to distinguish the identification. One situation where this may be observed is with stereoisomers. The structural similarity of stereoisomers often means that they have very similar elution behavior and RI with standard columns, as well as very similar mass spectral patterns, leaving ambiguity in the identification. Distinguishing stereoisomers can be important, however, as they sometimes have distinctly different aroma characteristics. Adding olfactory detection to the GC-MS analysis takes advantage of the different odor characteristics and may be useful to clarify this ambiguity. This combination of analytical tools and the benefits of using them together are demonstrated for the distinction of S-carvone and R-carvone in essential oils in this application note.

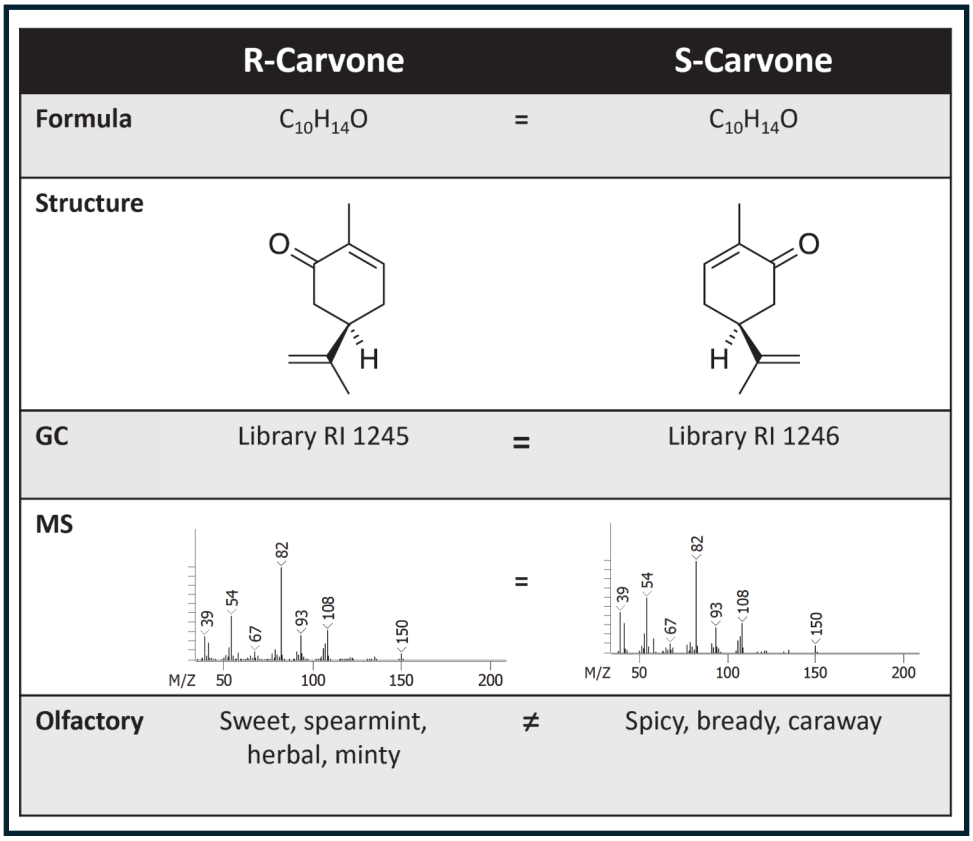

Figure 1. S-carvone and R-carvone have similar GC (with semi-standard non polar columns) and MS behavior, but they have distinct olfactory descriptions. Using GC, MS, and olfactory information together may help clarify which isomer is present in a sample of interest.

Experimental

Caraway and spearmint essential oils were diluted to 1% in acetone and analyzed by GC-MS-O with conditions listed in Table 1. An alkane standard was analyzed with the same analytical conditions for RI determinations.

Table 1. Instrument (*Pegasus* BT) Conditions

Auto Sampler	**LECO L-PAL 3 Autosampler**
Injection	1 µL
Gas Chromatograph	**LECO GC**
Inlet	250 °C
Carrier Gas	He @ 1.4 mL/min
Column	HP-5ms, 30 m x 0.25 mm i.d. x 0.25 µm coating
Temperature Program	40 °C, ramp 10 °C/min to 280 °C
Transfer Line	280 °C
Mass Spectrometer	**LECO *Pegasus* BT**
Ion Source Temperature	250 °C
Mass Range	35-500 m/z
Acquisition Rate	10 spectra/s
Olfactory Device	**GL Sciences Phaser Pro**

Results and Discussion

In many cases, GC and MS combine to give reliable analyte determinations. These tentative identifications can be achieved by matching the observed RI and observed MS spectral patterns to library databases, which is often sufficient to address analytical questions about a sample of interest. In some cases, a confirmed identification may be needed, and this can often be done with analysis of a validated standard or by utilizing high-resolution mass spectrometry. Occasionally, however, the similarities in both RI and spectral patterns can leave ambiguity in the identification, even with analysis of standards or formulae determinations. For example, the isomers R-carvone and S-carvone, shown in Figure 1, are difficult to distinguish. Their chromatographic behavior (on a standard non-polar column) is the same with RI values of 1245 and 1246, respectively. Additionally, their library MS patterns are visually the same and their chemical formula are identical. While these metrics are similar, their aroma contribution to a sample is quite different and confusing one isomer for the other could change conclusions and interpretation of a sample. The addition of olfactory detection can help clarify this ambiguity, as demonstrated with the analysis of caraway and spearmint essential oils, shown in Figures 2 and 3.

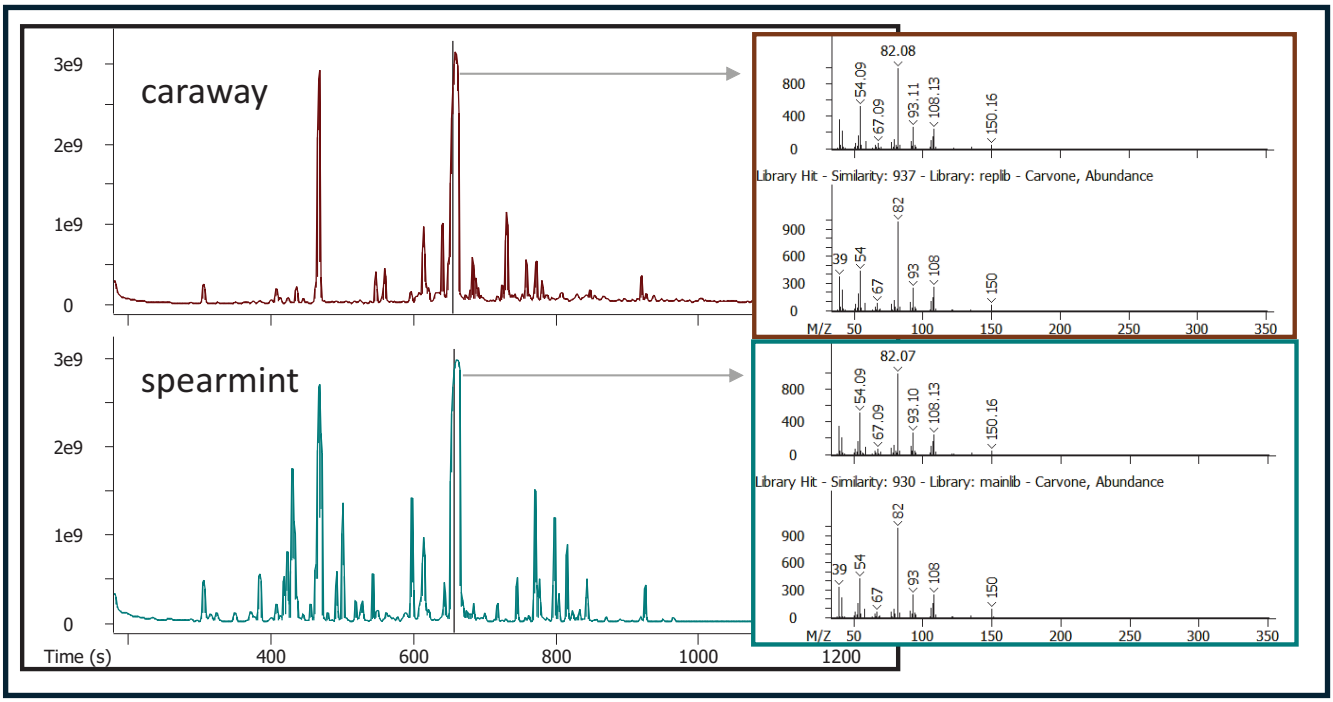

Figure 2. A large peak was observed in both the caraway and spearmint essential oils. Based on RI and MS data, it appeared that both samples had the same analyte, carvone.

TIC chromatograms for spearmint and caraway essential oils are shown in Figure 2. Based on RI data and MS data, the large peak indicated with a vertical line peak marker in each sample appears to be the same. Both peaks match to carvone (CAS 99-49-0) with similarity scores of 937 and 930 for caraway and spearmint essential oils, respectively. The observed RI values, 1253 and 1252 in caraway and spearmint, respectively, agree with each other and with the library value of 1242. By these analytical metrics, it would be reasonable to conclude that both samples contain the same analyte.

With GC-MS-O, however, the effluent splits at the end of the column to both the MS and to an olfactory port leading to better insight to the sample. Splitting to the olfactory port allows the analyst to sense olfactory notes concurrent with the MS acquisition.

As shown in Figure 3, this revealed a clear difference between the samples. The observed olfactory notes for the peak in the caraway essential oil were of caraway or rye, while the observed olfactory notes for the peak in the spearmint sample were minty. These features were not distinguishable by RI or MS information with this stationary phase, but the olfactory data was distinctly different and provided information to update the library hits to a specific, and different, isomer of carvone in each sample. The updated identifications are R-carvone (CAS 6485-40-1) for spearmint, with a similarity score of 928 and observed RI of 1252 compared to library RI of 1245, and S-carvone (CAS 2244-16-8) for caraway essential oil, with a with a similarity score of 928 and observed RI of 1253 compared to library RI of 1246.

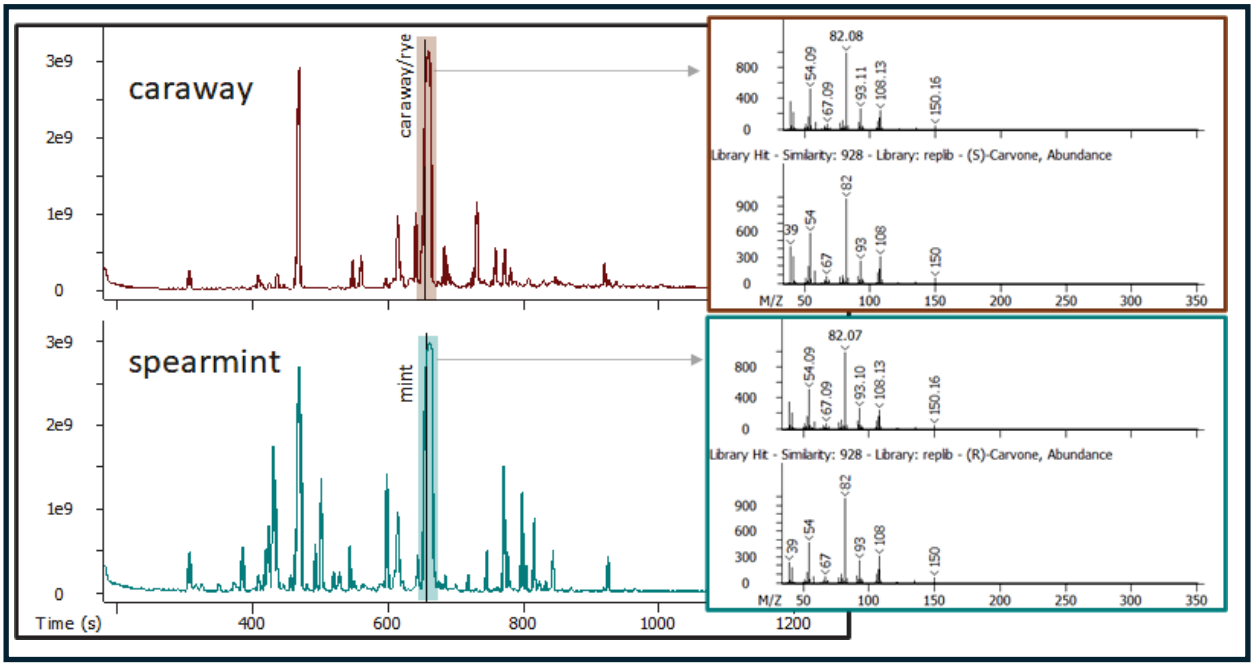

Figure 3. Olfactory data is distinctly different for these peaks in each sample clarifying the identifications as specific isomers.

Conclusion

In this work, we demonstrate how the use of GC, MS, and olfactory detection can combine to add clarity to analyte identifications. GC separates analytes within a complex mixture and provides elution information to support identifications. MS data can be library searched for tentative identifications. In instances of ambiguity, olfactory detection may add clarity to the identification as demonstrated with S-carvone and R-carvone in caraway and spearmint essential oils. Combining these complementary analytical tools leads to a better understanding of your sample.

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