Application Note SI-02388

Determination of Phthalate Compounds in Plastic Toys Using the Varian 225-MS Ion Trap Mass Spectrometer and V:Results™ GC/MS software

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Introduction

The health hazard caused by phthalate esters in polyvinyl chloride (PVC) toys has become a major concern for safety regulators. In December of 1999, the European Union (EU) placed an emergency ban on six phthalate esters in soft PVC toys and childcare products meant to be placed in the mouth of children under the age of three (1): dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), diethylhexyl phthalate (DEHP), di-n-ocyl phthalate (DNOP), diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP). In August 2008, the US Congress enacted the Consumer Product Safety Improvement Act (CPSIA 2008) (2), which established a 0.1% (w/w) limit for these six phthalate esters. The US Consumer Product Safety Commission (CPSC) subsequently introduced a test method for the analysis of phthalate content in childcare items and toys using GC/MS (3).

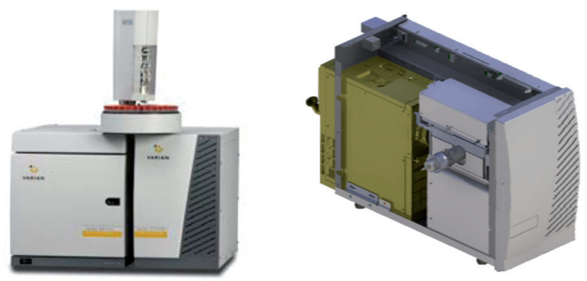

Figure 1. Varian 225-MS ion trap mass spectrometer with 431-GC gas chromatograph and 8400 AutoSampler (left). The 225-MS has a fully integrated vacuum module, eliminating the need for a foreline pump on the laboratory floor (right).

This note presents an analytical procedure for the quantitative determination of six regulated phthalates using the Varian 225-MS GC/MS Ion Trap in electron impact ionization (EI) full scan mode, based on the framework of the original CPSC method. In addition, the use of low-pressure chemical ionization (CI) with MS/MS provides a unique advantage in the analysis i.e. the ability to unambiguously identify and verify target compounds in a complex matrix without sample preparation using the Varian ChromatoProbe™ sample introduction device.

Materials and Method

Phthalate esters and benzyl benzoate stock standards were purchased from Ultra Scientific (North Kingstown, RI). Five calibration solutions at 0.25, 0.5, 1, 2.5 and 10 µg/mL were prepared by dilution in cyclohexane, along with one calibration blank (cyclohexane). Each standard solution contains 1 µg/mL of benzyl benzoate as internal standard.

Sample preparation: Toy extracts were provided by the California Department of Toxic Substances Control (DTSC). Ground plastic toy samples were extracted with a Soxhlet in dichloromethane for 16 hours at 60 °C based on their proprietary procedure.

Intrumentation

- Varian 225-MS Ion Trap Mass Spectrometer
- Varian 431-GC Gas Chromatograph
- 8400 AutoSampler
- V:Results GC/MS software

GC Conditions

Column:	FactorFour™ VF-5ms 30 m × 0.25 mm x 0.25 µm (Part No. CP8944)
Inlet Temperature:	280 °C
Injection Volume:	1 µL
Carrier Gas Mode:	Helium at 1 mL/min
Injection Mode:	Splitless, pulse injection at 35 psi for 0.6 min
Oven Program:	50 °C for 2 min, to 280 °C at 30 °C/min, to 310 °C at 15 °C/min and hold for 3.33 min, for a total run time of 15 min
Washing Solvent:	Cyclohexane

MS Conditions

Filament Delay:	5 min
Ion Trap Temp:	220 °C
Manifold Temp:	50 °C
Transfer Line Temp:	280 °C

Results and Discussion

CPSC Analytical Method

These six regulated phthalate compounds are all phthalate esters with different saturated alkyl side chains. The base peak in the EI ionization mass spectrum of all phthalate esters studied is *m/z* 149 (Figure 2) except for dimethyl phthalate, which has a base peak at *m/z* 163. A typical total ion chromatogram (TIC) and extracted ion chromatogram (EIC) of these six regulated phthalate esters, and several other closely related compounds at 10 µg/mL are shown in Figures 3 and 4. As indicated in the chromatogram, di-n-octyl phthalate (DnOP), diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP) were partially co-eluting. The quantitation ions in the CSPC method for DnOP, DINP and DIDP were low abundance ions at *m/z* 279, *m/z* 293 and *m/z* 307, respectively.

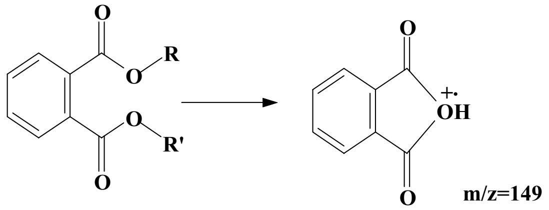

Figure 2. Major fragmentation of phthalate esters in EI ionization. The dominant ion in the EI spectrum is typically *m/z* 149.

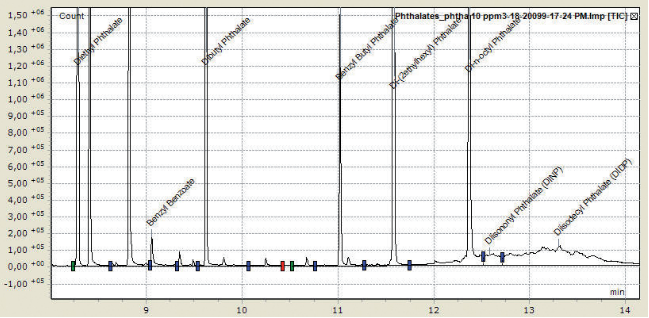

Figure 3. TIC of phthalates at 10 ppm.

The quantitative determination of phthalate esters was conducted at concentrations ranging from 0.25 to 10 µg/mL using quantitation ions listed in Table 1.

Table 1. Calibration of phthalates.

Compound Name	Correlation Coefficient (r^2)	Quantitation Ion
Dibutyl phthalate	0.9997	TIC
Benzyl benzoate	Internal standard	105
Benzyl butyl phthalate	0.9999	206 +149
Di-(2ethylhexyl) Phthalate	0.9994	279
Diethyl Phthalate	0.9990	177+149
Diisodecyl Phthalate (DIDP)	0.9993	307
Diisononyl Phthalate (DINP)	0.9984	293
Di-n-octyl Phthalate	0.9984	279

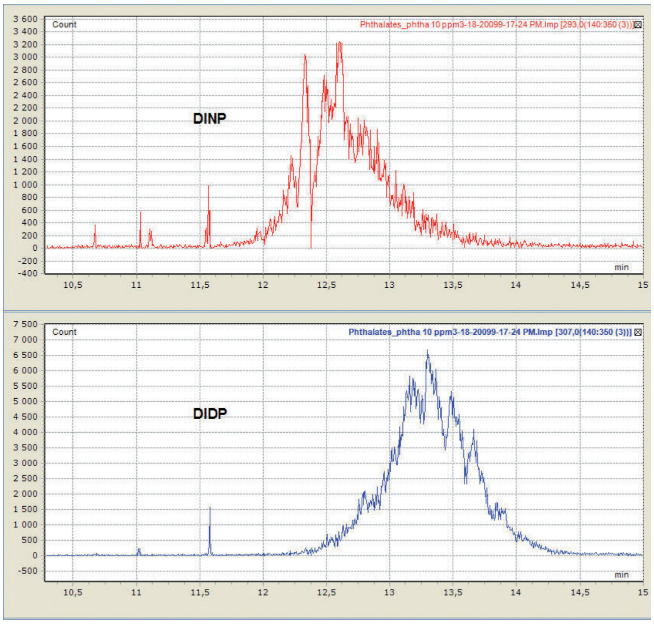

Figure 4. Extracted ion chromatogram of DINP at *m/z* 293 and DIDP at *m/z* 307.

Results showed that all of the compounds have excellent calibration coefficient and relative standard deviation, including DINP and DIDP, as shown in Figure 5. Results in Figure 6 demonstrate excellent reproducibility from injection to injection. A PVC toy extract and matrix spike extract are shown in Figure 7.

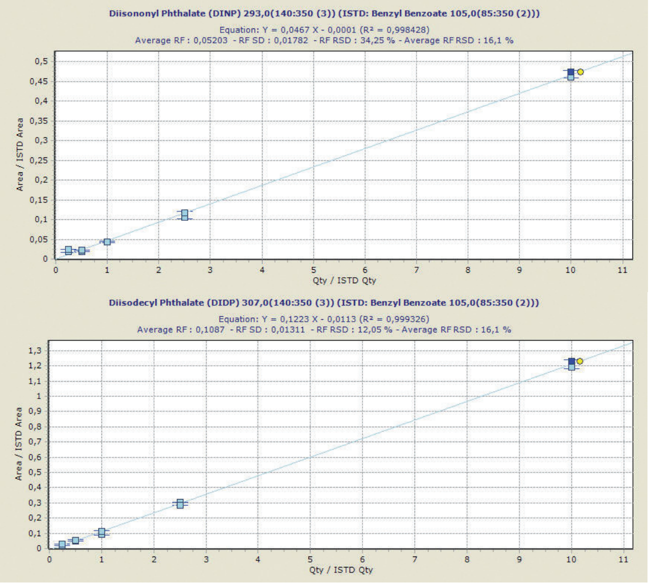

Figure 5. Calibration curves of DINP (top) and DIDP (bottom) from 0.25 µg/mL to 10 µg/mL.

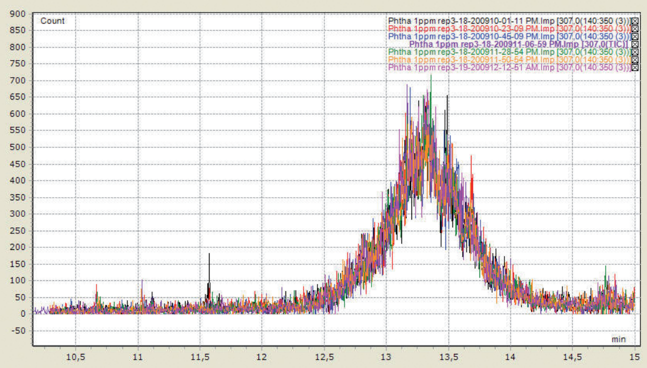

Figure 6. Reproducibility of DIDP from seven injections at 1 ppm.

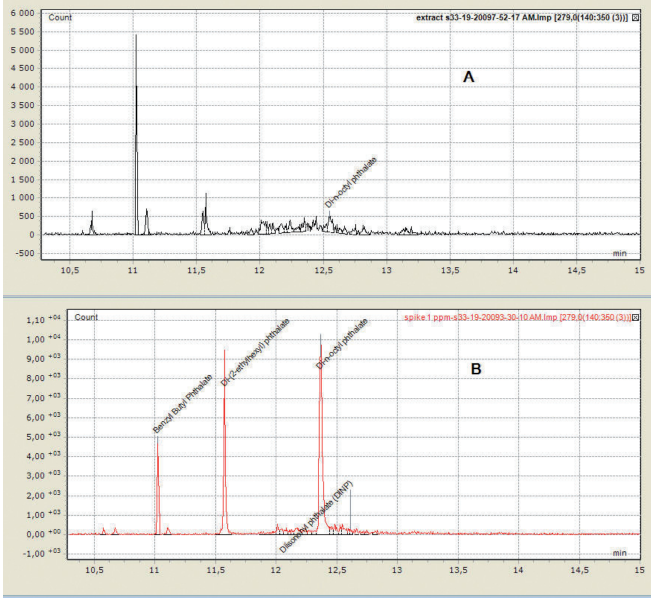

Figure 7. EIC at *m/z* 279 in a PVC toy extract (A) and toy extract spiked with 1-ppm phthalate mixture (B).

Figure 8 shows two plastic extracts with a broad peak eluting between 11.5 to 13.5 minutes. EI full scan analysis shows that extract 1 had a base ion at *m/z* 155, while the spectrum in extract 2 had a base ion at *m/z* 149 and a distinctive ion at *m/z* 293. The broad peak in extract 2 is the banned chemical, diisononyl phthalate, while the broad peak with base ion at *m/z* 155 and ion at m/z 299 in extract 1 was identified as 1, 2-cyclohexanedicarboxylic acid diisononyl ester. This chemical is approved for use as a plasticizer and impact modifier for plastics in food contact applications and is not considered to pose a risk to the environment based on its reported use pattern (4).

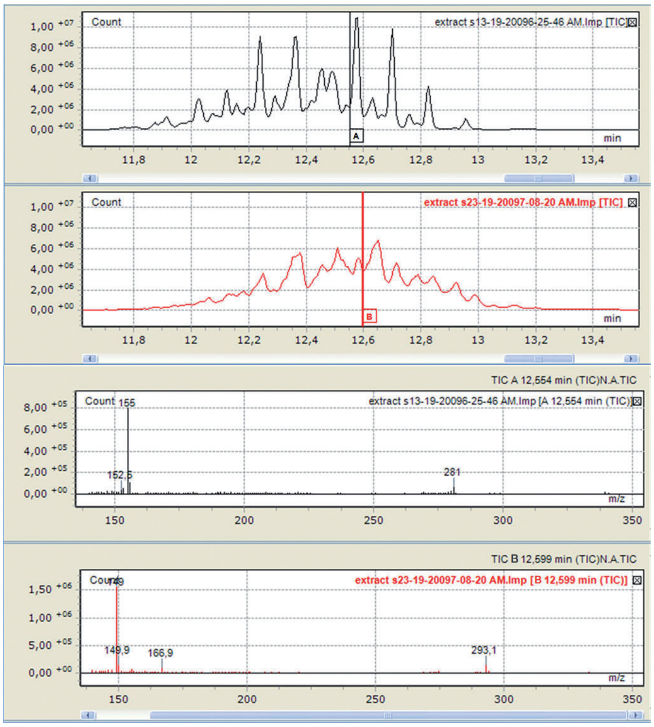

Figure 8. Broad peaks in extracts 1 and 2 and their corresponding spectra..

Low-pressure Chemical Ionization

An added benefit of the Varian 225-MS is the ability to perform low-pressure chemical ionization for the determination of phthalate esters. The result is a higher abundance of the protonated molecule that provides additional qualitative information.

It was determined that softer liquid CI reagents, such as liquid methyl t-butyl ether (MTBE), provided significant amounts of the protonated molecule for all six phthalate esters. Methanol used as a liquid CI reagent was also studied and found to be effective to a lesser extent. As shown in Figure 9, diisodecyl phthalate and diisononyl phthalate displayed protonated ions at *m/z* 447 and *m/z* 419, respectively. The corresponding EI spectra essentially look the same, showing the dominant ion at *m/z* 149.

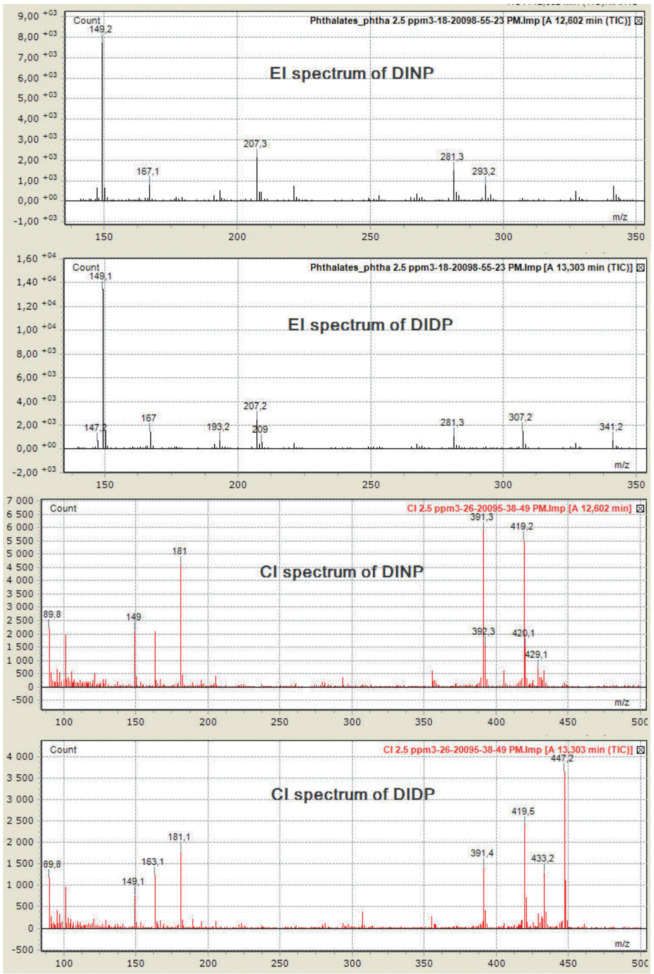

Figure 9. EI and CI spectra of diisononyl phthalate and diisodecyl phthalate.

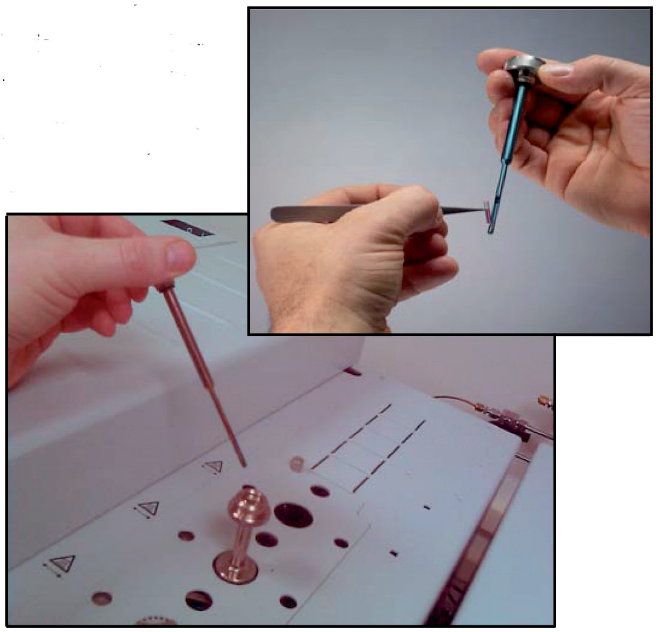

Figure 10. ChromatoProbe™ with sample vial (top right). ChromatoProbe is placed directly into the GC injection port (bottom left). The Varian 1079 programmable temperature vaporizing (PTV) injector is temperature programmable, allowing thermal desorption of the sample.

Because of the unique spectra generated by low-pressure CI, plastic from toy samples can be directly analyzed without sample preparation. The Varian ChromatoProbe sample introduction device allows for direct sampling of plastic in the GC/MS system (Figure 10).

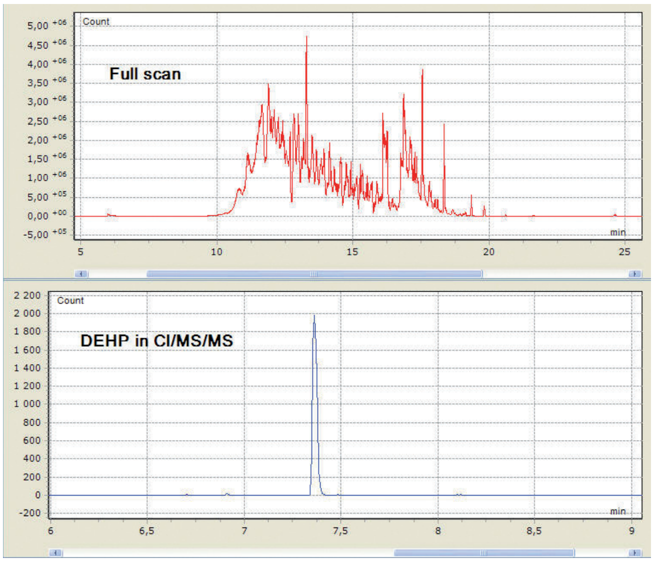

Figure 11. Full scan (top) of plastic ball sample analyzed directly with ChromatoProbe device and CI/MS/MS for DEHP (bottom), 349>149 of the same sample.

This direct sampling approach results in complex chromatograms in EI mode that would be extremely difficult to interpret. However, use of CI, combined with the power of MS/MS, simplifies the data immensely and provides confidence in results, (Figure 11).

Conclusion

The method developed on the Varian 225-MS Ion Trap Mass Spectrometer and 431-GC Gas Chromatograph in EI full scan acquisition provided excellent results in the determination of phthalate esters in PVC toy extracts using the approved CPSC method. In addition, low-pressure chemical ionization using CI liquid reagents provides these unique advantages:

- Produces mass spectra with a high abundance of the characteristic protonated molecule
- Easy to distinguish phthalates from each other in complex mixtures resulting in increased confidence in results
- Combined with MS/MS, low-pressure CI enables direct analysis and screening of plastic samples using the ChromatoProbe sample introduction device

References

1. Official Journal of the European Communities Decision 198/815/EC. 1999, European Commission; European Union Scientific Committee on Toxicology, Ecotoxicology, and the Environment.
2. U.S. Congress enacted the Consumer Product Safety Improvement Act (CPSIA 2008). http://www.cpsc.gov/cpsia.pdf
3. The US Consumer Product Safety Commission (CPSC) http://www.cpsc.gov/about/cpsia/cpsia.html
4. http://crl-fcm.jrc.it/index.php?option

These data represent typical results.
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