



# Chemical Analysis of Polymer Microbeads in Toothpaste by TD- and Py-GC×GC-TOFMS

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## 1. Introduction

Plastic microbeads were used increasingly in personal care products from toothpaste to facial cleansers up until 2013 when mounting pressure from many international environmental groups led to legislation banning their use. As a result, some industry leaders began phasing microbeads out of their products over the next few years. Microbeads are commonly made of polyethylene and other petrochemical-based plastics. In toothpaste, many people have complained about these plastic beads becoming embedded in their gums. This application note focuses on the direct analysis of a brand-name toothpaste containing polyethylene to determine the additives or inactive ingredients by consecutive thermal techniques. The toothpaste was analyzed first by thermal desorption (TD) at 250°C, and then by flash pyrolysis (Py) at 750°C via a CDS Pyroprobe 5200 coupled to a LECO Pegasus® 4D for comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GC×GC-TOFMS).

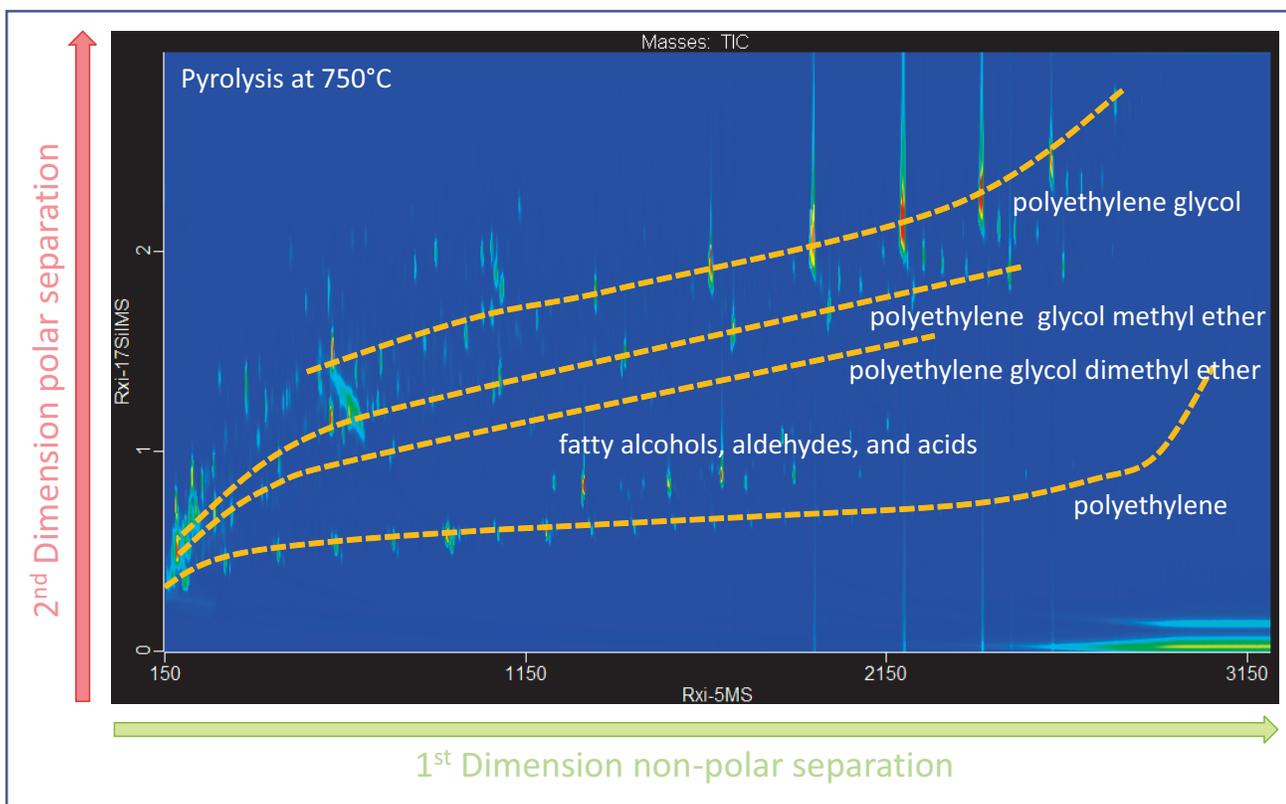


Figure 1. Contour plot from Py-GC×GC-TOFMS analysis of a name-brand toothpaste identified to contain polymer microbeads. Polyethylene was listed under the inactive ingredients on the product label and was detected as indicated by the oligomers eluting in the lower portion of the contour plot.

## 2. Experimental

About 20 mg of toothpaste was loaded into a quartz tube, plugged with quartz wool, and loaded into a CDS Pyroprobe 5200 series coupled to a LECO Pegasus 4D according to the method details below.

Thermal Desorption: 50°C to 250°C at 100°C/min, held for 2 min

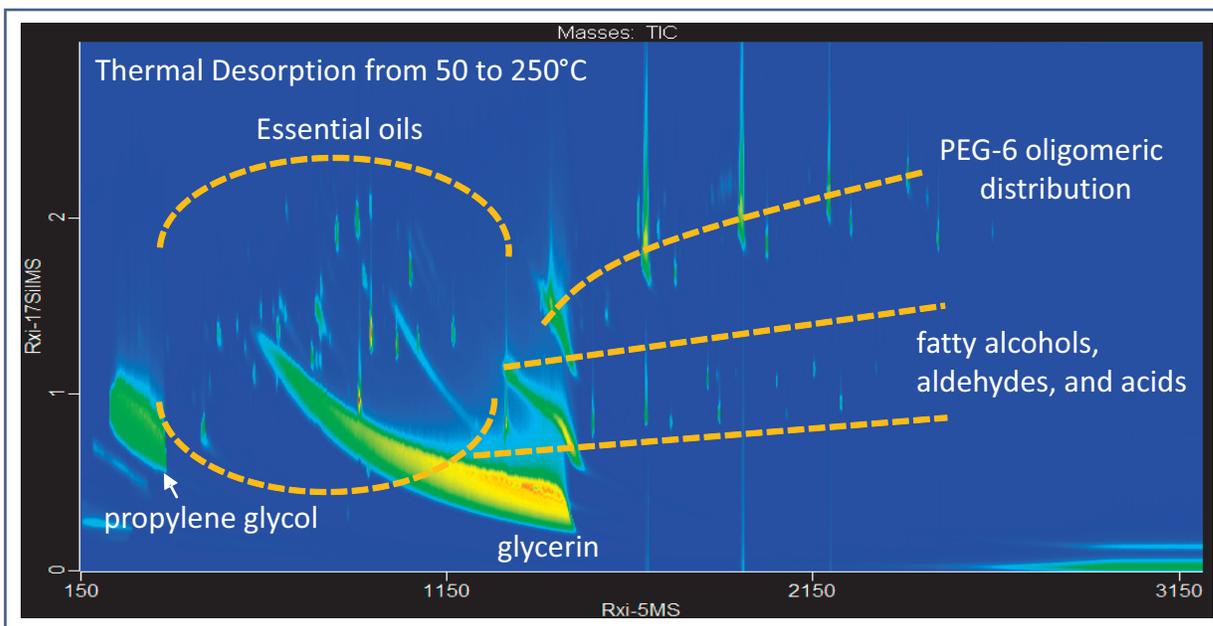
Pyrolysis: 250°C to 750°C at 100°C/s, held for 2 min

**Table I. GC×GC-TOFMS (Pegasus 4D) Conditions**

Gas Chromatograph	Agilent 7890 with Dual Stage Quad Jet Modulator and CDS Pyroprobe 5200
Injection	GC inlet, split 100:1 @ 325°C
Carrier Gas	He @ 1.0 ml/min, Corrected Constant Flow
Column One	Rxi-5ms, 30 m x 0.25 mm i.d. x 0.25 μm coating (Restek, Bellefonte, PA, USA)
Column Two	Rxi-17SilMS, 1.25 m x 0.18 mm x 0.18 μm coating (Restek, Bellefonte, PA, USA)
Temperature Program	2 min at 40°C, ramped 6°C/min to 320°C, held 5 min Secondary oven maintained +20°C relative to primary oven
Modulation	3 s with temperature maintained +20°C relative to secondary oven
Transfer Line	290 °C
Mass Spectrometer	LECO Pegasus HT/4D
Ion Source Temperature	250 °C
Mass Range	35-1000 m/z
Acquisition Rate	200 spectra/s

## 3. Results and Discussion

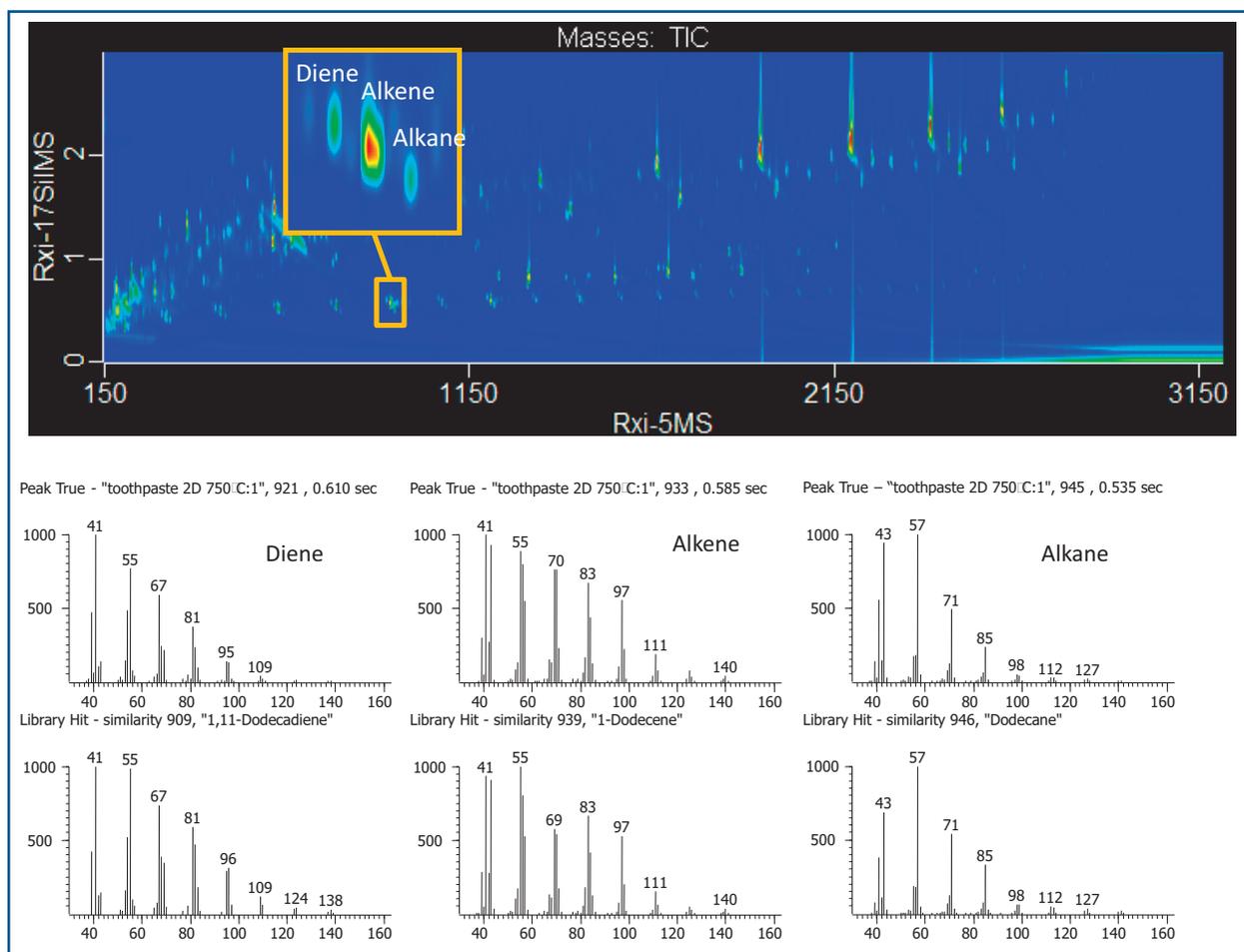
Thermal desorption (TD) was used to detect the volatile to semi-volatile components in the sample of toothpaste, whereas pyrolysis (Py) was used to analyze the non-volatile components by thermal decomposition and subsequent detection of the volatilized fragments. The data was processed using ChromaTOF® brand software, which included Automatic Peak Find with True Signal Deconvolution®, and library database searching for identification. Two library search options were available: 1) CDS Pyrolysis Database PYR2013 based on a thermogram of the integrated mass spectra, and 2) individual deconvoluted (Peak True) mass spectra searched against NIST 14 or Wiley 10 databases.



**Figure 2. Comprehensive TD-GC×GC-TOFMS contour plot for the direct analysis of a name brand toothpaste.**

Essential oils such as menthol, Wintergreen oil, carvone, anethole, and eugenol were identified by TD-GC×GC-TOFMS based on NIST 14 library similarity searching with a hit greater than 800 (out of 1000), as well as a number of inactive ingredients listed on the product labeling including glycerin, propylene glycol, PEG-6, and saccharin derivatives (Figure 2). A number of C<sub>12</sub> and C<sub>14</sub> fatty acids, alcohols, and aldehydes were also detected, which may have been formed by the decomposition of other inactive ingredients during TD, or were additional ingredients not listed.

The subsequent Py-GC×GC-TOFMS revealed many remnants of the TD analysis (i.e. PEG-6), however, the polymer profile of polyethylene was also observed (previously shown in Figure 1). Polyethylene has a characteristic diene, alkene, alkane profile, with dodecene being the most prominent peak in this instance (Figure 3). The advantage of 2D chromatography for this polymer analysis was the ability to separate the polymer profile from the sample matrix. The advantage was two-fold in that both the additives and the polymer spectra became more easily identifiable.



**Figure 3.** Py-GC×GC-TOFMS contour plot from the analysis of a toothpaste containing polyethylene. The highlighted region shows a C12-diene, -alkene, and -alkane. The Peak True (Deconvoluted) mass spectrum for each is included along with NIST 14 similarity scores which were greater than 900 out of 1000. This hydrocarbon profile is a characteristic of polyethylene.

#### 4. Conclusions

LECO's Pegasus 4D platform is uniquely suited for thermal desorption and pyrolysis applications due to the complexity of the pyrograms which are generated. The added peak capacity of GCxGC and the automated peak find and true signal deconvolution capabilities made possible by TOFMS help to effectively detect and identify components which make up these pyrograms. An additional feature making the Pegasus 4D well-suited for these types of analyses is its robust, low-maintenance ion source. Pyrolysis samples can rapidly dirty closed ion sources resulting in down-time for cleaning and maintenance, while the open ion source on the Pegasus HT/4D is extremely robust, increasing productivity by comparison.



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