

Summary

This application note describes a test method developed at CPG for the identification and quantification of plasticizer in PVC by gas chromatography/mass spectrometry (GC/MS). For a sample mass of 5-10g, the uncertainty in determining the percent plasticizer content is typically less than 1%.

Background

Plasticizers are typically added to polymers (especially PVC) to increase material flexibility. Such materials are found in a broad range of applications, such as construction materials, cosmetics, medical devices, children's toys. The type and percent content of plasticizer directly affects the material's mechanical properties.

However, substantial concerns have been raised over the safety of some plasticizers. Several ortho-phthalates, for example, have been classified as potential endocrine disruptors that may cause developmental toxicity. Other concerns have been raised about possible carcinogenicity and the effects of plasticizers on the environment.

Because of the possibility that such plasticizers may leech out of a given material, the use of some plasticizers has been restricted or banned in cosmetics, medical devices, and children's toys within the EU and the state of California.

Therefore, it is often desirable to identify and quantify the plasticizers used within a polymer, to ensure that banned compounds are not used, and that restricted substances are below allowable limits.

Experimental

A sample containing an unknown plasticizer is first cryomilled to increase the surface area prior to extraction. The sample is weighed on a precision balance and then is extracted with ethyl ether for six hours within a Soxhlet apparatus. After this time, the extract solvent is evaporated on a rotary evaporator and placed in a vacuum desiccator for one hour to ensure no ethyl ether remains in the samples. The sample extracts are weighed again to determine the extract mass and percent extract.

A small portion of the extract is then reconstituted in chloroform and GC/MS analysis is performed on an Agilent 6890 series gas chromatograph under the following conditions:

Column: Phenomenex ZB-5ms, 30 m x 0.25 mm ID x 0.25 μ m film thickness

Detector: Agilent 5973 mass selective detector

Injection parameters: Split injection (50:1 Split Ratio)

Injection volume: 1 μ L

Inlet temperature: 250 °C

Helium flow: 1 mL/min

Oven temperature program: Start at 50 °C, ramp 10 °C/minute to 300 °C, hold for 10 minutes

Solvent delay: 4.00 minutes

EI scan mode: Scan (m/z 50-550)

Mass spectra are measured for each peak detected in the chromatogram and then compared against the NIST/EPA/NIH Mass Spectral Library, using the NIST Mass Spectral Search Program v2.0a.

A typical chromatogram and mass spectrum of a PVC sample containing an unknown plasticizer is shown in Figure 1. The measured mass spectrum was compared against the NIST Mass spectral library, and the results of that search are shown in Figure 2. The closest spectral match to the sample's mass spectrum, with a match probability of 95.9%, was Trioctyl Trimellitate (TOTM), a common plasticizer used in PVC.

After identification is performed, a calibration curve for the identified compound(s) is prepared to determine the GC/MS response factor for the compound. A typical calibration curve for TOTM, ranging from 500ppm – 725ppm, is shown in Figure 3 and tabulated in Table 1. From the GC/MS response to the unknown sample, the percent plasticizer content within the sample is calculated.

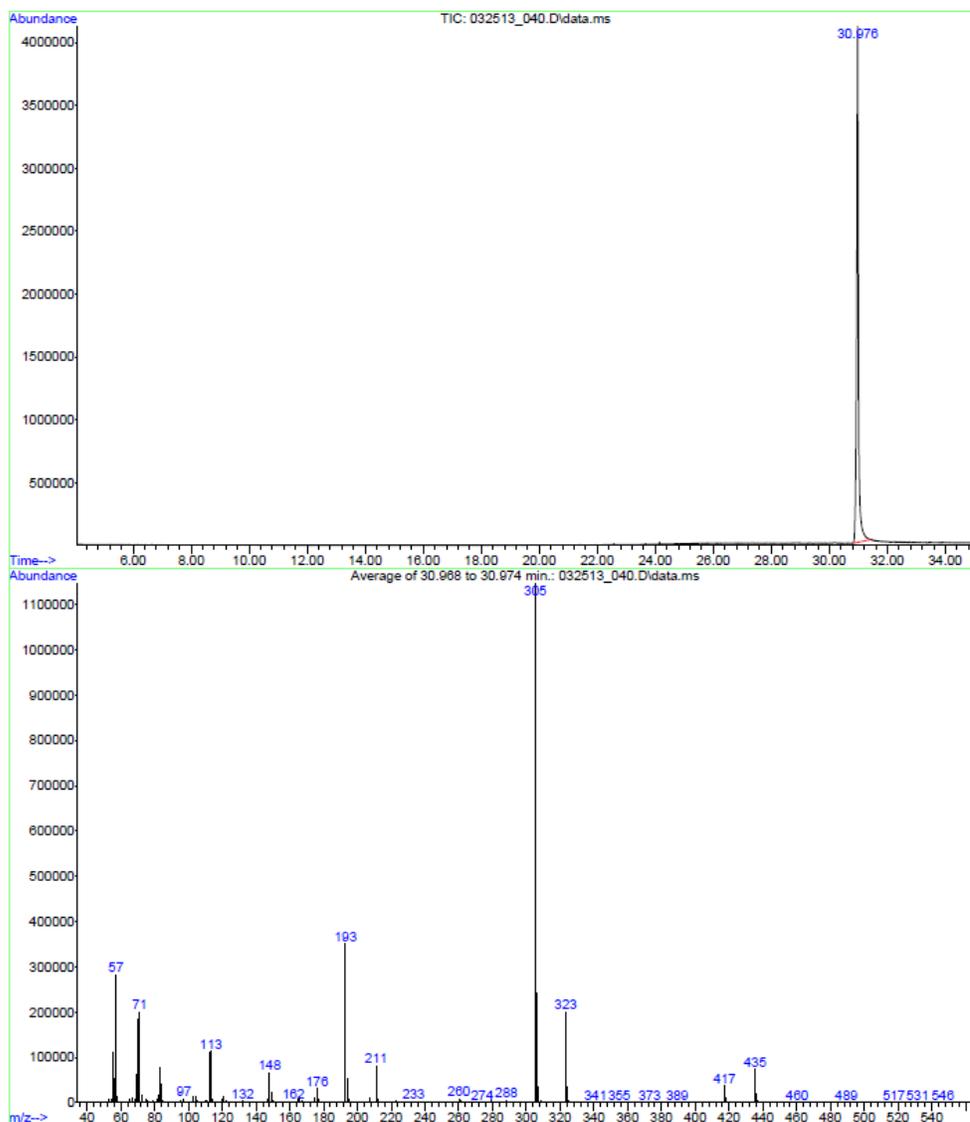
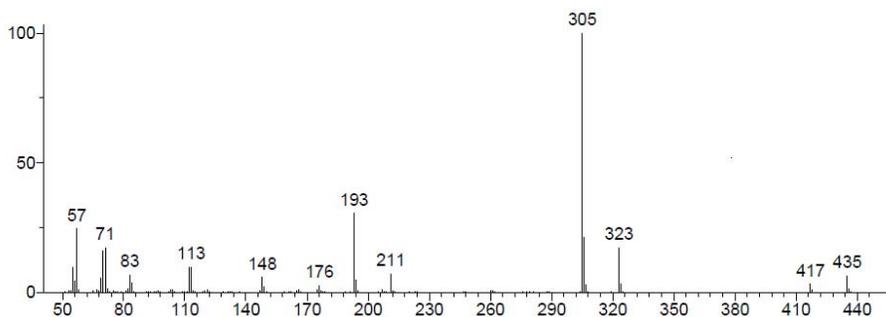


Figure 1: Total ion chromatogram (top plot) and mass spectrum of the peak at 30.976 min (bottom plot) of a PVC sample containing an unknown plasticizer.

Unknown: Average of 30.968 to 30.974 min.: 032513_040.D\data.ms
 Compound in Library Factor = 1810



Hit 1 : tri(2-Ethylhexyl) trimellitate
 C33H54O6; MF: 946; RMF: 947; Prob 95.9%; CAS: 3319-31-1; Lib: mainlib; ID: 136800.

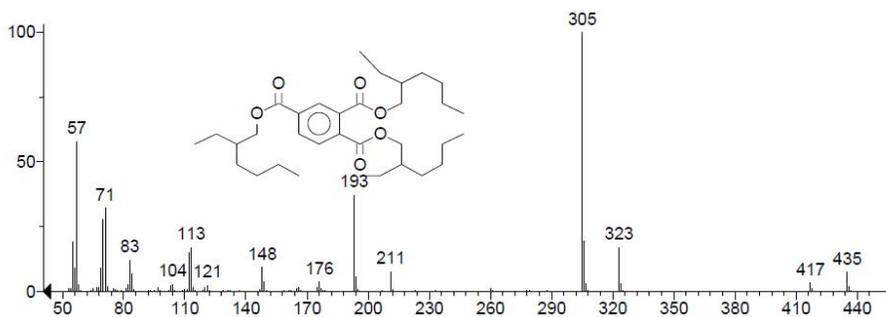


Figure 2: The closest spectral match to the dominant peak of the PVC sample containing an unknown plasticizer. The top plot is the mass spectrum of the peak at 30.976 min, while the bottom plot is the closest spectral match from the NIST library (bottom).

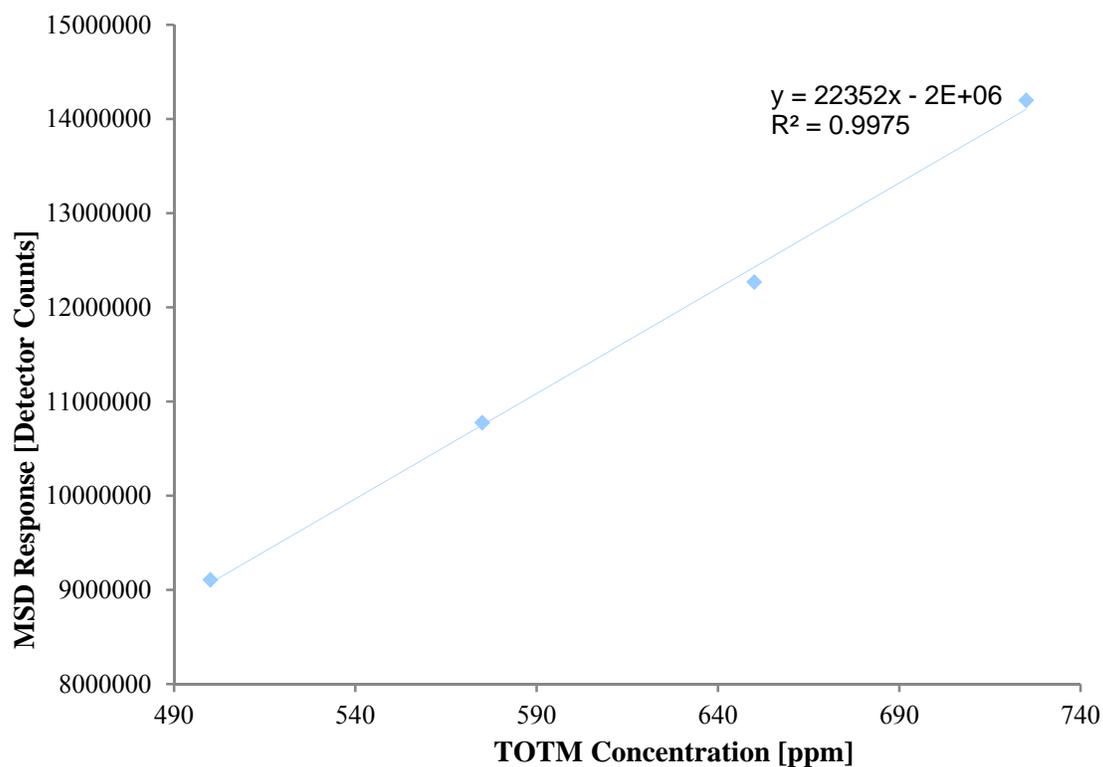


Figure 3: Sample calibration curve used for quantitation of TOTM within the concentration range of 500-725ppm.

Table 1: Tabulated calibration data for TOTM.

Concentration [ppm]	Peak Area [Detector Counts]
500	9107173
575	10777165
650	12270028
725	14197445