# How Can We Improve Number of Compounds Found by Deconvolution in One Essential Oil Sample with GCMS?

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## Introduction

Chemists in the essential oil industry need to know as much as they can about the identity of compounds that comprise their essential oils. When packed columns were commonly used in gas chromatography, one could routinely separate up to 100 compounds. Today, with long silica capillary columns in a GC with mass spectrometry one can easily separate more than 400 chemical components in an essential oil. Yet even with very long, narrow bore capillary columns and a very slow temperature gradient, one still encounters compounds that elute together, resulting in mixed spectra that do not produce a good library match. This problem can be solved with software tools that deconvolute individual spectra from a co-elution. In this study we will show the effect of a number of GCMS method parameters, like split ratio, oven ramp, and MS acquisition rate, as well as some deconvolution parameters, on the number of compounds successfully identified for the same essential oil sample.

## Experimental

For this study we use a GCMS 7890/5977 equipped with CTC PAL 3

The sample was Dolce Vita (Eau de Toilette) from Dior without dilution

Capillary column: 30m x 0.25mm x 0.25µm DB-5MS Ultra Inert (19091S-433)

Injector: split/splitless at 250 °C, injection volume 1 µl, liner for split, split ratio variable. We used split ratios of 200:1, 400:1 and 600:1

Column flow: 1.2 ml/min with helium at constant flow

Oven: 35 °C for 1 min then a linear ramp until 300 °C without hold. We tested oven ramps of 2, 5 and 10 °C/min.

Auxiliary Interface: 300 °C

MSD: EI Ultra Inert source at 300 °C, mass range 33 – 450 amu, threshold 50 and acquisition rate variable. We tested acquisition rates from 0.2 scans/sec to 16.1 scans/sec

Data acquisition and processing: For data acquisition, Masshunter GCMS Acquisition B.07.02; for Qualitative processing, Masshunter Qualitative Analysis B.07.00; and for deconvolution, Masshunter Unknowns Analysis B.07.01

## Experimental

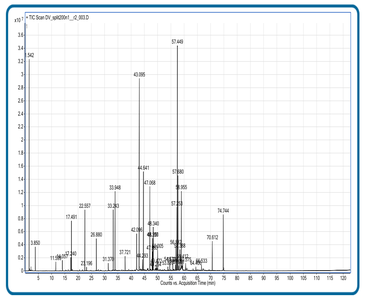

**Figure 1:** Chromatogram of Dolce Vita (Eau de Toilette) with an oven ramp of 2 °C/min and a split ratio of 200:1

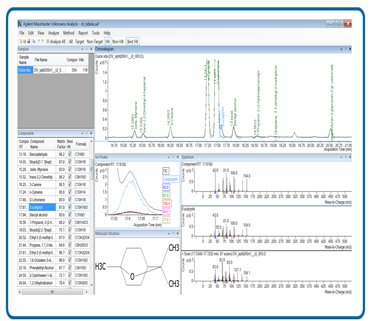

**Figure 2:** Masshunter Unknowns Analysis software used for deconvolution and search against the NIST library to generate a list of components and library hits

## Results and Discussion

Our first approach was to compare the same sample of Dolce Vita essential oil with three different oven ramp rates: 2, 5 and 10 °C/min. All conditions for these 3 analyses were the same, with a split ratio of 400:1. After analysis, we integrated all peaks with Masshunter Qualitative software to determine how many components could be enumerated for each oven ramp. Then, using Masshunter Unknowns software we did deconvolution to repeat the process for each oven ramp. After that, comparing with the NIST library we found hits for components with match factor higher than 60%. Figure 3 shows the chromatograms and Table 1 shows how many components were found for the 3 oven ramps. The greatest number of components and hits was found with the 5°C/min ramp.

Our next experiment was with split ratios of 200, 400 and 600:1. All other GCMS conditions were the same for these 3 analyses. Figure 4 shows the chromatograms and Table 2 shows how many components were found with regular integration in Qualitative software, and with deconvolution, followed by the number of NIST library hits. Using the same deconvolution process, we found more hits when we used a 200:1 split.

The data acquisition rate should always be sufficient to define the chromatographic peak, especially for quantitative analysis. To study the effect of data rate on this type of qualitative analysis, we acquired data at scan rates of 0.2, 0.5, 0.9, 1.8, 3.5, 6.5, 11.4 and 16.1 scans/sec. With Masshunter Qualitative Analysis, we integrated all peaks to enumerate the number of components. We then used deconvolution to find components and hits from the NIST library. Table 3 shows the number of components for integration, deconvolution and library hits. In the same table, we show the library match score, as a function of scan rate, for a component that elutes at 19.5 minutes. Figure 5 graphically illustrates the effect of the acquisition rate on the observed chromatographic peak shape.

In Masshunter Unknowns software, there are several parameters a user can set that affect the deconvolution results, including the number of components identified. The most important parameter to set correctly is the RT window. It is a relative parameter that defines how wide a chromatographic peak is assumed to be. If this value is set below 100 (narrower), more components will be reported, but that number may include repeats of the same component. If this value is set above 100 (wider), some narrow component peaks may be missed. Table 4 shows how the number of components and library hits varied as a function of the RT window value in this analysis.

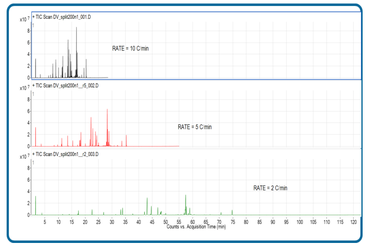


**Figure 3:** Chromatogram of the same essential oil using different oven ramp rates: 2, 5 and 10 °C/min

| Oven ramp | integration | deconvolution | hits | run time |
|---|---|---|---|---|
| 10 | 222 | 244 | 171 | 28 |
| 5 | 235 | 251 | 181 | 55 |
| 2 | 226 | 242 | 173 | 128 |

**Table 1:** Number of components and hits found when the GC oven ramp rate was changed

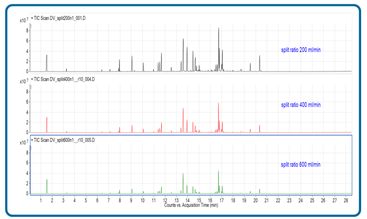


**Figure 4:** Chromatogram of the same essential oil using different split ratios at injection: 200, 400 and 600:1.

## Results and Discussion

| split | integration | deconvolution | hits |
|---|---|---|---|
| 200 | 222 | 244 | 171 |
| 400 | 183 | 190 | 142 |
| 600 | 178 | 183 | 134 |

**Table 2:** Number of components and library hits found when the split ratio at injection on GCMS was changed

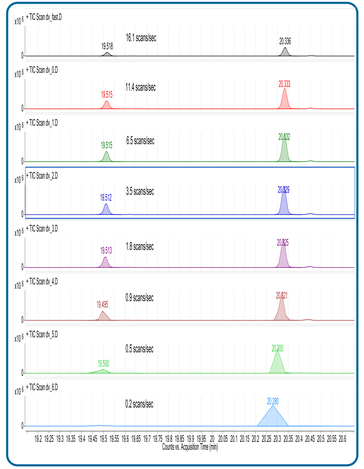


**Figure 5:** Chromatogram of the same essential oil at different scan acquisition rates

| acquisition time | integration | deconvolution | hits | NIST match -19.5 min |
|---|---|---|---|---|
| 16.1 scans/sec | 135 | 149 | 83 | 804 |
| 11.4 scans/sec | 141 | 209 | 105 | 919 |
| 6.5 scans/sec | 142 | 260 | 126 | 923 |
| 3.5 scans/sec | 141 | 281 | 149 | 933 |
| 1.8 scans/sec | 126 | 321 | 146 | 937 |
| 0.9 scans/sec | 83 | 301 | 137 | 940 |
| 0.5 scans/sec | 51 | 242 | 95 | 881 |
| 0.2 scans/sec | 24 | 159 | 61 | 674 |

**Table 3:** Number of components and library hits found when the scan acquisition rate was changed

| RT window | deconvolution | hits |
|---|---|---|
| 50 | 560 | 258 |
| 100 | 242 | 173 |
| 150 | 190 | 141 |

**Table 4:** Number of components and library hits found with Masshunter Unknowns Analysis software used for deconvolution and search against the NIST library for different values of the RT window parameter

## Conclusions

This study shows that, for the case of this sample and this analysis, a deconvolution software tool provides greater gains in the number of compounds enumerated than a long oven ramp aimed at decreasing the number of coelutions. The number of components found also increased as the split ratio decreased, though care should be taken not to overload the column, which would result in poor peak shapes. Scanning faster is not always better; a compromise exists between high speed for good chromatographic peak shape and low speed for better quality spectra. Finally, the RT window parameter is critical. Use of a low value and review of the results to eliminate duplicates may provide the best results.