

Fast Screening for Allergenic Compounds in Perfume Samples Using GC-TOFMS

LECO Corporation; Saint Joseph, Michigan USA
Sjaak de Koning; LECO European Technical Centre, Germany

Key Words: GC-TOFMS, Fragrance

1. Introduction

Many products used daily such as perfumes, housekeeping chemicals, cosmetics, etc., contain fragrances. Some of the fragrance compounds can cause allergic reactions on the human body. Starting in 2004 a new law will describe the use of 24 allergenic fragrance compounds. Because of this law, producers of mentioned products and controlling laboratories will need a fast and reliable method to test for these allergens.

Time-of-flight mass spectrometry (TOFMS) offers advantages for such a purpose. This technology allows full-scan screening with an extraordinarily high acquisition rate (up to 500 spectra/second) and sensitivities that scanning instruments can only achieve using single-ion-monitoring (SIM) mode. Additionally, intelligent software algorithms perform automatic data processing, looking for all present compounds in a given chromatogram while mathematically separating spectra of coeluting peaks. From this, analytes masked by matrix components can be easily identified and accurately quantified.

In this application note, a target screening method for the determination of several allergenic compounds in multiple perfumes is presented. The run time of the GC separation was less than 13 minutes.

In parallel, other compounds not present in the list of target compounds but present in the sample can generally be identified by standard library searching of the deconvoluted spectra. Thus, a target analysis is always combined with a sensitive full mass-range data acquisition.

2. Experimental Conditions

GC-Parameters: Agilent 6890
Column: DB-1ms; 20 m x 0.18 mm x 0.18 μ m
Injector Temp: 280°C
Injection: 1 μ l, split ratio 1:100
Oven Program: 60°C for 0 minutes, to 280°C at 20°C/minute
Flow Rate: 1 ml/minute Helium at constant flow
MS-Parameters: Pegasus® III GC-TOFMS
Mass Range: 10 to 450 amu
Acquisition Rate: 20 spectra/second
Ion Source Temp: 200°C
Transfer Line Temp: 250°C

Sample Preparation

Perfume oils were 10 to 100 times diluted in ethanol.

3. Results

A standard mixture containing several allergenic compounds was taken. A chromatogram of a standard mixture at 500 ppm is shown in Figure 1.

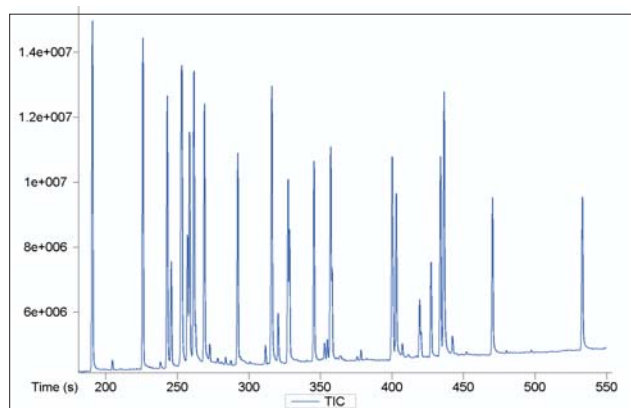


Figure 1. Total-ion-current (TIC) chromatogram of allergenic compounds at 500 ppm.

All allergenic compounds shown in Figure 1 were calibrated in the range of 1 to 1000 ppm. Calibration curves, as shown for Geranial in Figure 2, were automatically constructed by the LECO ChromaTOF® software. The calibration data of all compounds is listed in Table 1.

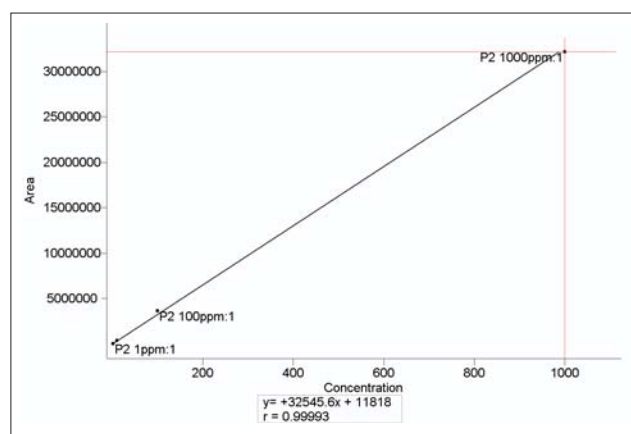
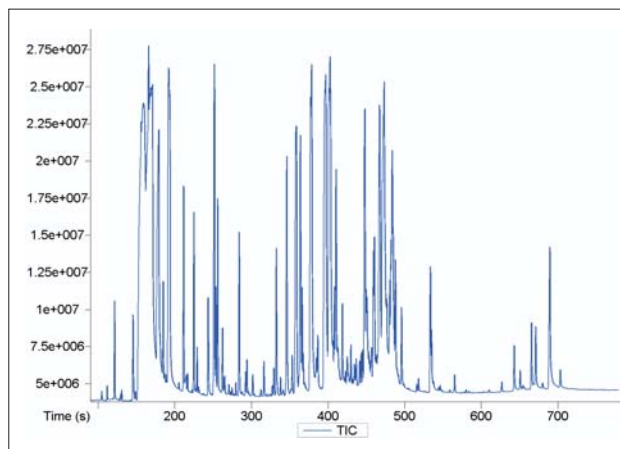


Figure 2. Calibration plot for Geranial in the range of 1 to 1000 ppm.

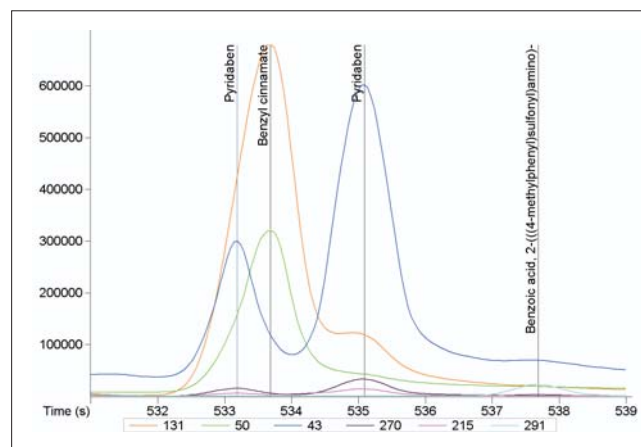
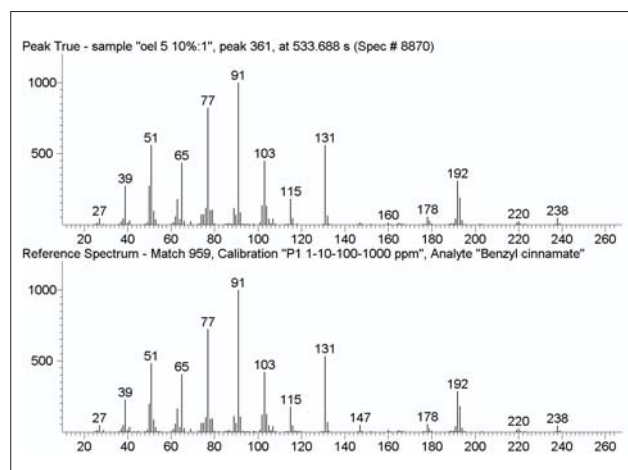
Table 1. Calibration data for selected allergenic compounds.

Name	Absolute R.T. (s)	Masses	Corr. Coeff.
Benzyl alcohol	157.4	108	0.9994
Limonene	165.5	68	0.9984
Linalool	190.4	71	0.9994
Methyl 2-octynoate	225.9	66	0.9993
Citronellol	242.9	69	0.9994
Nerol	243.5	69	0.9991
Neral	245.8	94	1.0000
Cinnamic aldehyde	252.5	131	1.0000
Geraniol	253.2	41	0.9994
Geranial	257.1	69	0.9999
p-Anisyl alcohol	258.2	138	1.0000
Hydroxycitronellal	261.4	59	0.9998
Cinnamic alcohol	268.7	92	0.9999
Eugenol	292.2	164	1.0000
Coumarin	315.7	118	0.9999
Isoeugenol	327.3	164	1.0000
à Isomethyl ionone	345.6	135	0.9999
Lilial	357.1	189	0.9999
à-Amylcinnamic aldehyde	400.1	129	1.0000
Lylal	400.6	59	1.0000
Lylal:2	402.9	136	1.0000
à-Amylcinnamic alcohol	413.0	115	1.0000
Farnesol	419.4	81	1.0000
Farnesol:2	427.3	69	1.0000
Hexyl cinnamic aldehyde	433.8	129	1.0000
Benzyl benzoate	436.2	105	1.0000
Benzyl salicylate	470.2	91	1.0000
Benzyl cinnamate	533.1	131	0.9999

The calibration data from Table 1 were used for quantitative screening of unknown samples. Figure 3 shows the TIC chromatogram of a typical perfume oil 10 times diluted prior to injection. The listed compounds are automatically searched, identified and quantified (see Table 2 for analysis data). As can be expected from such a chromatogram where many compounds coelute, data processing is usually very difficult and time consuming. The Automatic Peak Find and Deconvolution algorithm of the ChromaTOF software accomplishes the difficult tasks in only a short period of time. Figure 4 shows the peak of benzyl cinnamate coeluting with other compounds. The deconvoluted mass spectrum of this compound, compared to the Reference mass spectrum, is shown in Figure 5.


Figure 3. TIC chromatogram of a typical perfume oil diluted 10 times.
Table 2. Analytical data of a typical perfume oil.

Name	R.T. (s)	Concentration (ppm)	Match
Benzyl alcohol	158.0	37	913
Limonene	165.7	410	946
Citronellol	243.4	580	970
Geraniol	253.6	390	984
Hydroxycitronellal	262.3	250	989
Eugenol	292.5	115	990
Coumarin	316.3	110	966
à Isomethyl ionone	346.1	1700	983
à-Amylcinnamic alcohol	413.5	18	808
Hexyl cinnamic aldehyde	434.2	56	896
Benzyl benzoate	436.8	110	987
Benzyl cinnamate	533.7	940	959


Figure 4. Multiple coelution of benzyl cinnamate.

Figure 5. Deconvoluted (top) and Reference (bottom) mass spectra for benzyl cinnamate.

4. Conclusions

The described work demonstrates the use of GC-TOFMS for the target screening of allergenic compounds in perfume. The use of TOFMS in this work is an innovative approach, which demonstrates a number of advantages over other types of mass spectrometers.

The power of the Pegasus III GC-TOFMS lies in its automated data handling. Peak finding, deconvoluted spectrum determination, qualification, and quantification are all automatically performed, even when peaks are below the base line of the TIC. This is all possible due to the high degree of spectral continuity as well as the large data density provided by the fast acquisition rate of TOFMS.



LECO Corporation • 3000 Lakeview Avenue • St. Joseph, MI 49085 • Phone: 800-292-6141 • Fax: 269-982-8977
info@leco.com • www.leco.com • ISO-9001:2000 • No. FM 24045 • LECO is a registered trademark of LECO Corporation.