Quantification of Contact Allergens in Personal Care Products with GC and Full Mass Range TOFMS

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Key Words: Pegasus HT, Full m/z Range Acquisition, TOFMS, Deconvolution, Calibration

1. Introduction

Many cosmetic and personal care products contain fragrances and other analytes that can be allergens or irritants for some consumers. Manufacturers are often asked to provide information on the composition of their product, including potential allergens, to be compliant with various regulations. In particular, the European Cosmetics Directive has 26 regulated contact allergens that must be reported if present in a product above certain levels. Gas chromatography (GC) paired with mass spectrometry (MS) is well-suited to screen for these target allergens and is commonly used, often with selected ion monitoring (SIM) detection. Here, we highlight the benefits of full mass range acquisition with TOFMS for this application. TOFMS provides a solution to coeluting peaks, which is common and can cause confusion when targeting analytes within a matrix. Calibration data for regulated analytes, as well as representative examples of product screening for quantification of these analytes are demonstrated with LECO's Pegasus® HT GC-TOFMS. The *Pegasus* HT's full mass range sensitivity and speed with unparalleled deconvolution capabilities allow you to see peaks that may be hidden in a standard analysis.

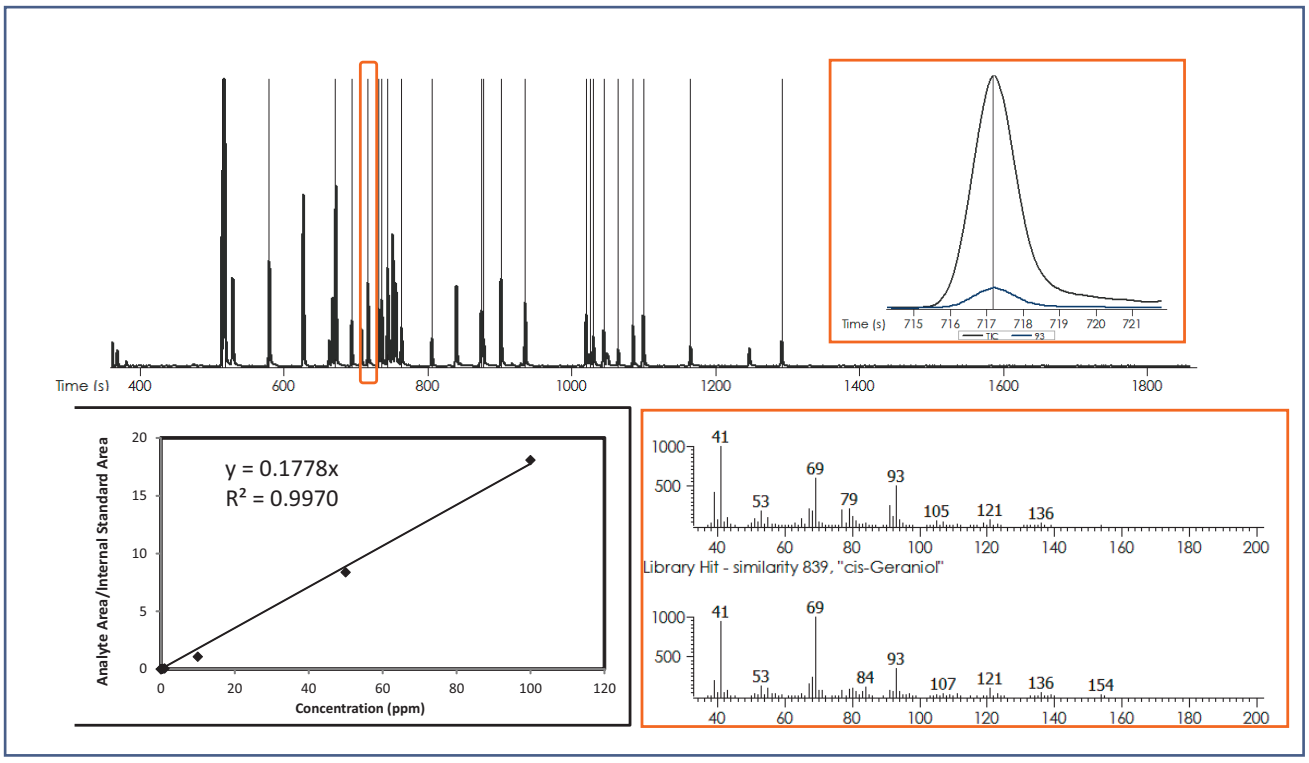

Figure 1. GC-TOFMS data were collected for an allergen standard, containing 24 of the regulated analytes. Allergens are indicated in the standard with vertical line peak markers, and geraniol is shown as a representative example. The peak profile, mass spectral information, and calibration data are compiled. Calibration equations for all analytes were determined with automated data processing, and can also be applied to subsequent unknown samples in an automated way.

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2. Experimental

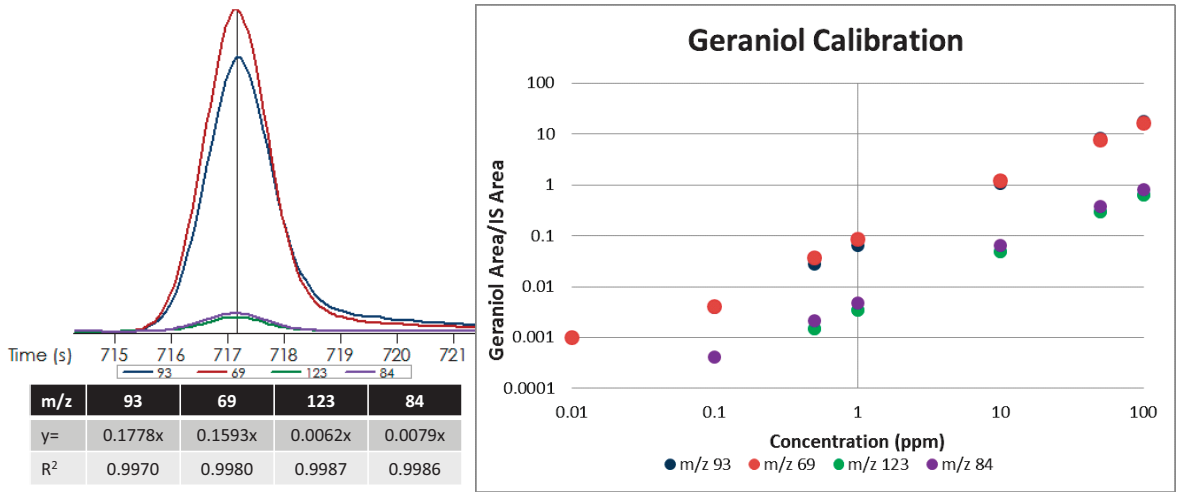
A set of calibration standards were prepared through serial dilutions of a fragrance allergen standard (Restek) in isooctane at concentrations of 10 ppb to 100 ppm. A perfume sample, characterized as a "leave-on" personal care product, was diluted 100x prior to analysis in order to be within the calibration range. Analytical conditions are listed in Table 1.

Table 1. GC-TOFMS (*Pegasus* HT) Conditions

Gas Chromatograph	**Agilent 7890 with MPS2 Autosampler**
Injection	1 µL splitless with inlet @ 250°C
Carrier Gas	He @ 1.4 ml/min, Constant Flow
Column	Rxi-5ms, 30 m x 0.25 mm i.d. x 0.25 µm coating (Restek)
Oven Program	2 min at 40°C, ramped 10°C/min to 280°C, held 5 min
Transfer Line	280°C
Mass Spectrometer	**LECO *Pegasus* HT**
Ion Source Temperature	250°C
Mass Range	33-500 m/z
Acquisition Rate	15 spectra/s

3. Results and Discussion

All target analytes, indicated with vertical line peak markers in Figure 1, were observed in the standard and identified through ChromaTOF® brand software's automated peak finding. Calibration data were compiled, and geraniol is shown as a representative example. The calibration range for all other standards was from low levels of 10 or 100 ppb (analyte dependent) through 100 ppm with an average R^2 of 0.9909, demonstrating the ability of the *Pegasus* HT to detect and quantify the known allergen standards at the necessary levels. These target analyses are often done with SIM detection, which may introduce the risk of skewed concentrations when unexpected or unknown interferences that contain shared m/z are present. Here, we present an example where the collection of only SIM data would lead to confusing and inconsistent concentration information due to an interference from the matrix that shares m/z with the target analyte. Full mass range TOFMS data were necessary to both recognize the interference and to accurately determine the concentration of geraniol, a regulated contact allergen.



m/z	93	69	123	84
y=	0.1778x	0.1593x	0.0062x	0.0079x
R^2	0.9970	0.9980	0.9987	0.9986

Figure 2. Geraniol is chromatographically isolated in the allergen standard and several m/z are unique and appropriate for determining calibration equations. m/z 93, 69, 123, and 84 are all free from interferences and provide reliable calibration information. SIM methods often suggest m/z 93, 69, and 123 for this analyte.

In the allergen standard, geraniol is chromatographically separated from all other allergen standards, and calibration equations can be determined using several different individual m/z. In Figure 2, XIC for m/z 93, 69, 123, and 84 are shown and all are free from interferences. Thus, all provide good calibration equations and R^2 values, with the major difference being the lowest detectable level due to differences in spectral intensity per m/z. When geraniol is targeted in a sample, however, a coelution from the matrix is observed. With full mass range data acquisition and *ChromaTOF's* deconvolution capabilities, this coelution is readily determined, as shown in Figure 3.

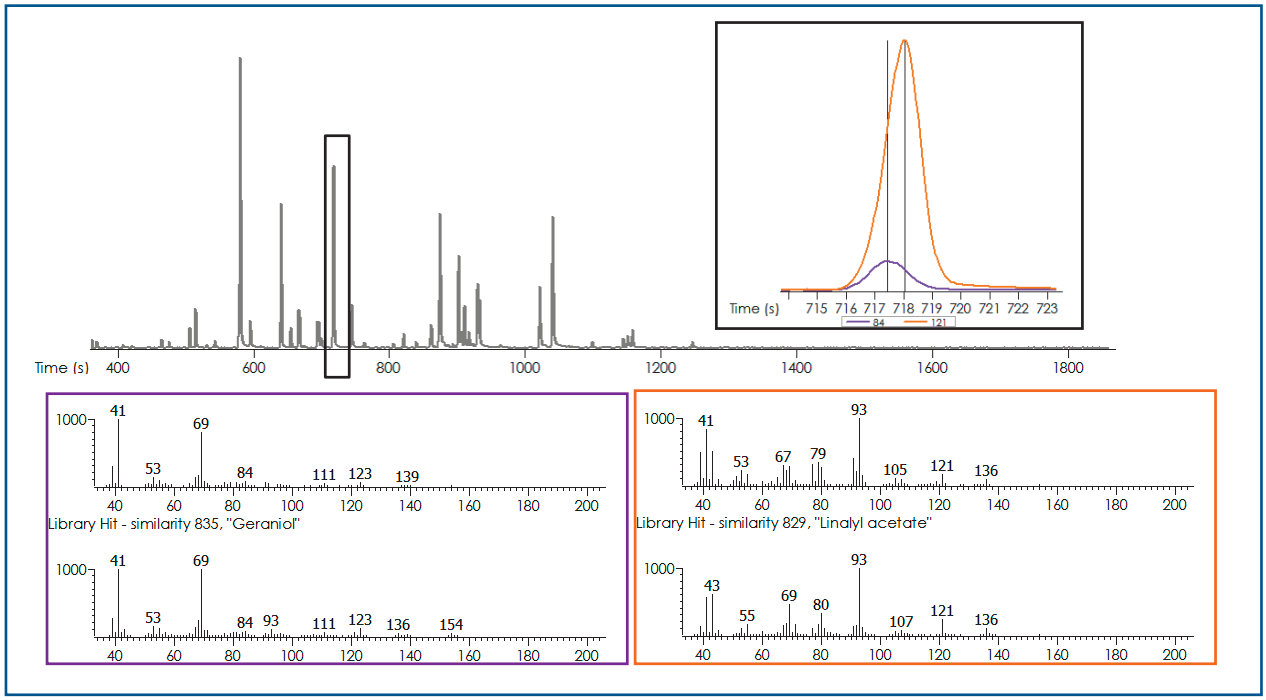


Figure 3. Geraniol, a target allergen, coelutes with a matrix analyte, tentatively identified as linalyl acetate. ChromaTOF's deconvolution capabilities mathematically separates this coelution and provides pure spectra and pure peak profiles for each analyte. There are several shared m/z between these analytes.

The coelution, tentatively identified as linalyl acetate, shares the recommended target analyte SIM m/z 93 and 69 (as well as numerous other m/z). If the quantification is done with an m/z that is shared between the analytes, the determined concentrations are over-reported due to the contribution of the interference for that particular m/z, as shown in Figure 4. If only the SIM data were collected, it may be difficult to note the presence of the interference and it may not be possible to select a different m/z unique to the target analyte for accurate quantification without the acquisition of additional data.

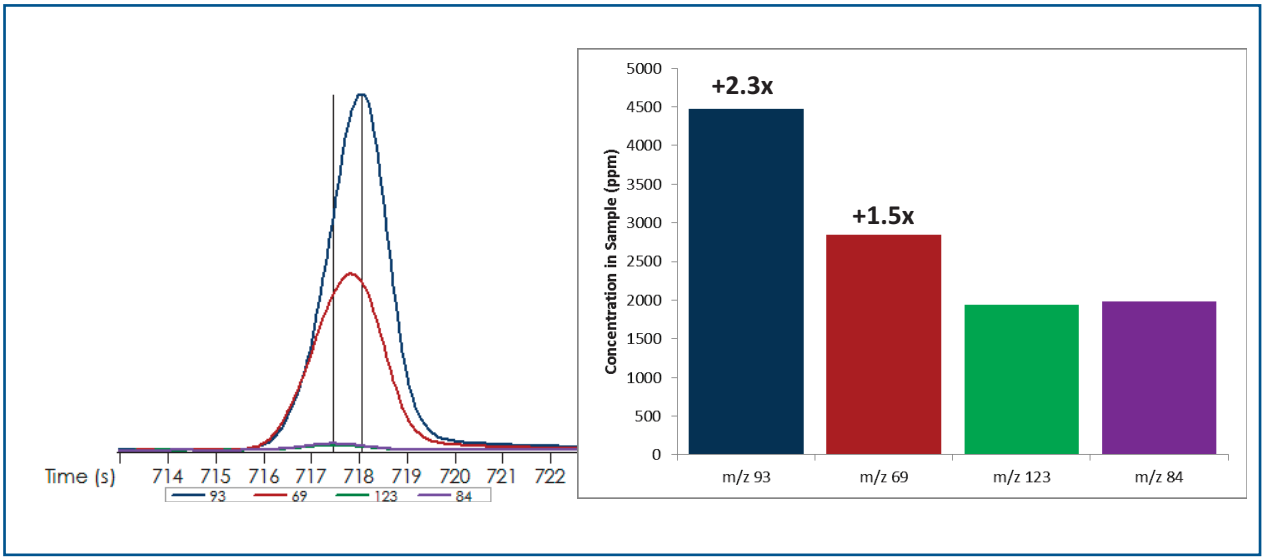


Figure 4. The target allergen and the coelution share multiple m/z, including m/z 93 and 69 that are recommended SIM masses. If quantification is done with these m/z, the reported concentration is skewed by the contribution of the matrix interference. m/z 123 and 84 have less interference from the coelution and provide more reliable quantification information.

Delivering the Right Results

4. Conclusion

This study demonstrates the benefits of LECO's *Pegasus* HT GC-TOFMS to provide targeted screening for contact allergens within a complex personal care product. Calibration data for regulated analytes, as well as representative examples of product screening for quantification of these analytes were demonstrated. The need for full mass range acquisition and deconvolution even in a targeted analysis are highlighted and provide the ability to retrospectively analyze a sample to see what you are missing without repeating injection. The need for these capabilities is demonstrated through the skewed concentrations that would be determined for the target analyte, geraniol, when a matrix coelution with shared m/z is present.

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