Cosmetic Products Analysis by Pyrolysis-Comprehensive Two-Dimensional Gas Chromatography with Time-of-Flight Mass Spectrometry Detection (Py-GCxGC-TOFMS)

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Key Words: GCxGC-TOFMS, Pyrolysis

1. Introduction

Cosmetics are part of everyday life. From moisturizers to sunscreens, lipsticks, mascaras, and hair dyes, this industry is increasing its market every day. New fashion trends as well as health concerns result in the rapid creation of new products. The increasing complexity of cosmetic formulations makes it harder for the analytical chemist to differentiate between minor differences in composition and/or to determine the presence of trace amounts of impurities in the products. Good analytical techniques are needed to either determine the quality of the products or to help in deformulating applications.

Pyrolysis (Py) is a useful technique for reproducibly degrading (under temperature-controlled conditions) organic materials to produce smaller, more volatile compounds. One of the main advantages of the technique is the fact that there is almost no sample preparation involved. Also the amount of sample necessary for the analysis is, in most cases, less than 1 mg. The combination of pyrolysis with the separation and identification capabilities provided by GC-MS can be a powerful analytical technique. The addition of yet another way to increase chromatographic separation can be the solution for complex sample analysis. Comprehensive two-dimensional gas chromatography (GCxGC) extends the separation power of a gas chromatograph to two different dimensions in a single run. Two columns employing different separation mechanisms provide a total peak capacity sufficient for chromatographic separation of hundreds of components. A combination of high acquisition rate capabilities and spectral continuity across the chromatographic peak profile gives Time-of-Flight Mass Spectrometry (TOFMS) the ability not only to fully characterize the narrow GCxGC peaks, but also to provide additional analytical separation through peak deconvolution.

2. Experimental Conditions

Sample Description

Three samples of different mascara brands from three different manufacturers were used for this study. About 1 mg of each of the samples was analyzed under conditions listed below. The samples were labeled as follows.

- Sample 1: Brand A black mascara
- Sample 2: Brand B black brown mascara
- Sample 3: Brand C blackened brown mascara

Instrumentation: Py-GC-TOFMS

Pyrolysis Unit:	CDS 2000
Temperature:	750°C for 15 seconds
Sample Size:	~1 mg
GC:	Agilent 6890 GC
Column:	Rtx-1MS, 30 m, 0.25 mm id, 0.25 µm film thickness
Oven Program:	40°C (2 minute hold) to 250°C (10 minute hold) at 5°C/minute
Inlet Temperature:	250°C
Split Ratio:	200:1
Carrier Gas:	He at a constant flow of 1 ml/minute
MS:	LECO Pegasus® TOFMS
Ionization:	EI at 70eV
Mass Range (u):	35 to 400
Acquisition Rate:	10 spectra/second

Instrumentation: Py-GCxGC-TOFMS

Pyrolysis Unit:	CDS 2000
Temperature:	750°C for 15 seconds
Sample Size:	~1 mg
GCxGC:	Agilent 6890 GC equipped with a LECO Thermal Modulator
Primary Column:	Rtx-1MS, 30 m, 0.25 mm id, 0.25 µm film thickness
Main Oven Program:	40°C (2 minute hold) to 250°C (10 minute hold) at 5°C/minute
Secondary Column:	DB-WAX, 1 m, 0.1 mm id, 0.1 µm film thickness
Secondary Oven Program:	30°C offset from main oven
Inlet Temperature:	250°C
Split Ratio:	200:1
Carrier Gas:	He at a constant flow of 1 ml/minute
Modulator Temperature:	30°C offset from main oven
Modulation Frequency:	6 seconds with a 1.2 second hot pulse time
MS:	LECO Pegasus TOFMS

With the exception of the acquisition rate that was increased to 200 spectra/second, all the parameters were kept the same as for the one-dimensional analysis.

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3. Experimental Results

One-Dimensional Analysis (GC-TOFMS)

Large differences between the three samples can be observed by visual comparison of the total ion current (TIC) chromatograms presented in Figure 1. Between 114 and 120 peaks were found when the data was processed at a S/N of 100. For fast, automated comparison of the samples the Compare feature available through the ChromaTOF® software was used. Sample 2 was arbitrarily selected as the reference sample, and then the other two samples were compared with it. Retention time, mass spectral information, and compound concentration are the three criteria used for a peak-by-peak comparison of the samples. Peaks that pass all criteria are considered matches. If both the retention time and the spectral match are within the user-defined threshold, but the concentration is outside the set limits, the peak will be labeled "out of tolerance". All the extra peaks found in the compared samples are labeled as "Contaminants". The peak table, as well as the chromatogram display can be filtered to selectively display one or more categories of peaks. The main differences in composition found between the three mascara samples are presented in Table 1.

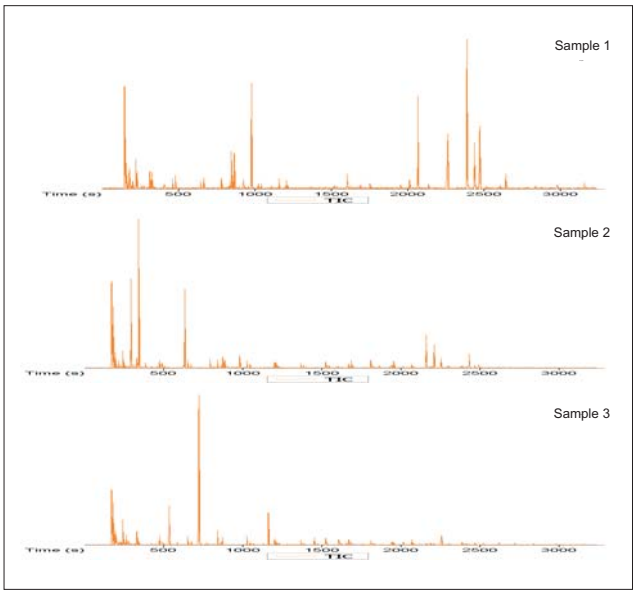

Figure 1. TIC chromatograms of the three mascara samples.

Table 1. Major differences between mascara samples obtained from three different vendors.

Compound	Sample 1	Sample 2	Sample 3
Butanol	-	+	-
Methyl methacrylate	-	+	+
Butyl acrylate	-	+	-
Isobutyl methacrylate	-	-	+
Vinylpyrrole	+	+	-
hexadecanol	-	+	-
Methyl hexadecanoate	-	+	-
Docosene	+	-	+
Methyl stearate	-	+	-
Palmidrol	+	+	-

Note: A (+) sign shows that the compound was present in the sample while a (-) sign shows the absence of the compound in a sample.

Two-Dimensional Analysis (GCxGC-TOFMS)

More than five times as many peaks were found in each of the samples when GCxGC technology was used for the chromatographic separation. Figure 2 shows the TIC chromatogram of Sample 1 in a contour plot representation. Regular class pattern can be easily observed in the chromatogram with a distinct alkane/alkene/diene region spanning from about C5 to C27 in all three samples.

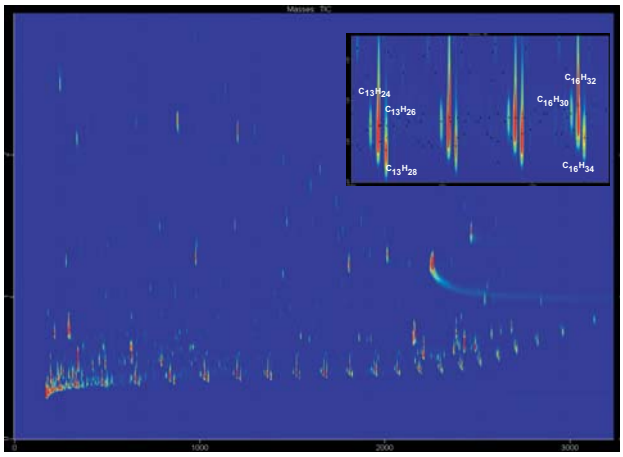

Figure 2. TIC chromatogram from Sample 1 presented as a contour plot. Inset shows the C13-C16 region for the alkanes/alkenes/dienes classes.

If only characteristic ions are plotted multiple chemical class regions can be easily seen. This is illustrated in Figure 3 where extracted ion chromatograms are shown for all three mascara samples in the nitriles and acids regions. The curvature observed in the class pattern for the alkane and alkene acids is caused by the oven reaching the final temperature before all components in the classes have eluted from the chromatographic system. Looking at characteristic ions makes the sample comparison task much easier. Visual examination of Figure 3 reveals that most of the nitriles are absent from Sample 2, while most of the acids are missing in Sample 3.

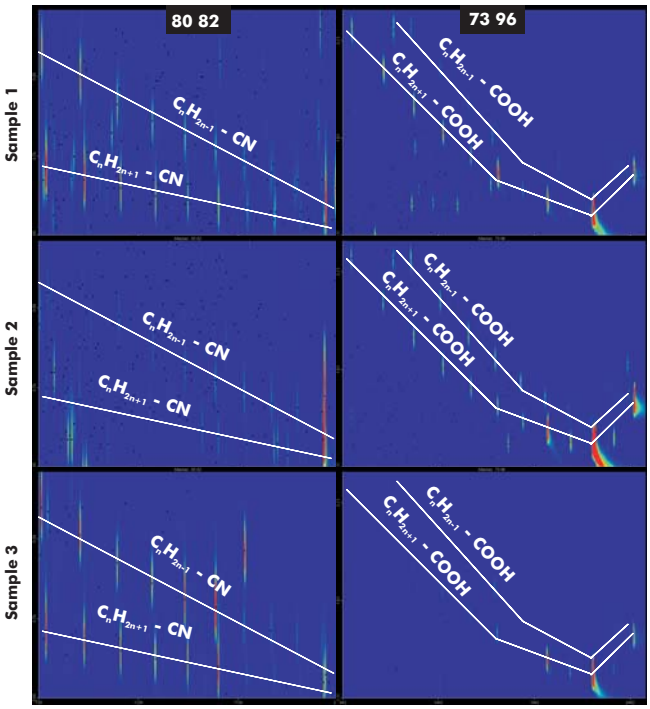

Figure 3. Extracted ion chromatograms presented for the nitriles and acids regions for the three mascara samples. The white lines highlight the presence of chemical class patterns.

4. Conclusions

Using GCxGC-TOFMS technology allowed the finding of more than 500 peaks in each of the three analyzed mascara samples. Using a mass spectrometer as the detector of choice gave the ability to display only selected masses in the two-dimensional chromatogram. This feature, combined with the characteristic chemical class pattern obtained from GCxGC systems, enabled easier visual comparison of the three samples. Results obtained show great potential for the application of this technique (Pyrolysis-GCxGC-TOFMS) in the analysis of samples from the cosmetic industry.

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