# Application Note

***Instrument: Pegasus® BT***

# Quantitation of Four Regulated Phthalates in Plastic Consumer Products by Gas Chromatography–Time-of-Flight Mass Spectrometry

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Key Words: Phthalates, GC-MS, Polymer Additives

## *Introduction*

Phthalates are a class of chemical compounds commonly used to soften and add pliability to plastic materials. Over the past decade, phthalates have come under increased scrutiny as concerns about their potentially harmful effects on human health have arisen. In 2015 the European Union announced a ban on four specific phthalates commonly used in consumer products such as toys, coated fabrics, building materials, and office supplies. The ban included the following phthalates: diisobutyl phthalate, dibutyl phthalate, benzylbutyl phthalate, and bis(2-ethylhexyl) phthalate. This application note demonstrates the use of LECO's Pegasus® BT GC-TOFMS system for quantitation of these phthalates in a range of commercial products including two children's toys, an ink pen barrel, and cross-linked high-density polyethylene (CL-HDPE) pipe used in residential plumbing applications.

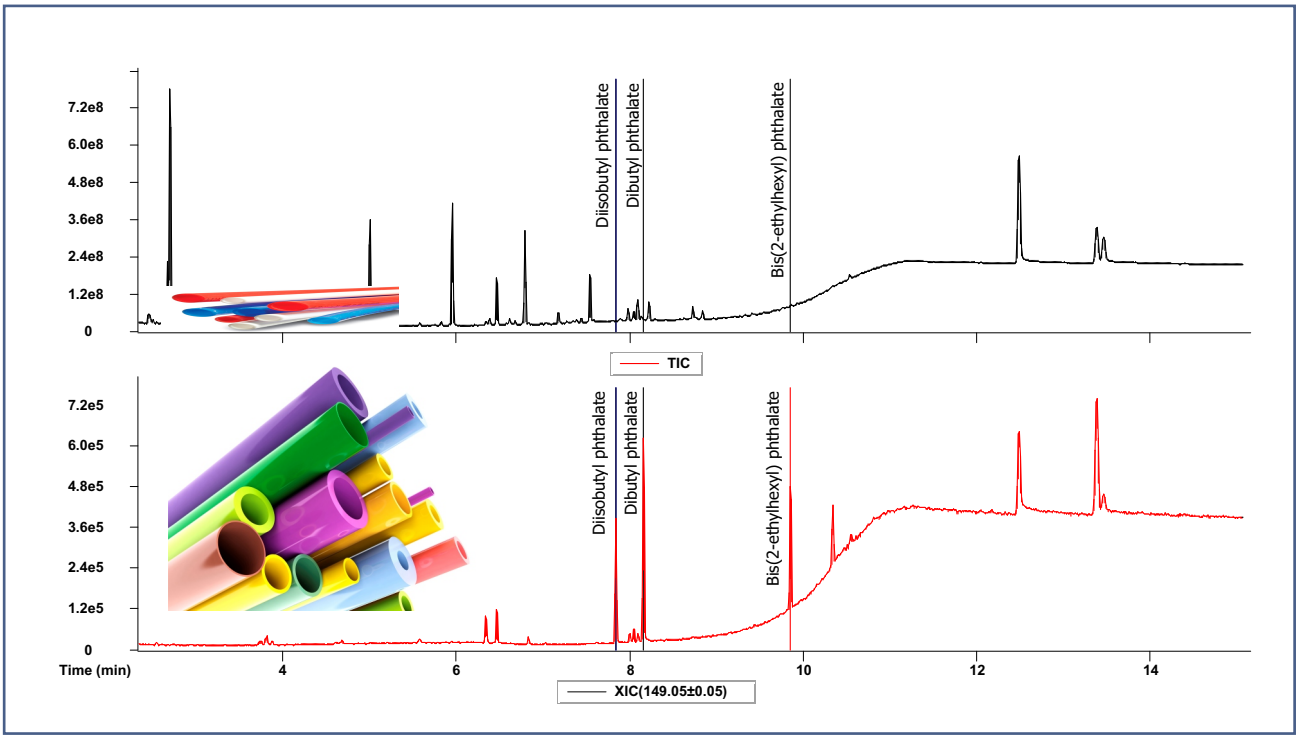


***Figure 1. Total Ion Chromatogram (TIC) and Extracted Ion Chromatogram (XIC m/z 149.05 ) Showing Detection of 3 out of 4 Regulated Phthalates in Cross-linked High-Density Polyethylene water pipe.***

## Experimental

Four different plastic products were tested for the regulated phthalates: two children's toys, an ink pen barrel, and pipe used in residential plumbing. The goal was to detect the phthalates present on the surface of these materials; therefore exhaustive extraction techniques requiring sample grinding prior to extraction were not employed. For each sample, a 1 to 2 gram portion was placed in a 15 mL scintillation vial and the weight recorded. A 10 mL aliquot of chloroform was added, and the vial was placed in an ultrasonic bath for 20 minutes. After sonication, a 1mL portion of each extract was transferred to GC autosampler vials for analysis. Calibration standards for each of the phthalates were prepared in chloroform at a concentration range from 20 to 10,000 pg/$\mu$L. Plastic extracts and standards were analyzed using the instrument conditions shown below in Table I. External standard calibration curves for each of the phthalates were generated within the ChromaTOF® brand software, and were used to quantitate the levels of each regulated phthalate in the extracts.

**Table I. GC-TOFMS *(Pegasus* BT) Conditions**

| **Gas Chromatograph** | **Agilent 7890 with L-PAL3 Autosampler** |
|---|---|
| Injection | 1$\mu$L, split 10:1 @ 300 °C |
| Carrier Gas | He @ 1.4 mL/min, Constant Flow |
| Column | Rxi-5ms, 30 m x 0.25 mm i.d. x 0.25 $\mu$m coating (Restek, Bellefonte, PA, USA) |
| Oven Program | 50 °C (1 min), to 330 °C @ 30 °C/min (20 min) |
| Transfer Line | 300 °C |
| **Mass Spectrometer** | **LECO *Pegasus* BT** |
| Ion Source Temperature | 250 °C |
| Mass Range | 40-700 m/z |
| Acquisition Rate | 10 spectra/s |

## Results and Discussion

Table II shows the quantitative results obtained from the surface extraction of the four plastic products. The values are expressed in ng/g.

**Table II. Quantitative Results in nanograms/gram for Regulated Phthalates in Four Plastic Products**

| Sample ID | Diisobutyl phthalate | Dibutyl phthalate | Benzyl butyl phthalate | Bis(2-ethylhexyl) phthalate |
|---|---|---|---|---|
| CL HDPE Pipe | 491 | 817 | n.d. | 1011 |
| Ink Pen Barrel | 2741 | 5077 | 973 | 114450 |
| Children's Toy #1 | 3728 | 5457 | 404 | 6894 |
| Children's Toy #2 | 1858 | 1934 | 619 | 9561 |

Results shown in ng/g

The GC-MS method used for this analysis demonstrated excellent linearity across the entire calibration range for all four of the phthalates measured. Table III shows the phthalates and their corresponding linearity values. Figure 2 shows a representative calibration plot and spectra for Bis(2-ethylhexyl) phthalate.

**Table III. Phthalates and their corresponding linearity values**

| Phthalate | $R^2$ Value |
|---|---|
| Diisobutyl phthalate | 0.99999 |
| Dibutyl phthalate | 0.99995 |
| Benzyl butyl phthalate | 1 |
| Bis(2-ethylhexyl) phthalate | 0.99999 |

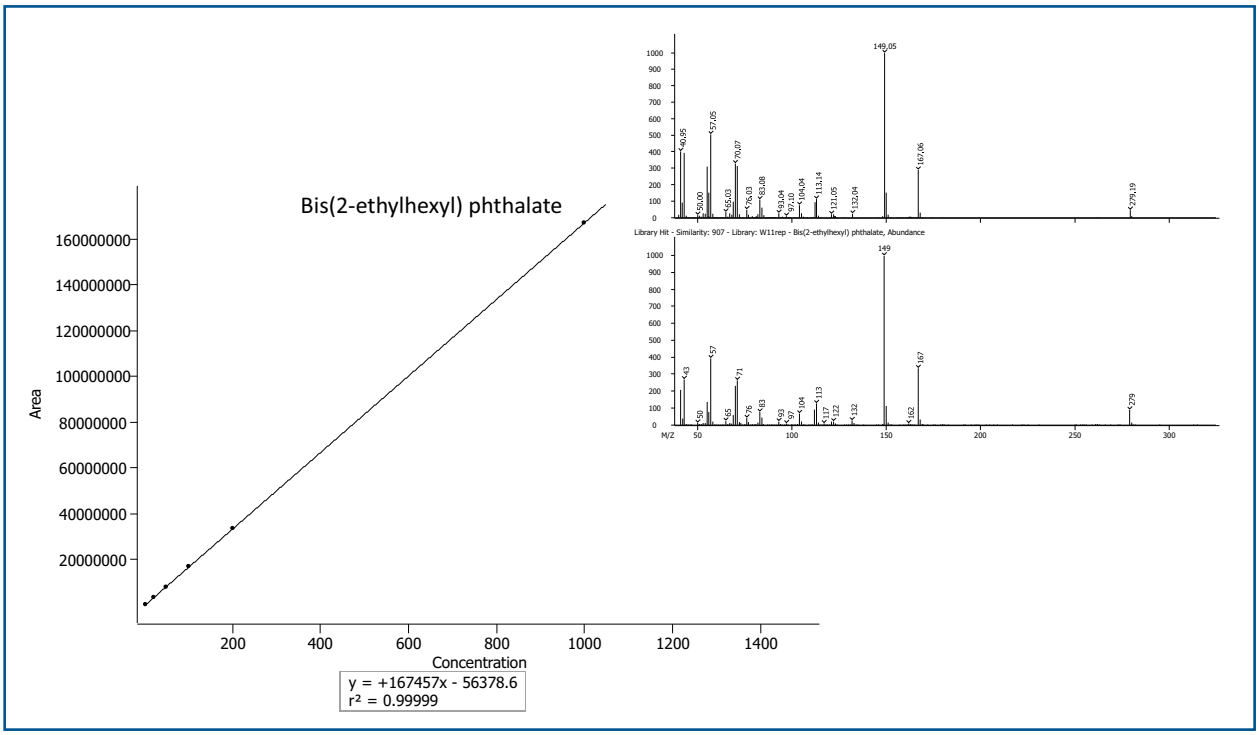


***Figure 2. GC-MS Calibration Curve and Mass Spectra (Deconvoluted and NIST Library match) for Bis(2-ethylhexyl) Phthalate.***

A representative GC-MS total ion chromatogram (TIC) and extracted ion chromatogram (XIC) of m/z 149.05 for the regulated phthalates in Children's Toy #1 are shown in Figure 3.

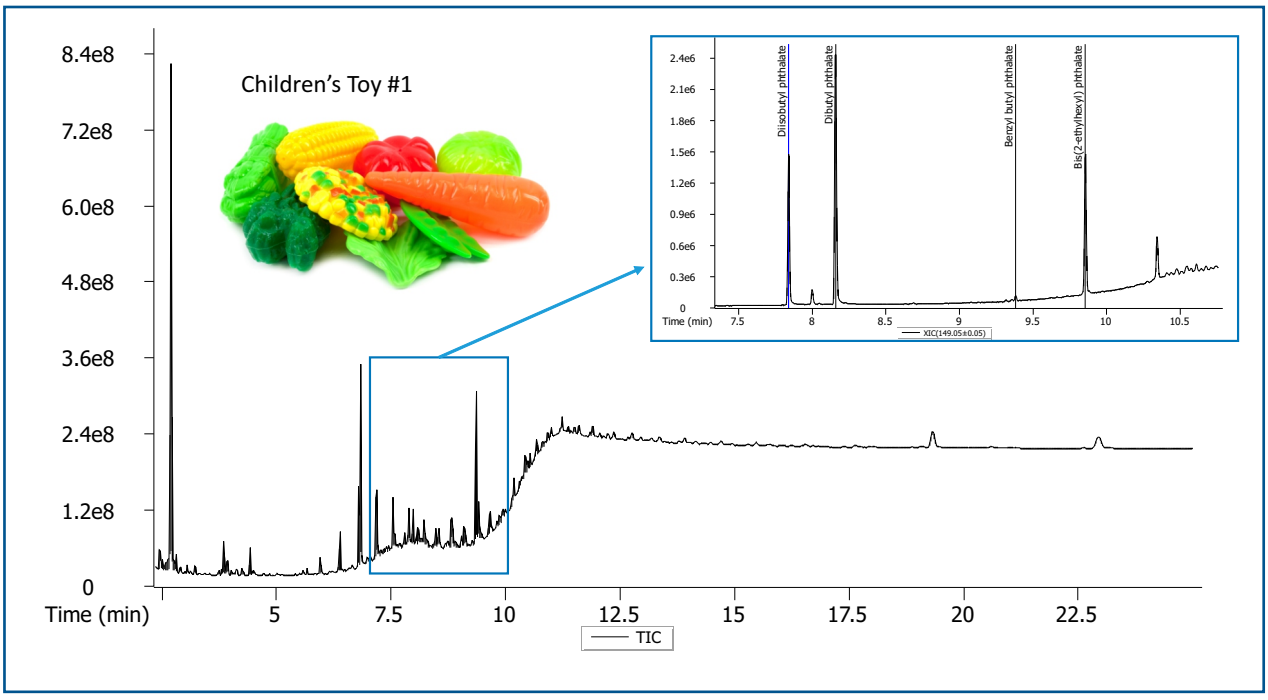


***Figure 3. GC-MS Chromatograms for Toy #1 Extract.***

Since the *Pegasus* BT offers maximum sensitivity and reproducibility with full mass range data acquisition, the same analyses used for the targeted phthalate quantitation can also be interrogated for other untargeted compounds of interest. A representative example is shown in Figure 4 where several additional polymer additive-type compounds were identified.

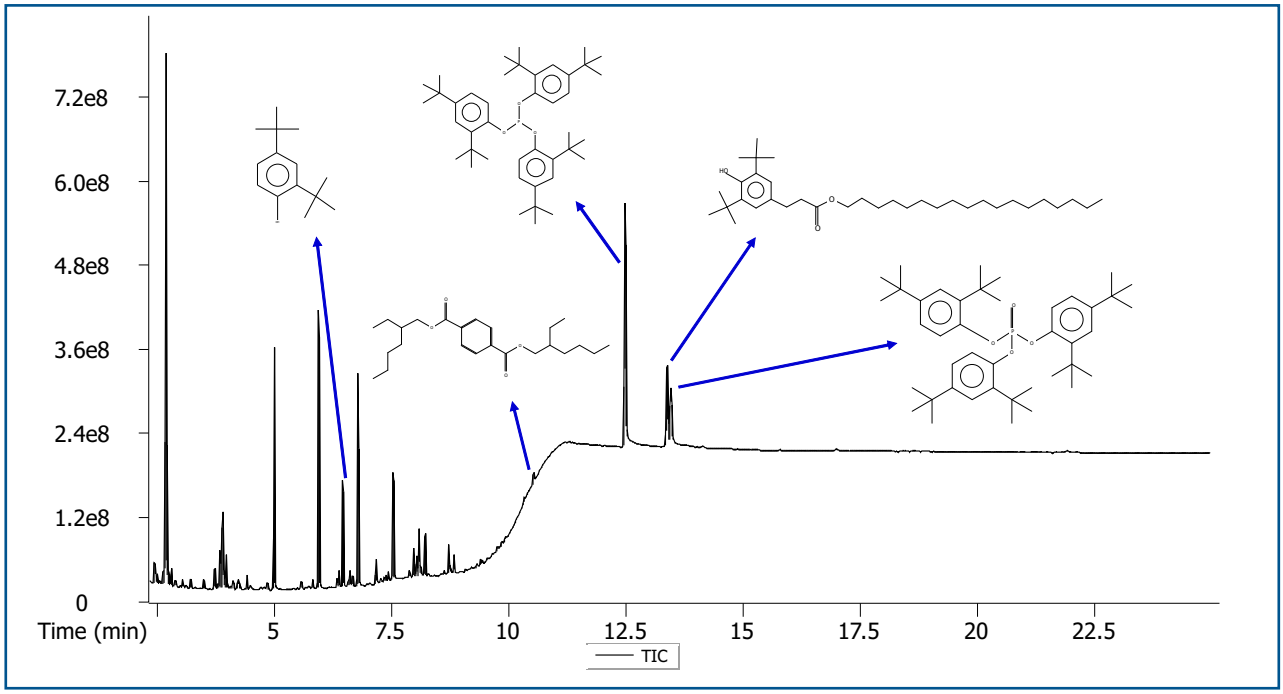


***Figure 4. Example showing the automated identification of several non-targeted compounds within the CL HDPE Extract.***

Another important attribute of the system is NonTarget Deconvolution® (NTD®). Non-Target analysis is a rapidly expanding area of importance in analytical sciences. The *Pegasus* BT was built from the ground up to support these types of investigations. *NTD* is an automated function within the *ChromaTOF* brand software and very effectively identifies known unknowns (known to be in the NIST library but not known to be in the sample a priori). The *Pegasus* BT, being a time-of-flight mass spectrometer, provides data perfectly suited for mass spectral deconvolution algorithms (note scanning instruments are challenged due to spectral skewing). The example shown in Figure 5 demonstrates the ability of *ChromaTOF's NTD* to effectively identify two analytes that were not separated chromatographically. This was done in a fully automated fashion and resulted in excellent spectral similarity scores against the NIST 2017 database. Bis(2-ethylhexyl)Phthalate and 2,4-bis(1-methyl-1-phenylethyl)-Phenol were identified with similarity scores of 901/1000 and 863/1000, respectively.

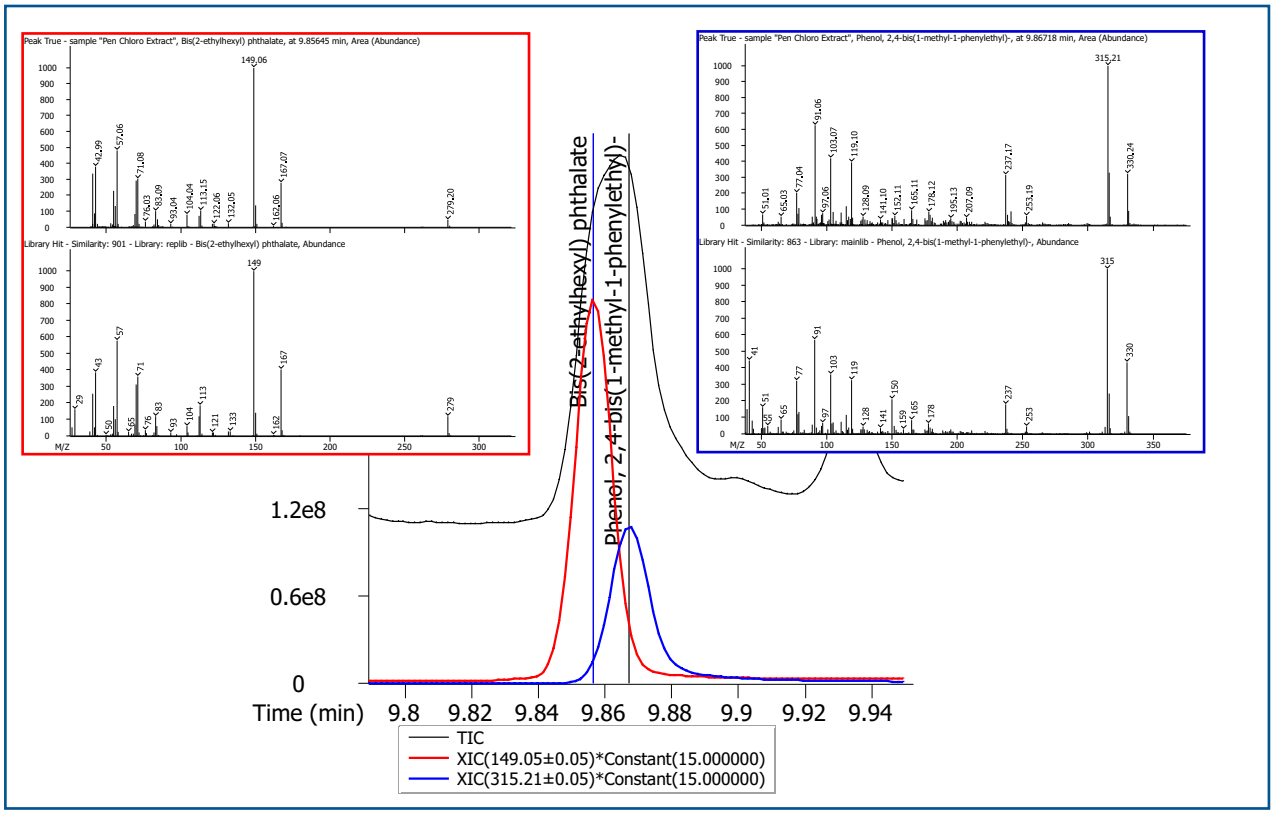


***Figure 5. Example demonstrating effective deconvolution of Bis(2-ethylhexyl)Phthalate and 2,4-bis(1-methyl-1-phenylethyl)-Phenol.***

## *Conclusion*

This application note effectively demonstrates the ability of the *Pegasus* BT GC-TOFMS system to quantitate four regulated phthalates in plastic consumer products. The Time-of-Flight MS system demonstrated excellent sensitivity and linearity for this application. The ability to quantitate targeted analytes while still maintaining the ability to identify other relevant compounds within the same analytical data file shows the *Pegasus* BT GC-TOFMS to be a powerful tool for not only routine screening of regulated components, but also additional characterization of consumer product formulations.

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Form No. 203-821-553 1/26—REV2 