Determination of Phthalate Esters in Child Care Products and Children's Toys by Gas Chromatography / Mass Spectrometry (GCMS)

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Introduction

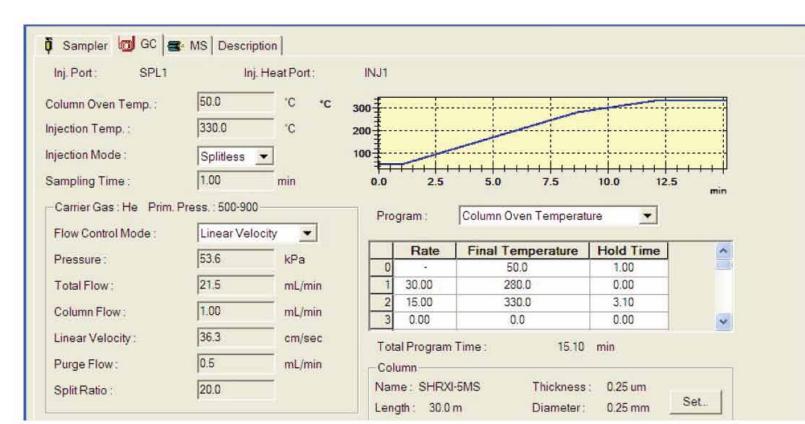
The Consumer Product Safety Improvement Act of 2008 (CPSIA) requires testing of child care products and toys for phthalate esters by GCMS. The CPSC test method specifies GCMS analysis in the SIM mode to monitor for low-intensity ions that are unique to specific phthalate esters. However, full scan mass spectra are extremely valuable in making unequivocal qualitative identification of specific isomers or homologs. Operation of the mass spectrometer in the FASST Scan/SIM mode allows concurrent acquisition of full-scan and SIM mass spectral data.

Two of the regulated analytes, di-isononyl phthalate (DINP) and di-isodecyl phthalate (DIDP), are mixtures of isomers (despite their isomer-specific nomenclature), and quantitation ions for these compounds are of very low relative intensity. So trace detection for these two substances is significantly more challenging than for the other regulated compounds.

Terephthalate esters (non-regulated compounds with similar structures) are frequently present at high concentrations in real-world samples; terephthalates interfere with identification and quantitation of DNOP, DINP and DIDP, An alternate chromatographic column has been investigated in an effort to provide chromatographic resolution of interferences from the regulated phthalate esters.

Analyses were conducted using a Shimadzu GCMS-QP2010S operated in the FASST (Scan/SIM) mode. Two chromatographic columns were employed: RXI-5MS and RXI-17Sil MS (Restek Corporation).

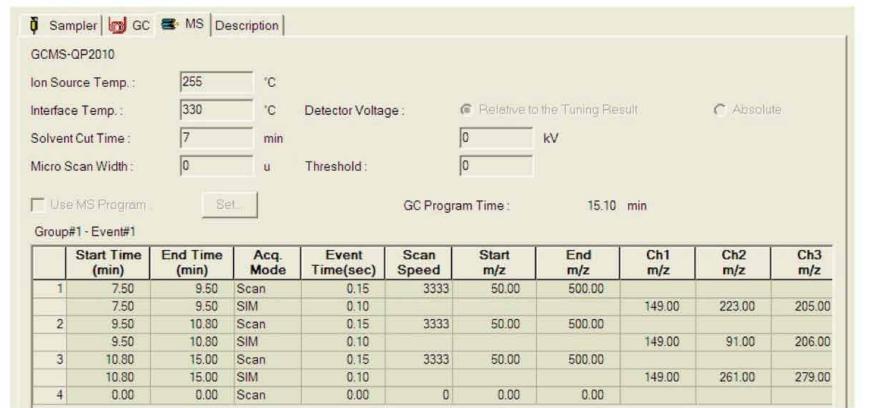
Analytical Conditions



The GC is operated in the splitless mode, using a RXI-5MS 30M x 0.25mm x 0.25µ capillary column (Restek), as specified by the CPSC method. Analysis using a RXI-17Sil MS 30M x 0.25mm x 0.25µ capillary column (Restek) is conducted using the same chromatographic conditions.

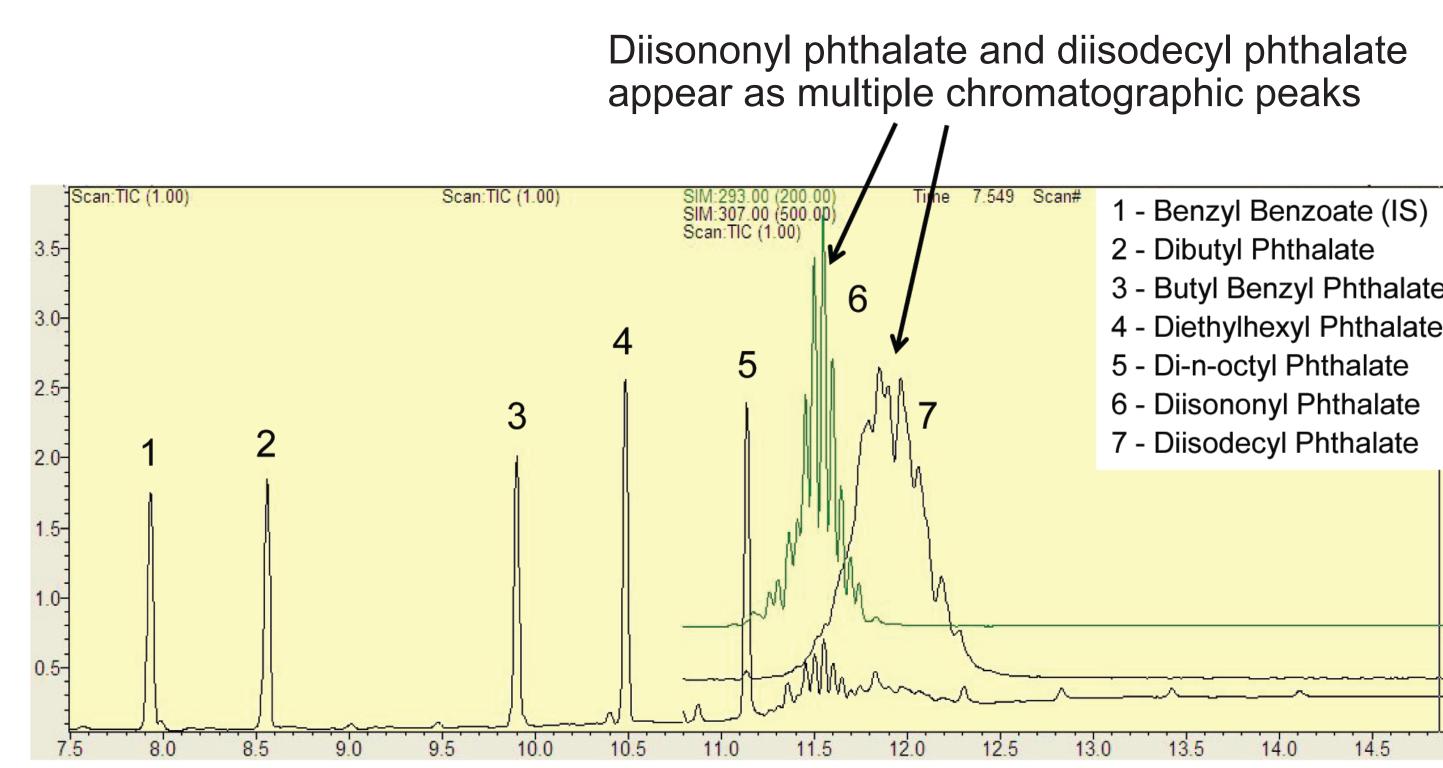
MS Conditions

The MS is operated in the EI Scan/SIM ("FASST") mode to while still providing full-scan mass spectra for unequivocal qualitative identification.



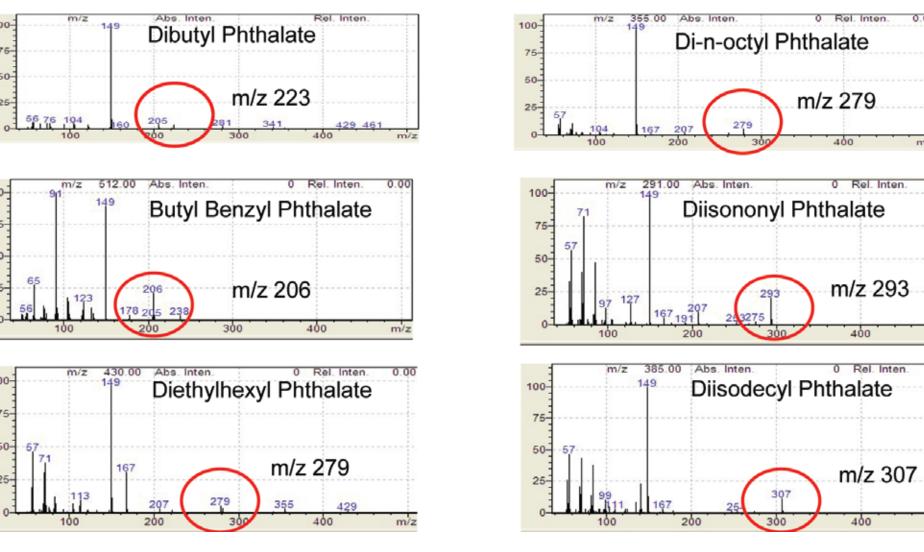
Chromatography of Phthalates on RXI-5MS Column

RXI-5MS Column 30M x 0.25mm x 0.25µ (Restek Corp)



Quantitation lons for the Phthalate Esters

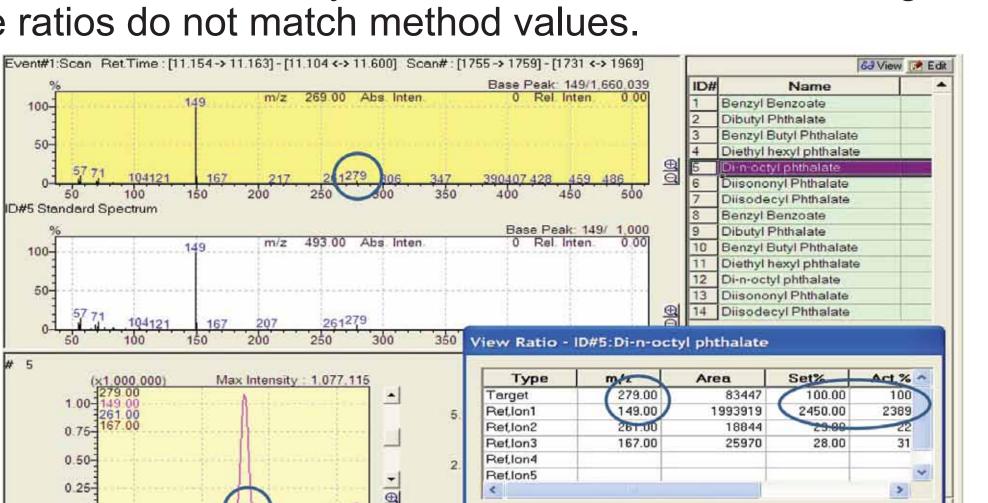
Unique quantitation ions are specified in the CPSC method for unequivocal identification of the regulated phthalate esters. In several cases, the relative abundance of the specified quantitation ion is relatively low. The low relative abundance quantitation ion is particularly significant for diisononyl phthalate and diisodecyl phthalate, which show multiple chromatographic peaks.



91 243275 200 300 400 Diisodecyl Phthalate

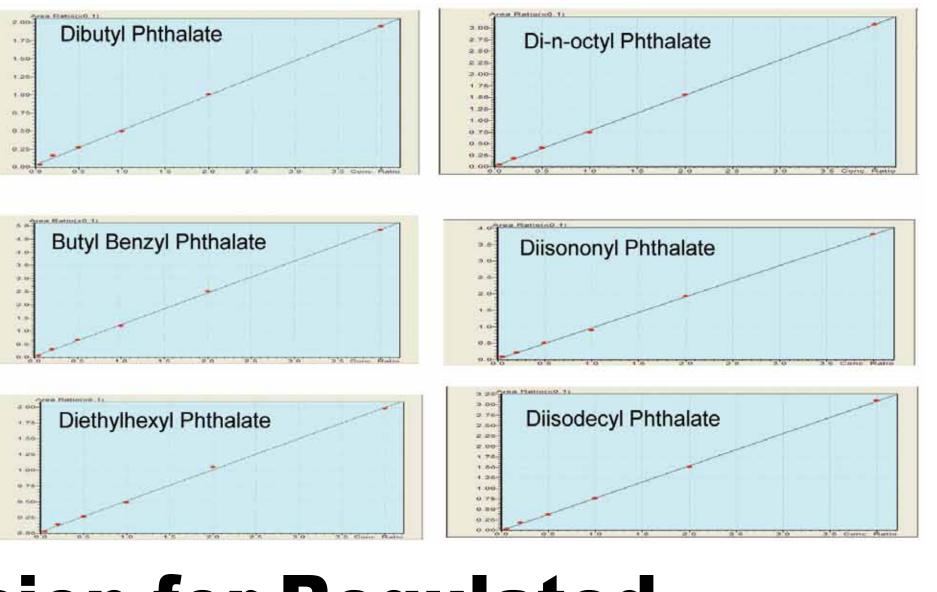
Quantitation lons for the Phthalate Esters

- When ions of low relative abundance are used as quantitation ions, large abundance ratios result for the major peaks in the mass spectrum.
- Discrepancies between abundance ratios can easily result in misidentification of target compounds because abundance ratios do not match method values.
- A software feature that displays method and actual ion abundances is a convenient way to monitor relative abundance ratios and make method adjustments if necessary.
- Example shown below for di-n-octyl phthalate



Calibration Curves for Regulated **Phthalate Esters**

Calibration curves are linear from 0.25-20ug/ml (corresponding to detection of the analytes well below the regulatory limit) for each of the regulated phthalate



Trace-Level Precision for Regulated **Phthalate Esters**

The precision of the GCMS analytical method was evaluated by injecting eight aliquots of the lowest-level analytical standard. Results are tabulated below:

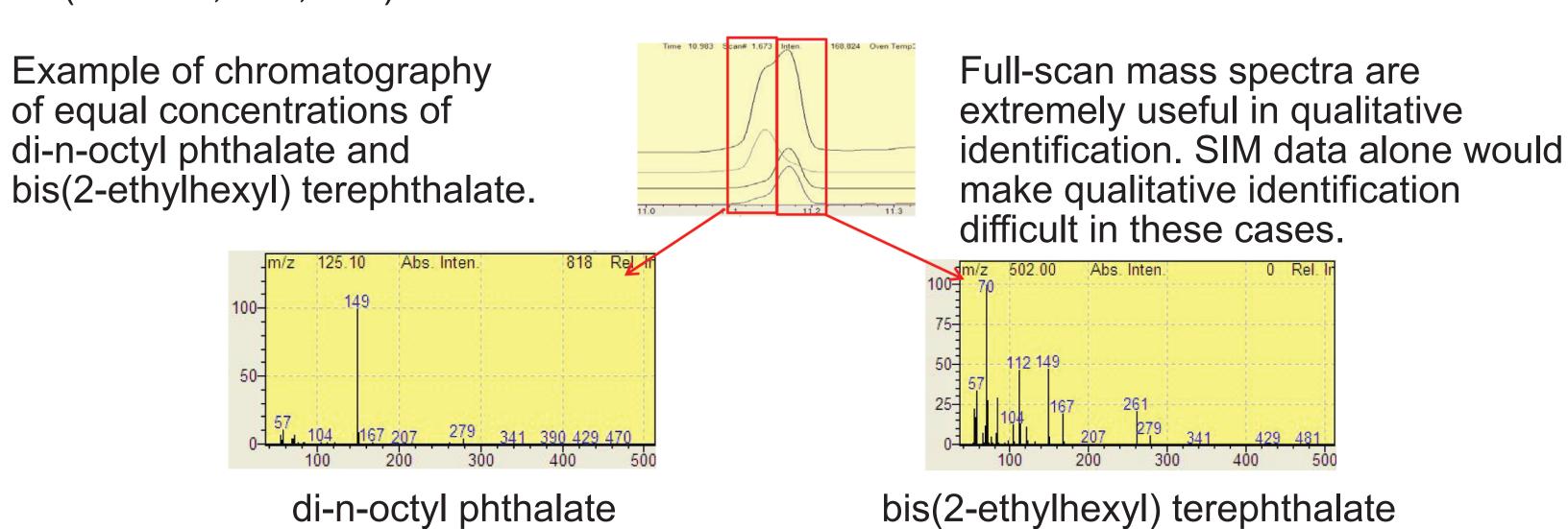
owest-level analytical standard. Results are tabulated below.												
	Compound	Mode	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Mean	RSD (%)
D	ibutyl Phthalate	Scan	0.30	0.29	0.31	0.28	0.25	0.30	0.30	0.27	0.29	6.9
В	utyl Benzyl Phthalate	Scan	0.26	0.26	0.24	0.24	0.25	0.23	0.25	0.25	0.25	4.2
D	iethylhexyl Phthalate	Scan	0.24	0.27	0.28	0.25	0.27	0.25	0.25	0.31	0.27	8.6
D	i-n-octyl Phthalate	Scan	0.25	0.22	0.23	0.24	0.24	0.24	0.25	0.25	0.24	4.5
D	iisononyl Phthalate	Scan	0.21	0.22	0.20	0.20	0.21	0.21	0.18	0.19	0.20	6.3
D	iisodecyl Phthalate	Scan	0.27	0.22	0.21	0.28	0.22	0.27	0.21	0.23	0.24	12.4
D	ibutyl Phthalate	SIM	0.30	0.29	0.29	0.28	0.28	0.32	0.30	0.30	0.30	4.4
В	utyl Benzyl Phthalate	SIM	0.25	0.25	0.24	0.23	0.24	0.24	0.23	0.24	0.24	3.1
D	eiethylhexyl Phthalate	SIM	0.27	0.27	0.27	0.25	0.25	0.26	0.27	0.26	0.26	3.4
D	i-n-octyl Phthalate	SIM	0.24	0.24	0.23	0.22	0.23	0.24	0.23	0.23	0.23	3.0
D	iisononyl Phthalate	SIM	0.20	0.20	0.20	0.20	0.25	0.20	0.20	0.19	0.21	9.0
D	iisodecyl Phthalate	SIM	0.20	0.22	0.21	0.20	0.20	0.22	0.20	0.23	0.21	5.7
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Method Performance

- Fundamental method performance is satisfactory:
- Good chromatography, with excellent linearity and precision Excellent sensitivity with FASST (Scan/SIM)
- Issues with method implementation:
- Background contamination with phthalate esters from various sources method blanks are very critical
- Interferences from non-regulated phthalate esters and related compounds chromatographic and mass spectral interferences with detection and quantitation of regulated phthalate esters (example following)
- Variable homogeneity of solid samples gives rise to questions of method reliability

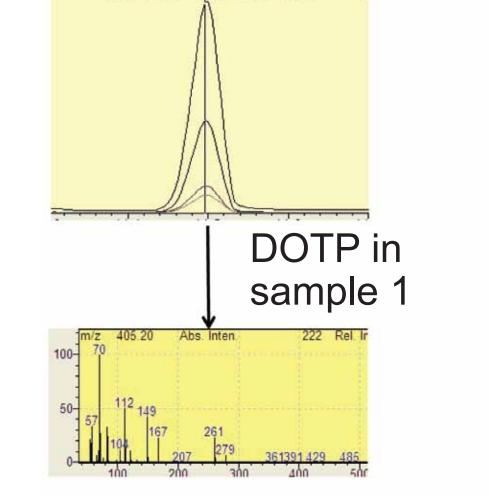
Method Performance Issues (Interferences)

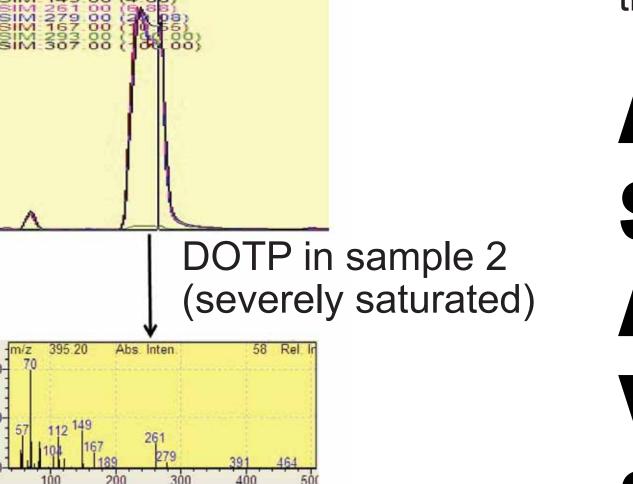
- Interference from non-regulated phthalate esters and related compounds masks trace detection of the regulated phthalate esters.
- Noteworthy is interference of bis(2-ethylhexyl) terephthalate (a commonly-used, non-regulated plasticizer) with detection of di-n-octyl phthalate; these compounds co-elute on the RXI-5MS column and have key mass spectral fragment ions in commo (m/z 149, 167, 279).



Method Performance Issues (Interferences)

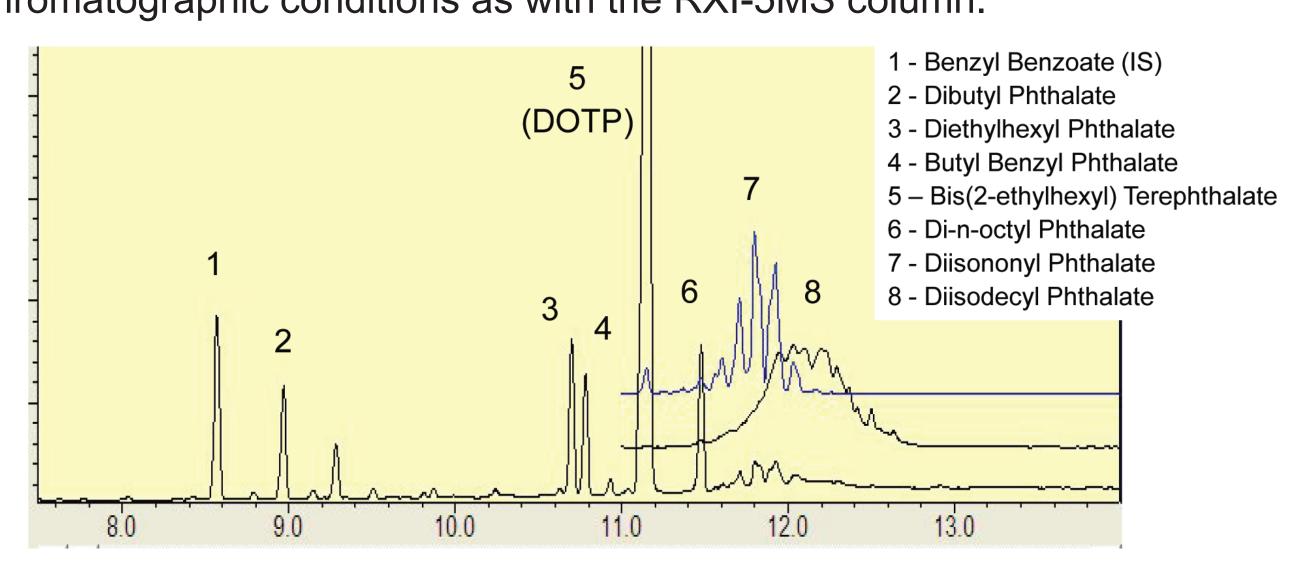
Examples of "real-world" sample data – samples contain bis(2-ethylhexyl) terephthalaite (DOTP) which masks the chromatographic signal for di-n-octyl phthalate (DNOP).





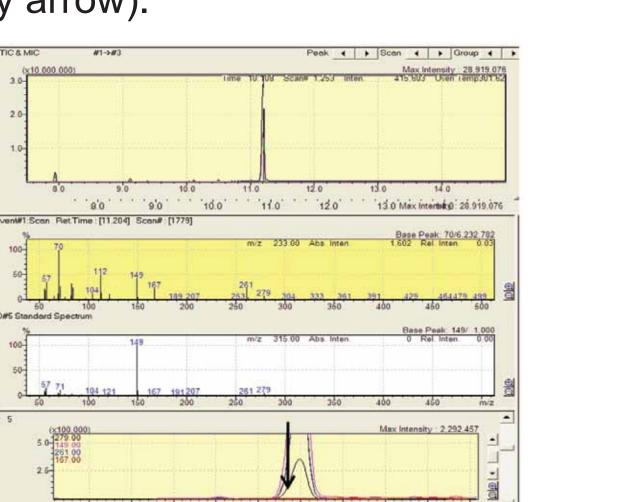
Chromatography of Phthalates on RXI-17Sil MS Column

Bis(2-ethylhexyl) terephthalate ("DOTP") is well-resolved from the regulated phthalate esters on a RXI-17Sil MS 30M x 0.25mm x 0.25µ capillary column (Restek), using the same chromatographic conditions as with the RXI-5MS column.

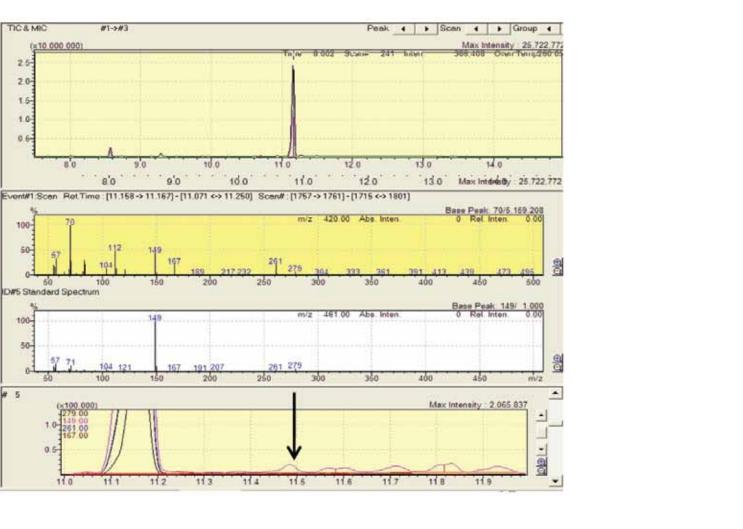


Real-World Sample Results (Sample 1)

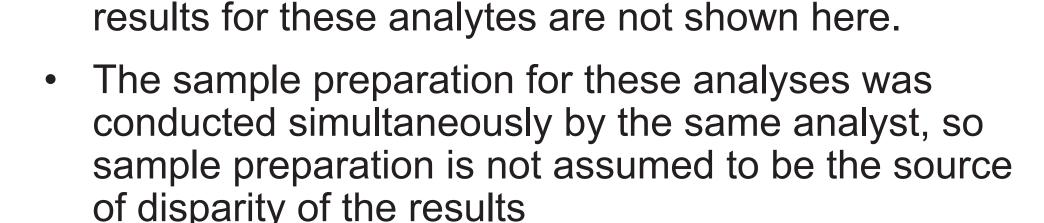
When an RXI-5MS column is used. detection of di-n-octyl phthalate (DNOP) is masked by high concentration of bis(2-ethylhexyl) terephthalate (expected RT of DNOP is indicated by arrow)



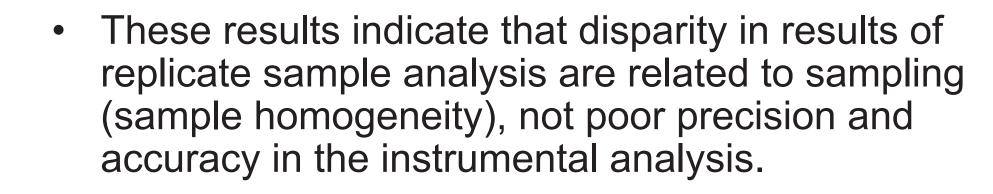
When an RXI-17Sil MS column is used, there is no interference in detection of di-n-octyl phthalate (DNOP) by bis(2-ethylhexyl) terephthalate (expected RT of DNOP is indicated by arrow – trace-level peak does not correspond to DNOP).



instrument precision (Std Dev, shown by the amber bars in the graphic) is considerably better than precision between aliquots. Results for dibutyl phthalate and butyl benzyl phthalate are very low (single-digit precision), so



Graphical representation of the results show



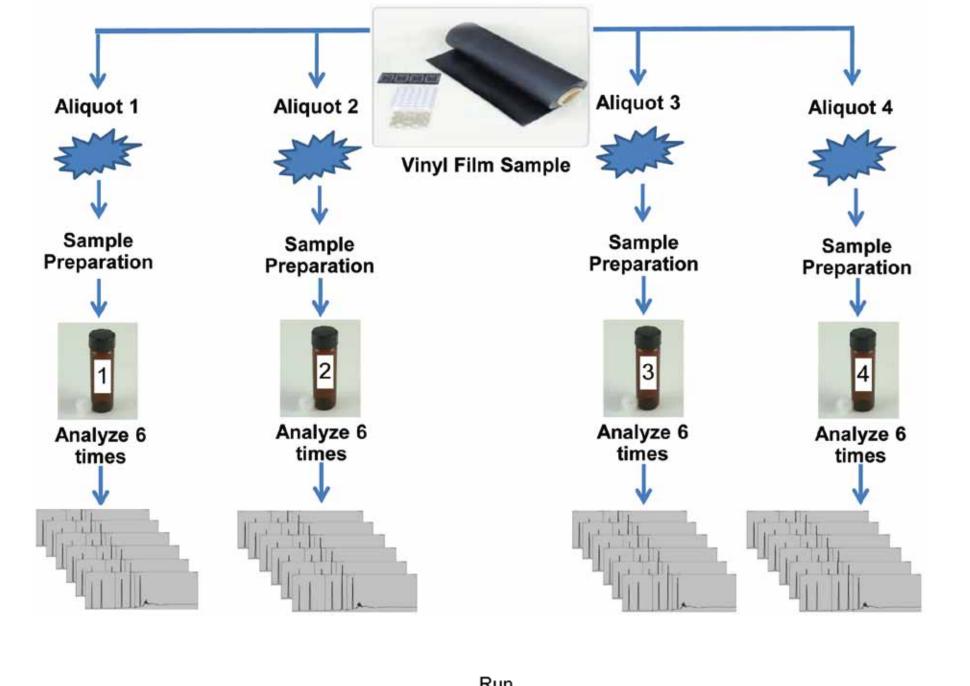
Method Performance Issues (Disparate Results)

Disparate results have been reported for multiple analyses of the same samples by different laboratories. These results have given rise to concerns about laboratory credibility, instrument reliability, and method performance. Example results are presented below for a vinyl film sample analyzed by three separate laboratories:

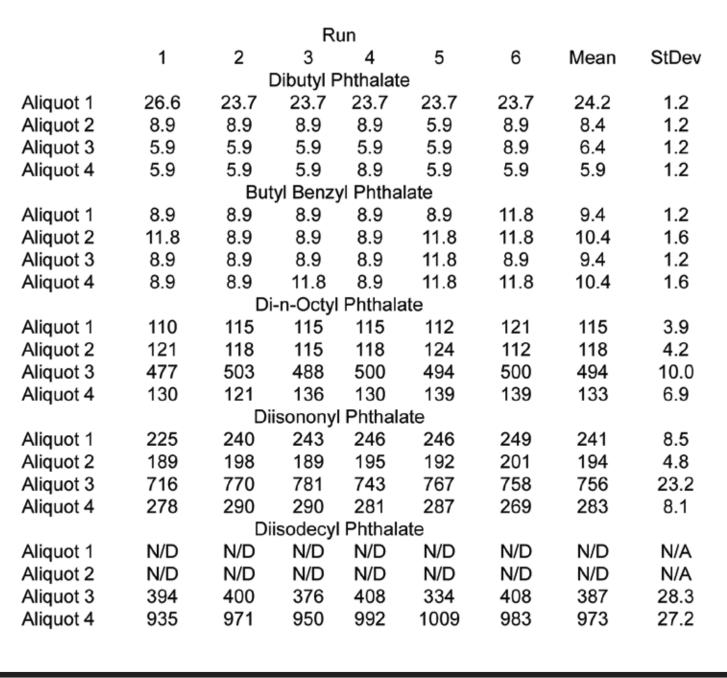
Compound	Lab 1	Lab 2	Lab 3
ibutyl Phthalate	5	13	19
Butyl Benzyl Phthalate	ND	10	ND
ethylhexyl Phthalate	34	215	725
i-n-octyl Phthalate	ND	ND	ND
iisononyl Phthalate	1500	325	17900
iisodecyl Phthalate	609	354	543

To further define the problem of disparate results, four aliquots of the vinyl film sample were prepared and analyzed six times each. Results are summarized in the table below. and are also presented graphically in figures following; sampling/analysis is illustrated in the following graphic.

Analytical Scheme for **Analysis of** Vinyl Film Sample



Sample Results -Replicate Analyses of Vinyl Film Sample



Solutions for Method Performance Issues

Method Performance Issue

- Difficulties in qualitative identification of regulated phthalate esters with SIM data
- Low-level detection of some analytes difficult due to low relative abundance of quantitation ions and multiple chromatographic peaks.
- Monitoring of low abundance ions for quantitation gives rise to large variations in relative abundance ratios.
- Chromatographic and spectral interferences are encountered from non-regulated phthalate esters and terephthalate esters.
- Disparate results are frequently obtained for analysis of replicate analyses of solid

Conduct analyses using Scan/SIM

- function (FASST) for unequivocal qualitative identification. Excellent sensitivity is achieved using
- Scan/SIM function (FASST), even for analytes with multiple chromatographic peaks (DINP, DIDP).
- Use of a convenient software feature to monitor ion abundance ratios allows easy modification of method parameters.
- One major interfering compound is easily resolved by using an RXI-17Sil MS chromatographic column (Restek).
- Results indicate that difficulties are related to sampling rather than analysis. Sample homogenization and analysis of replicate sample aliquots is highly

Summary

The CPSC test method has been demonstrated using a Shimadzu GCMS-QP2010S operated in the FASST (Scan/SIM) mode. Excellent basic method performance was demonstrated: specifically, excellent sensitivity, linearity, and precision at low levels was demonstrated. Two of the regulated compounds, di-isononyl phthalate (DINP) and di-isodecyl phthalate (DIDP), are mixtures of isomers (despite their isomer-specific nomenclature), and quantitation ions for these compounds have very low relative intensity. So, trace detection for these two substances is more difficult than for the other regulated compounds, but adequate sensitivity is attained using the FASST Scan/SIM technique.

Interferences from terephthalate esters (non-regulated compounds with similar structures) have been encountered in real-world samples; terephthalates interfere with identification and quantitation of DINP and DIDP. An alternate chromatographic column was employed to resolve the interferences from terephthalate esters.

Disparate results have been observed for replicate analyses of real-world solid samples. To cast light on this issue, replicate aliquots of a vinyl film sample were prepared and analyzed six times each. Replicate analyses of each aliquot showed good statistical agreement, but variable results were obtained for each of the sample aliquots. The results suggest that disparity in the results can be attributed to homogeneity of solid samples. Sample homogenization and analysis of replicate aliquots is recommended to obtain representative analytical results.

Acknowledgement

 The authors wish to thank Gary Stidsen, Restek Corporation for supplying columns for this investigation.