Rapid Determination and Quantification of Sensitizers and Skin Irritants in Fragrances by GC-TOFMS

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Key Words: GC-TOFMS, Quantification, Rose Oil

1. Introduction

Fragrances have been used for centuries for medicinal, religious, and ceremonial purposes. Scented oils were used by the elite and rich to enhance beauty or as a symbol of status. In the past, fragrances were mainly obtained from plant and animal sources. Modern fragrances, however, are manufactured primarily from synthetic materials.[1]

A number of the synthetic materials used in modern perfumes have been shown (as stated in their respective MSDS) to be respiratory and skin irritants, respiratory and skin sensitizers, possible carcinogens, and even possible hormone disrupters. In this application, a common fragrance was rapidly analyzed using the Pegasus® GC-TOFMS platform so that a number of these offending analytes could be quantified. Calibration curves were made to obtain reliable results on the quantities of these analytes in the perfume.

Target Compounds

Methyl Eugenol	Methyl Chavicol
Benzyl Alcohol	Cinnamyl Alcohol
Eugenol	Isoeugenol
Benzyl Salicylate	Cinnamaldehyde
Coumarin	Linalool
Benzyl Benzoate	Citronellol
Limonene	BHT

2. Experimental Conditions

GC-Parameters: Agilent® 6890 (EPC Mode)

Column:
DB-WAX; 10 m x 0.18 mm x 0.33 µm film
Injector Temperature: 250°C
Split Ratio: 10:1
Oven Program:
40°C for 0.5 minute to 250°C at 60°C/minute, hold 0.75 minute
Flow Rate:
Constant flow at 2.0 ml/minute
Transfer Line: 240°C

MS-Parameters: Pegasus II GC-TOFMS (EI Mode)

Mass Range: 35 to 400 amu
Acquisition Rate: 50 spectra/second
Source Temperature: 200°C
Acquisition Time: 4.75 minutes

3. Results and Discussion

Calibration samples were prepared by dissolving the pure materials (shown in the target list) in ethyl acetate solvent. A four-point calibration, ranging from 200 ppb to 200 ppm, was generated using the method listed above. Good response and linearity was observed for all the analytes in the list, as demonstrated by their regression coefficients.

Figure 1 shows a chromatogram of the reference material at the 2.0 ppm level with its peak table (Table 1). Two of the calibration plots are shown in Figure 2.

When quantification is requested, three parameters must be specified for the quantification to be successful. First, a retention time deviation has to be set. This specifies the vicinity where the peaks are to be found. Second, a spectral match factor must be specified that shows how well the spectra of the analyte matches the reference. Third, a signal-to-noise (S/N) threshold is specified that instructs the software to ignore peaks below that threshold.

A common rose oil fragrance was analyzed in less than 5 minutes and processed against the calibration curves previously established to quantify the analytes of interest. The chromatogram for the rose oil is shown in Figure 3 along with a quantification table (Table 2) for the analytes of interest. As the peak table shows, two peaks in the target list were not present in the rose oil. The rose oil sample was processed using a S/N rejection ratio of 50:1. This means that peaks with S/N ratios of lower than 50:1 are ignored by the processing algorithm. The Peak Find algorithm identified 201 analytes and any coelution was deconvoluted away from the target analyte spectra to prevent matrix masking effects.

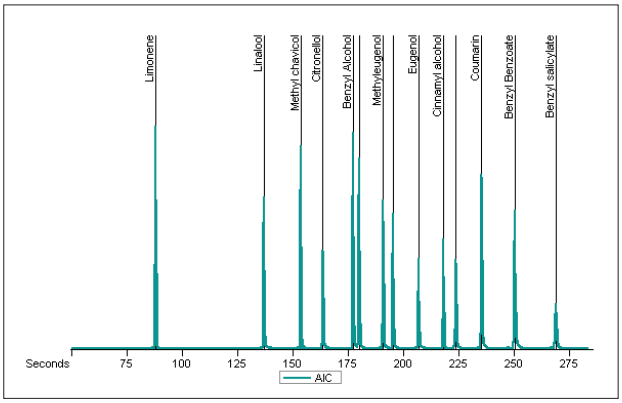

Figure 1. Chromatogram of 2.0 ppm Standard Sample.

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Table 1. Peak Table for Quantification Analytes.

PEAK #	NAME	R.T.	QUANT MASS
1	LIMONENE	88.24	68
2	LINALOOL	137.1	71
3	METHYL CHAVICOL	153.78	148
4	CITRONELLOL	163.84	67
5	BENZYL ALCOHOL	177.4	79
6	BUTYLATED HYDROXYTOLUENE	180.18	205
7	METHYLEUGENOL	191.06	178
8	CINNAMALDEHYDE	195.48	131
9	EUGENOL	207.06	164
10	CINNAMYL ALCOHOL	218.3	134
11	ISOEUGENOL	223.96	164
12	COUMARIN	235.56	118
13	BENZYL BENZOATE	250.56	105
14	BENZYL SALICYLATE	269.14	91

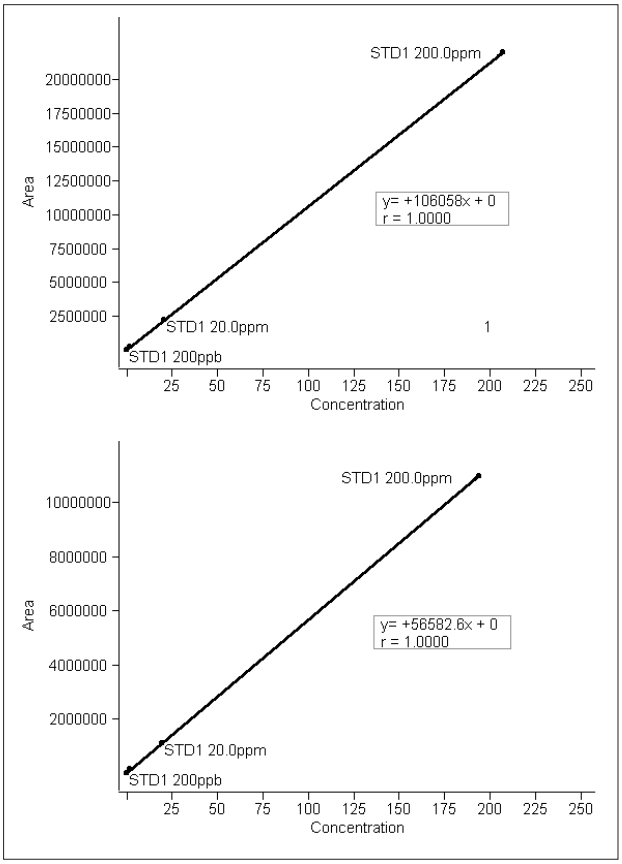

Figure 2. Calibration Plots for Limonene and Linalool (200 ppb to 200 ppm).

The rose oil fragrance sample illustrates the advantages of the Pegasus platform in analyzing complex samples using the spectral continuity generated by TOF instruments. Since the ion ratios for a given peak do not change across the peak, spectral deconvolution can be used to extract the spectrum of coeluting peaks using the unique software algorithm in LECO's ChromaTOF® package.

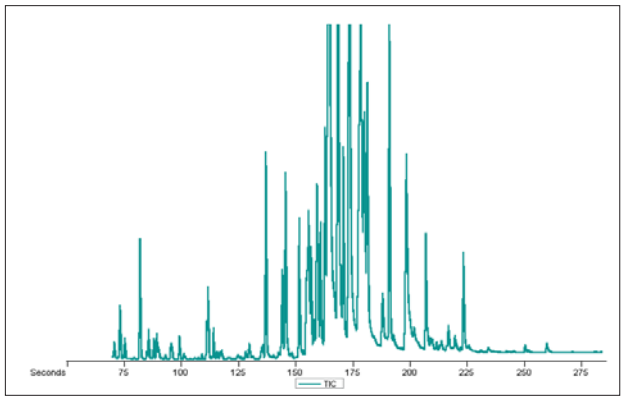

Figure 3. Chromatogram of Rose Oil Fragrance.

Table 2. Target Analytes in the Rose Oil Fragrance.

PEAK #	NAME	R.T.	QUANT MASSES	CONCENTRATION	MATCH	QUANT S/N	AREA
9	D-LIMONENE	88.06	68	9.70 NG/µL	976	970.71	1,024,800
50	Á-LINALOOL	137.08	71	151.94 NG/µL	974	3855.1	8,597,600
	METHYL CHAVICOL	153.68	148	NOT FOUND			
91	CITRONELLOL	164.26	69	OUT OF CALIBRATION RANGE: 989.24 NG/µL	910	3660.8	51,197,000
114	BENZYL ALCOHOL	177.36	79	3.81 NG/µL	818	282.29	473,250
	BUTYLATED HYDROXYTOLUENE			NOT FOUND			
138	METHYLEUGENOL	191.08	178	254.15 NG/µL	960	42802	14,688,000
142	CINNAMALDEHYDE	195.40	131	0.64 NG/µL	856	157.08	57,549
154	EUGENOL	207.00	164	110.16 NG/µL	966	19638	4,921,400
174	CINNAMYL ALCOHOL	218.18	92	0.58 NG/µL	825	18.115	22,531
	ISOEUGENOL			NOT FOUND			
190	COUMARIN	235.42	118	0.50 NG/µL	813	171.53	71,934
194	BENZYL BENZOATE	250.46	105	6.31 NG/µL	949	471.48	1,134,600
198	BENZYL SALICYLATE	269.06	91	0.45 NG/µL	810	21.2	67,202

Figure 4 shows a coelution of benzyl alcohol with nonadecane, where the nonadecane is at a very high concentration relative to the benzyl alcohol. The benzyl alcohol is below the TIC and under the canopy of the nonadecane, yet the software is able to detect the benzyl alcohol peak and extract the spectrum for good library matching and quantification. The benzyl alcohol spectrum is shown in the insert.

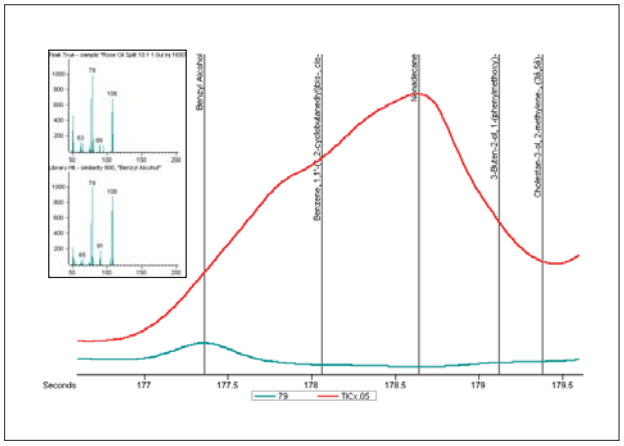

Figure 4. Coelution of Benzyl Alcohol with Nonadecane.

4. Conclusions

This application note shows that suspected skin and respiratory sensitizers found in common fragrances can be accurately quantified in less than 5 minutes. The Pegasus GC-TOFMS platform is ideally suited for this type of analysis since it can detect and quantify target analytes, (even when they are present below the baseline of the TIC—as is the case in a complex sample such as a fragrance), as well as give additional information on unknown components after their spectra has been deconvoluted and extracted for proper library identification.

This is all possible due to the spectral continuity and high data density offered by the Pegasus. Fast data acquisition (up to 500 spectra/sec.) permits the accurate profiling of very narrow peaks that can be generated by faster GC methodology. The strength of the Pegasus GC-TOFMS for the analysis of these complex mixtures lies in its automated data handling capabilities, which allow very rapid determinations, thus improving analytical results and productivity.

5. References

[1]http://www.eisc.ca/fragrance-rebut.html

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