Screening of Plastics for Phthalates

Introduction

With regulations becoming stricter regarding the presence of phthalates in children's toy and other materials a DART method has been developed to screen for banned phthalates. Traditional GC/MS methods require extensive sample preparation (10-20 minutes) and have long analysis times (> 20 minutes). This new method allows for rapid analysis (< 2 minutes) with no sample preparation required.

Materials & Method

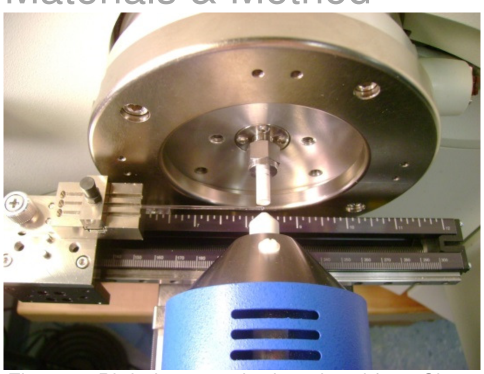
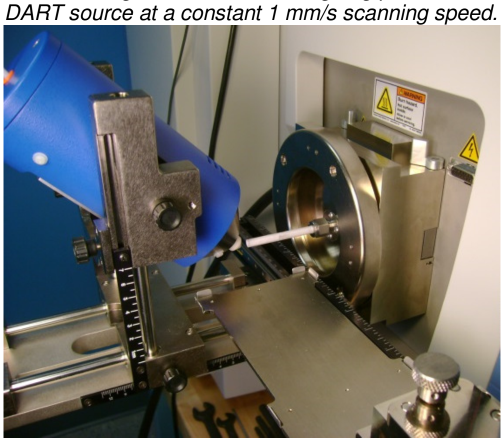


Figure 1: Phthalate standards ordered from Sigma Aldrich and all (except DMTP) were directly sampled as liquids on closed end glass capillary tube as pictured here.
Figure 2: (Below) The DART source was operated at 200 °C. The 3+D stage was moved in a zig-zag pattern under the DART source at a constant 1 mm/s scanning speed.



Phthalate Name	Elemental Composition	Exact Mass	Allowed?	
Benzyl butyl phthalate (BBP)	$C_{19}H_{20}O_4$	312.13561	No	CA Prop 65
Bis(2-ethylhexyl) phthalate (DEHP)	$C_{24}H_{38}O_4$	390.27646	No	CA Prop 65
Di-n-butyl phthalate (DBP)	$C_{16}H_{22}O_4$	278.15126	No	CA Prop 65
Diisodecyl phthalate (DiDP)	$C_{28}H_{46}O_4$	446.33906	No	CA Prop 65
Diisononyl phthalate (DiNP)	$C_{26}H_{42}O_4$	418.30776	No	CA Prop 65
Di-n-octyl phthalate (DnOP)	$C_{24}H_{38}O_4$	390.27646	No	CA Prop 65
Diisobutyl phthalate (DiBP)	$C_{16}H_{22}O_4$	278.15126	No	EU
Di-n-hexyl phthalate (DnHP)	$C_{20}H_{30}O_4$	334.21386	No	EU
Dioctylterephthalate (DOTP)	$C_{24}H_{38}O_4$	390.27646	OK	

Table 1: Shown above are the major phthalates of interest in this study. Those highlighted in yellow are isomeric phthalates of the allowed DOTP phthalate

Experimental

Liquid standards were analyzed directly on an ion trap MS to optimize the temperature of the DART ionization gas as well as the activation energies required to fragment each of the phthalates. The activation energies were ramped from 20-45% in increments of 5%.

Fragmentation was necessary for this experiment due to isomers, which include a banned and allowed phthalate. These two isomers, DnOP and DEHP, were found to have two different optimum activation energies. DOTP did not require fragmentation confirmation, as the main ion that was observed was its ammonium adduct. The optimum energies for the all of the phthalates can be seen in table 2

Phthalate Name	[M+H]+	Activation Energy (%)
Benzyl butyl phthalate (BBP)	312.80	30
Bis(2-ethylhexyl) phthalate (DEHP)	390.90	25
Di-n-butyl phthalate (DBP)	279.16	25
Diisodecyl phthalate (DIDP)	447.35	25
Diisononyl phthalate (DINP)	419.32	25
Di-n-octyl phthalate (DnOP)	391.28	40
Diisobutyl phthalate (DIBP)	279.16	25
Dipentyl phthalate (DPP)	307.19	25
Dipropyl phthalate (DPrP)	251.13	30
Dioctylterephthalate (DOTP) *	407.86	45
Dimethylterephthalate (DMTP)	195.07	30

Table 2: Optimum activation energies for phthalate standards.

Figures 3 and 4 shows the two easily differentiable fragmentation patterns of the isomers.

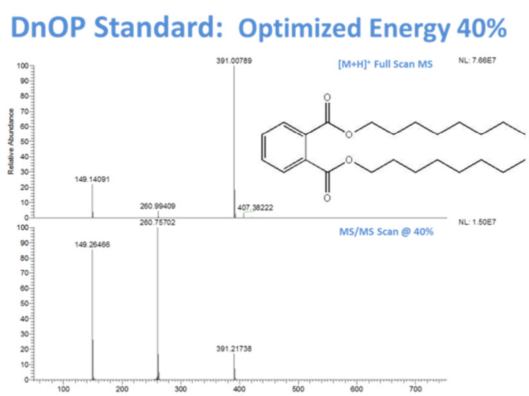
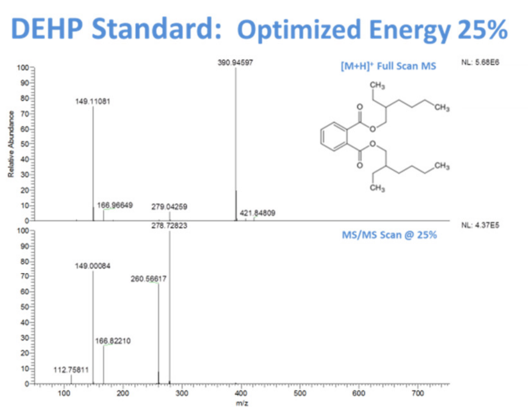


Figure 3: DEHP parent and product ions.
Figure 4: (Below) DnOP parent and product ions.



A plastic handle piece was analyzed to demonstrate the direct analysis capabilities of DART. Figure four shows the spectrum and the chromatogram from the data collected off the plastic. The spectra show a strong ion response at 391m/z which was confirmed via MS/MS fragmentation pattern to be DEHP and DnOP.

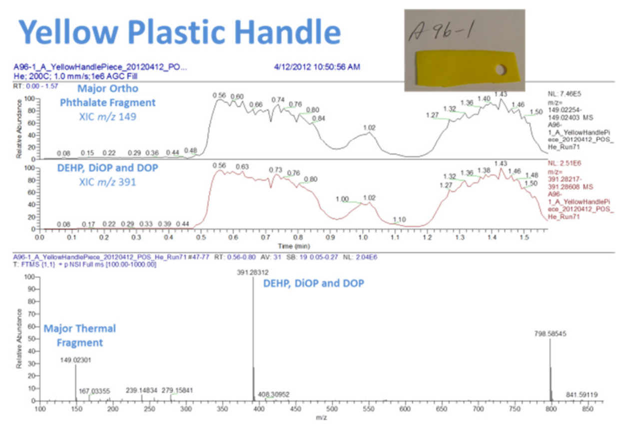


Figure 5: Chromatogram and spectrum for a plastic yellow handle.

Conclusion

Direct sample analysis of phthalates with no sample preparation is possible with the utilization of a DART-MS. Phthalate isomers can become easily distinguishable via their fragmentation pattern providing confirmatory results.

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