Analysis of phthalates using gas chromatography mass spectrometry and application to multiple passive sampling matrices

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Abstract

The demand for the production of phthalate plasticizers has accelerated over the last century due to the discovery of their unique properties that were feasible for businesses to use for their products. Phthalates are used in a wide array of everyday consumer items. Due to increasing demand and more awareness of environmental health impacts of phthalates within the last thirty years, regulations have been implemented across the globe for particular phthalates. A gas chromatography mass spectrometry (GC-MS) method was developed and will be established to determine the phthalate in a wide array of sample matrices. This method, 31 compounds total, includes 3 alternative (non-phthalate) plasticizers and does not incorporate derivative steps. These matrices range from passive sampling devices such as silicon wristbands and low density polyethylene samplers. These compounds were analyzed via Agilent 8890 GC 5977B MS. The target compounds were analyzed via scan and selected ion monitoring (SIM) modes. Analytic method validation includes standard spiked passive samplers in replicates of three on three different days.

Introduction

Phthalates known as dominant plasticizers are found in everyday consumer items from auto interiors, food packaging, home furniture items, and consumer products. Phthalates are additives that make products more flexible, durable, and regulate temperature changes. Since they are not chemically bound to polymer(s), they are therefore able to leach out. Over the years, more phthalates have been synthesized as well as alternative phthalates.

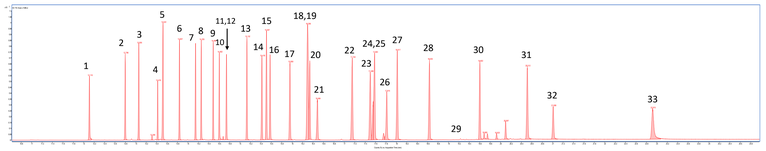


Figure 1: Full chromatograph of all 31 compounds including 3 alternative (non-phthalate) plasticizers run in ethyl acetate on a DB 5MS column. Far left peak is dimethyl phthalate with a molecular weight of 191 g/mol. Far right peak is ditridecyl phthalate with a molecular weight 531 g/mol. Peaks are numbered according to retention time.

There are 31 phthalates, including 3 alternative compounds, in this GC-MS method (Figure 1). For a full analyte list see Table 5.

Calibration Range

- Most target's calibration range is from 0.5 ppm to 25 ppm, based on an eight point curve.
  - Potential for lower Limit of Detection (LOD) with some compounds: bis (2-ethylhexyl) adipate, di-n-butyl phthalate, diallyl phthalate to name a few.

LOD	Minimum RSD%	Maximum RSD%
0.5 ppm	1.63	9.88
1 ppm	2.99	8.65
2 ppm	6.79	7.50

Table 1: Relative Standard deviation (RSD%) range seen over the three different LOD levels.

- Relative standard deviation (RSD%) was calculated over 3 days for each level.
- Four compounds have quadratic fits (dipropyl phthalate, di-n-butyl phthalate, bis (2-ethylhexyl) terephthalate, ditridecyl phthalate).
- All other compounds have a linear fit.

Spiked Matrices

- Aliquots of random blank low density polyethylene (LDPE) and silicone wristbands (WB) spiked with a 5 ppm solution of the full curve.
- LDPE response was 26% higher than WB.
- Concentrations for both matrices were on average 16 to 20 times higher than original spike.
- This will lead to optimizing inlet parameters.

	Avg Conc. (ppm)	Avg RSD%
WB	80.4	3.88
LDPE	98.0	12.3

Table 2: Concentrations and RSD% for spiked LDPE and WB

Instrumentation

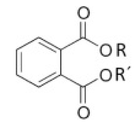
Instrument Parameters	Settings
MS Source	300 °C
MS Quad	180 °C
MSD transfer line	300 °C
Function type	Full Scan and SIM
Full Scan Range	50-600 m/z
Dwell time	20 ms per peak
Gain Factor	0.75
Injection Volume	1 µL
Inlet mode	Pulsed splitless
Pulse Pressure	25 psi
Inlet temperature	290 °C
Liner	4 mm single taper w/glass wool
Column	J&W DB 5MS 30m x 250µm x 0.25µm
Gas	Helium 99.99%
Flow rate	1.157 mL/min
Source type	Xtr EI Source

Table 3: GC-MS parameter table

Analyte List

Retention Time order	Analyte	CAS Number	Chemical formula	Retention Time (min)	Molecular Weight (g)	Sim Ion	Qualifier Ions	r^2	LOD (ppm)
1	Dimethyl phthalate	131-11-3	C10H10O4	12.115	194.2	163	133, 194	0.997	1.0
2	Diethyl phthalate	84-66-2	C12H14O4	12.802	222.2	149	177, 105	0.998	0.5
3	Diisopropyl phthalate	605-45-8	C14H18O4	13.064	250.3	149	122, 167	0.993	0.5
4	Diallyl phthalate	131-17-9	C14H14O4	13.431	246.3	149	132, 189	0.998	0.5
5	Dipropyl phthalate	131-16-8	C14H18O4	13.538	250.3	149	191, 209	0.998	1.0
6	Diisobutyl phthalate	84-62-8	C16H22O4	13.854	278.3	149	104, 223	0.991	0.5
7	Di-n-butyl phthalate	84-74-2	C16H22O4	14.166	278.3	149	205, 160	0.999	0.5
8	Bis (2-methoxyethyl) phthalate	117-82-8	C14H18O6	14.279	282.3	149	176, 167	0.999	0.5
9	Diisopentyl phthalate	605-50-5	C18H26O4	14.509	306.4	149	237, 104	0.995	0.5
10	Bis (2-ethoxyethyl) phthalate	605-54-9	C16H22O6	14.630	310.3	149	176, 193	0.990	0.5
11	Diamyl phthalate d-4	358730-89-9	C18H22D4O4	14.766	310.4	153	241, 223	-	-
12	Diamyl phthalate	131-18-0	C18H26O4	14.766	306.4	149	306, 219	0.991	1.0
13	Bis (4-methylpentyl) phthalate	146-50-9	C20H30O4	15.165	334.5	149	251, 167	0.995	0.5
14	Dihexyl phthalate	84-75-3	C20H30O4	15.458	334.4	149	150, 233	0.994	1.0
15	Benzyl butyl phthalate	85-68-7	C19H20O4	15.546	312.4	149	206, 150	0.997	1.0
16	Bis (2-ethylhexyl) adipate*	103-23-1	C22H42O4	15.612	370.6	129	147, 130	0.998	0.5
17	Bis (2-butoxyethyl) phthalate	117-83-7	C20H30O6	16.000	366.4	149	193, 176	0.998	0.5
18	Bis (2-ethylhexyl) phthalate	117-81-7	C24H38O4	16.346	390.6	279	149, 167	0.999	0.5
19	Diheptyl phthalate	3648-21-3	C22H34O4	16.346	362.5	247	149, 265	0.998	0.5
20	Dicyclohexyl phthalate	84-61-7	C20H26O4	16.386	330.4	249	149, 167	0.999	0.5
21	Diphenyl phthalate	84-62-8	C20H14O4	16.535	318.3	225	226, 153	0.997	1.0
22	Bis (2-ethylhexyl) isophthalate	137-89-3	C24H38O4	17.2	390.6	149	167, 261	0.997	0.5
23	Di-n-octyl phthalate	117-84-0	C24H38O4	17.547	390.6	149	261, 279	0.994	1.0
24	Diphenyl isophthalate	744-45-6	C20H14O4	17.606	318.3	225	141, 104	0.996	2.0
25	Bis (2-ethylhexyl) terephthalate*	6422-86-2	C24H38O4	17.632	390.6	149	112, 261	0.999	2.0
26	Dibenzyl phthalate	523-31-9	C22H18O4	17.862	346.4	107	149, 91	0.997	0.5
27	Bis (2-propylheptyl) phthalate	53306-54-0	C28H46O4	18.056	446.7	149	167, 307	0.996	0.5
28	Dinonyl phthalate	84-76-4	C26H42O4	18.667	418.6	149	150, 293	0.994	0.5
29	Diisodecyl phthalate d-4	1346604-79-2	C28H42D4O4	19.261	450.7	153	311, 171	-	-
30	Didecyl phthalate	84-77-5	C28H46O4	19.627	446.7	149	167, 307	0.994	0.5
31	Diundecyl phthalate	3648-20-2	C30H50O4	20.539	474.7	149	167, 321	0.996	0.5
32	Tri (2-ethylhexyl) trimellitate*	3319-31-1	C33H54O6	21.029	546.8	305	193, 323	0.996	1.0
33	Ditridecyl phthalate	119-06-2	C34H58O4	22.950	530.8	149	150, 349	0.976	1.0

Table 5: Full analyte list with r^2 values and LOD's. Compounds with an asterisk are alternative plasticizers.



Representative Phthalate Structure

Oven Profile	Rate (C/min)	Value (C)	Hold time (min)
Initial		40	2
Ramp 1	10	100	0
Ramp 2	25	200	0
Ramp 3	40	280	3
Ramp 4	20	335	7
Post run		340	5

Table 4: Oven profile for Agilent 8890 GC 5977B MS

Oven Profile

- Developed to improve resolution between coelutions and to preserve the Gaussian peak shapes of the high molecular weight phthalate compounds.
- A five minute post run was added to the oven profile to prevent silicon matrix carry over.
- Total run time is 31.75 minutes.

Peaks of Interest

- Two coelutions exist in this method: bis (2-ethylhexyl) phthalate and diheptyl phthalate, diphenyl isophthalate and bis (2-ethylhexyl) terephthalate. Both can be mass resolved.

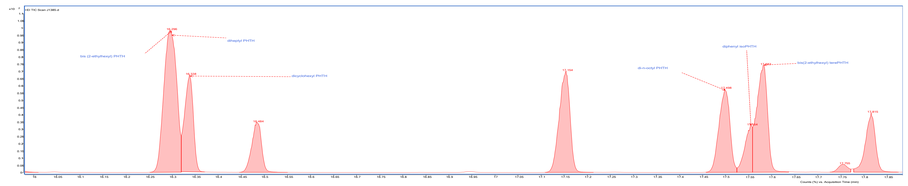


Figure 2: Coelutions in the method: bis (2-ethylhexyl) phthalate and diheptyl phthalate, diphenyl isophthalate and bis (2-ethylhexyl) terephthalate.

- Diphenyl phthalate and diphenyl isophthalate both have a break down product of phenol which is earlier at the chromatograph.

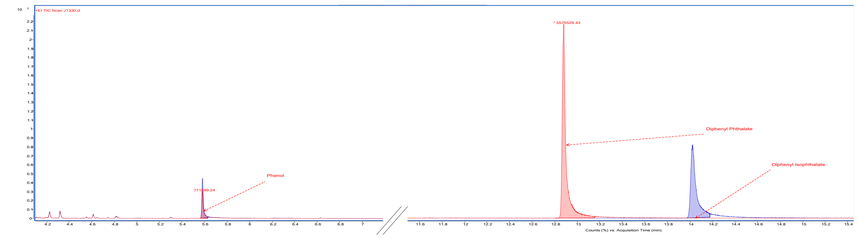
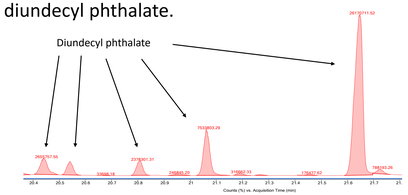


Figure 3: Phenol breakdown from diphenyl phthalate (red) and diphenyl iso phthalate (blue).

- Diundecyl phthalate breaks down into four additional smaller peaks. In order to quantify the compound, the 5 peaks are integrated to contribute the concentration of diundecyl phthalate. No other compounds in this method are retained during the expected retention time of diundecyl phthalate.

Figure 4: The 5 peaks of diundecyl phthalate. Main peak on far right.



Conclusion and Next Steps

- This robust GCMS SIM method has the capability to quantify phthalate content in matrices such as silicon wristbands and LDPE without any additional derivative steps.
- Next steps:
  - Potential pulse split injection mode with different split ratios for multiple matrices.
  - Further method detection limit studies.
  - Matrix spiked calibration curves.
  - Conduct storage stability studies.

Acknowledgements

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