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Analysis of Phthalates Using GC/MS With Hydrogen Carrier Gas: The Importance of Reducing Interferences and Contamination

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Introduction

Due to the price of helium (He), many laboratories are looking for alternative carrier gases for their gas chromatography/mass spectrometry (GC/MS) methods. This work describes the evaluation of a single quadrupole GC/MS method for the analysis of 19 phthalates using hydrogen carrier gas and an EI source [1]. The method provides excellent peak shape, resolution, sensitivity, and a 13 min run time. Calibration curves were linear for 16 of the phthalates, with the remaining 3 alkoxy phthalates requiring a quadratic fit. Except for DINP and DIDP (mixtures of isomers), all compounds could be quantitated at low pg levels. Specific attention to the consumables used and their preparation before use is discussed and is important for reaching the lowest calibration levels.

Experimental

Table 1. Method Parameters

GC	Agilent 8890 GC with Agilent 7693A automatic liquid sampler and tray
Inlet	Multimode inlet (MMI), Pulsed Splitless Mode, Injection Volume 1.0 µL
Injection Pulse Pressure	25 psi until 0.90 min, Purge Flow to Split Vent 50 mL/min at 1.0 min
Inlet Temperature	280 °C
Inlet Liner	Agilent universal Ultra Inert mid-frit liner (p/n 5190-5105)
Column	Agilent HP-5MS UI 20 m x 0.18 mm id x 0.18 µm (p/n 19091S-577UI)
Column Temperature Program	60 °C (1.5 min), 50 °C/min to 220 °C, 12.5 °C/min to 320 °C (0.3 min hold)
Carrier Gas and Flow Rate	Hydrogen, 0.9 mL/min constant flow
MSD	Agilent 5977C Inert Plus GC/MSD
Source	Inert Plus Extractor EI source with optional 9 mm lens (G3870-20449)
Temperatures	Transfer line 280 °C, Ion Source 300 °C, Quadrupole 150 °C
EM voltage Gain Mode	Gain, 1.0
Mode	SIM
Tune; Solvent Delay	ETUNE.U; Solvent Delay: 3.5 min.

Table 2. Names, abbreviations, CAS numbers, retention times, target and qualifiers ions of phthalates studied.

RT	Name	Abbreviation	CAS Number	Target m/z	Q1 m/z	Q2 m/z	Q3 m/z
4.177	Dimethyl phthalate	DMP	131-11-3	163	77	194	133
4.530	Diethyl phthalate	DEP	84-66-2	149	177	105	222
4.896	Diallyl phthalate	DAP	131-17-9	149	41	132	189
5.206	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	DIBP	84-69-5	149	223	167	104
5.480	Dibutyl phthalate	DBP	84-74-2	149	223	205	104
5.602	Bis(2-methoxyethyl) phthalate	DMEP	117-82-8	149	176	104	59
5.876	1,2-Benzenedicarboxylic acid, bis(4-methylpentyl) ester	BMPP	146-50-9	149	251	167	85
5.993	1,2-Benzenedicarboxylic acid, bis(2-ethoxyethyl) ester	DEEP	605-54-9	149	72	104	193
6.128	Diamyl phthalate	DPP	131-18-0	149	237	219	104
6.915	1,2-Benzenedicarboxylic acid, dihexyl ester	DHXP	84-75-3	149	104	233	251
6.971	Benzyl butyl phthalate	BBP	85-68-7	149	91	104	206
7.515	Bis(2-butoxyethyl) phthalate	DBEP	117-83-9	149	193	101	85
7.767	Dicyclohexyl phthalate	DCHP	84-61-7	149	167	104	249
7.858	Bis(2-ethylhexyl) phthalate	DEHP	117-81-7	149	167	113	104
8.777	Di-n-octyl phthalate	DNOP	117-84-0	149	279	104	261
9.292	Bis(2-propylheptyl) phthalate	DPHP	53306-54-0	149	55	167	307
9.779	1,2-Benzenedicarboxylic acid, dinonyl ester	DNP	84-76-4	149	293	275	150
8-10.3	Diisononyl phthalate	DINP	28553-12-0	293	149	167	
8.5-10.7	Diisodecyl phthalate	DIDP	26761-40-0	307	149	167	

Results and Discussion

Figure 1. 50 ppb phthalate standard. SIM 163 quantifier for DMP. SIM 149 for all others.

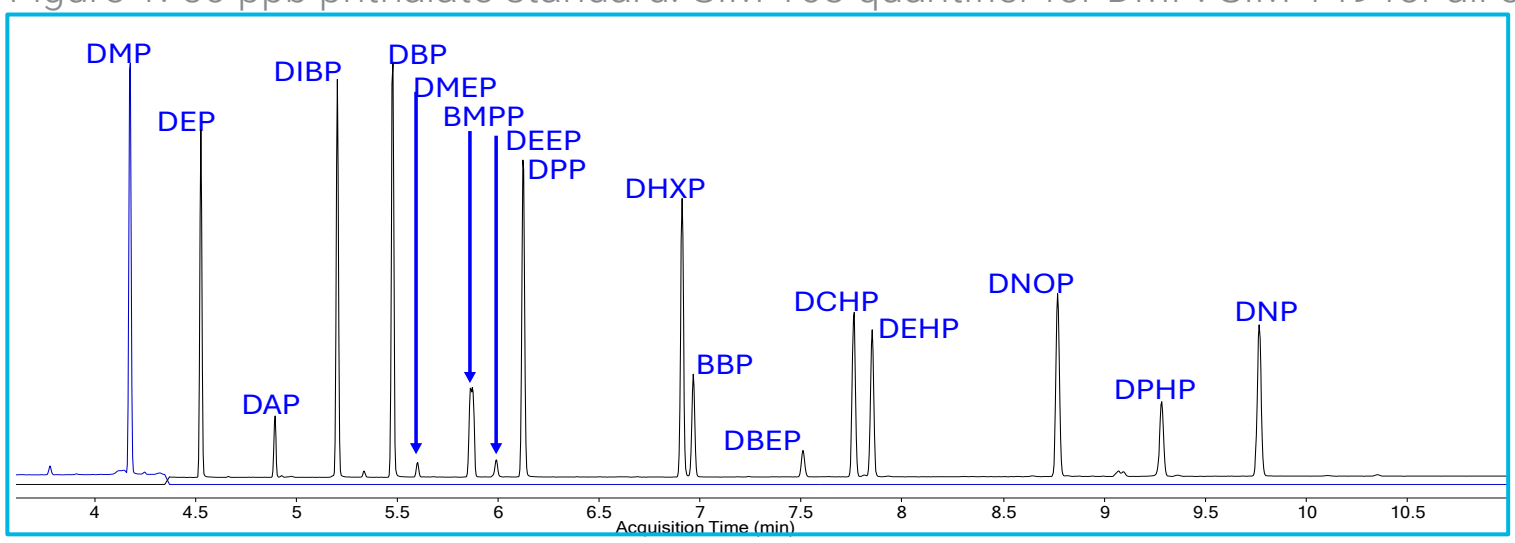


Figure 2. 1000 ppb diisononyl and diisodecyl isomers phthalate standard.

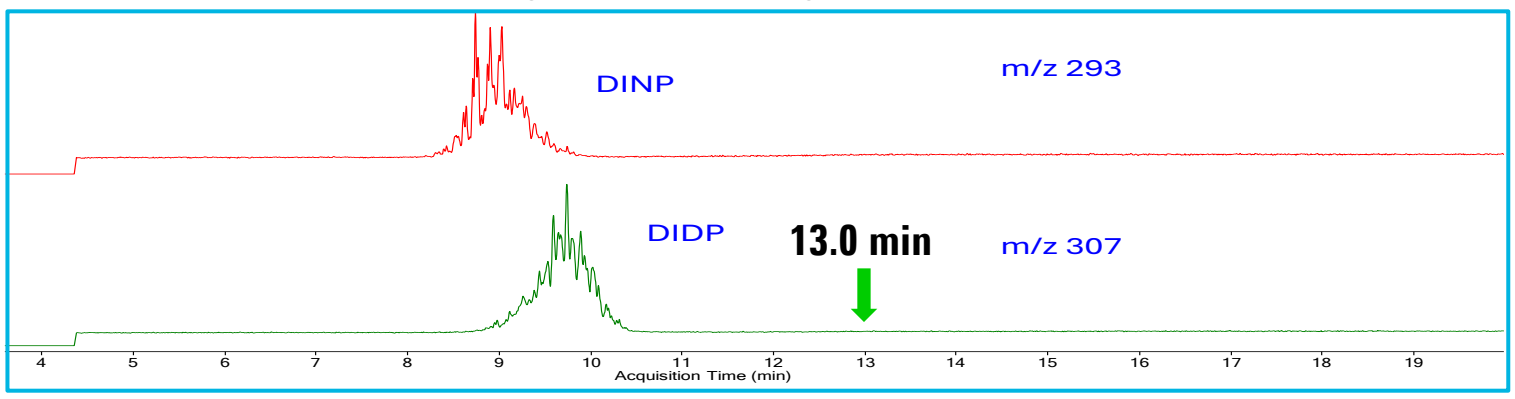


Figure 3. Example of interferences and contaminants initially observed in isooctane solvent blanks.

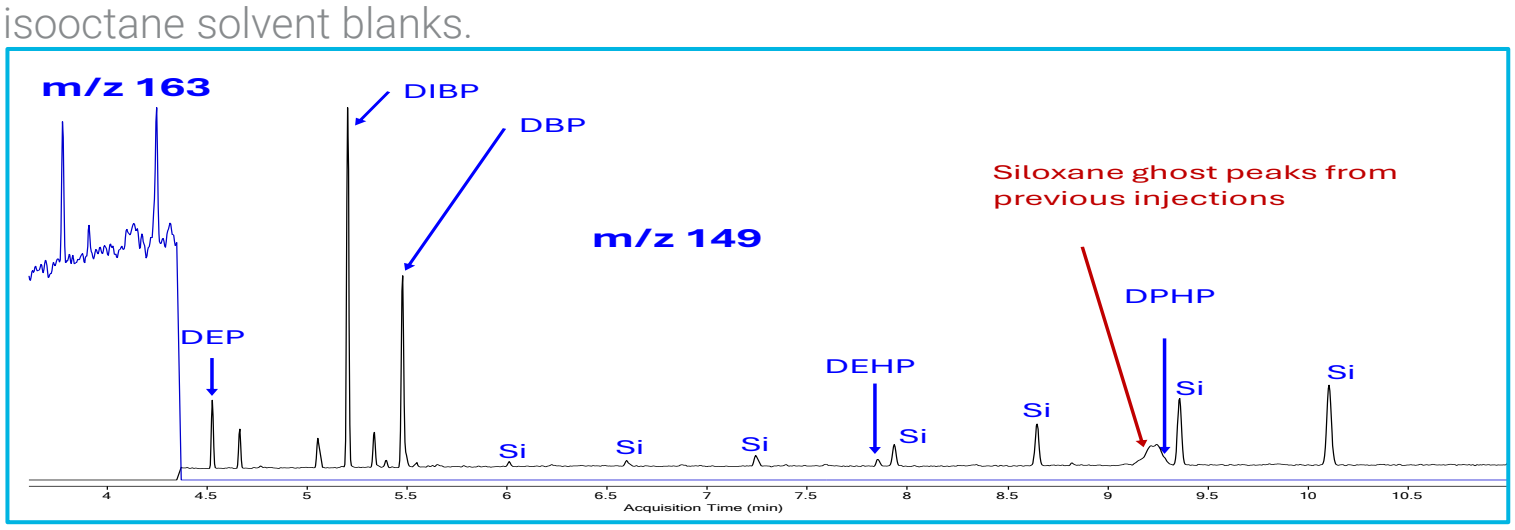
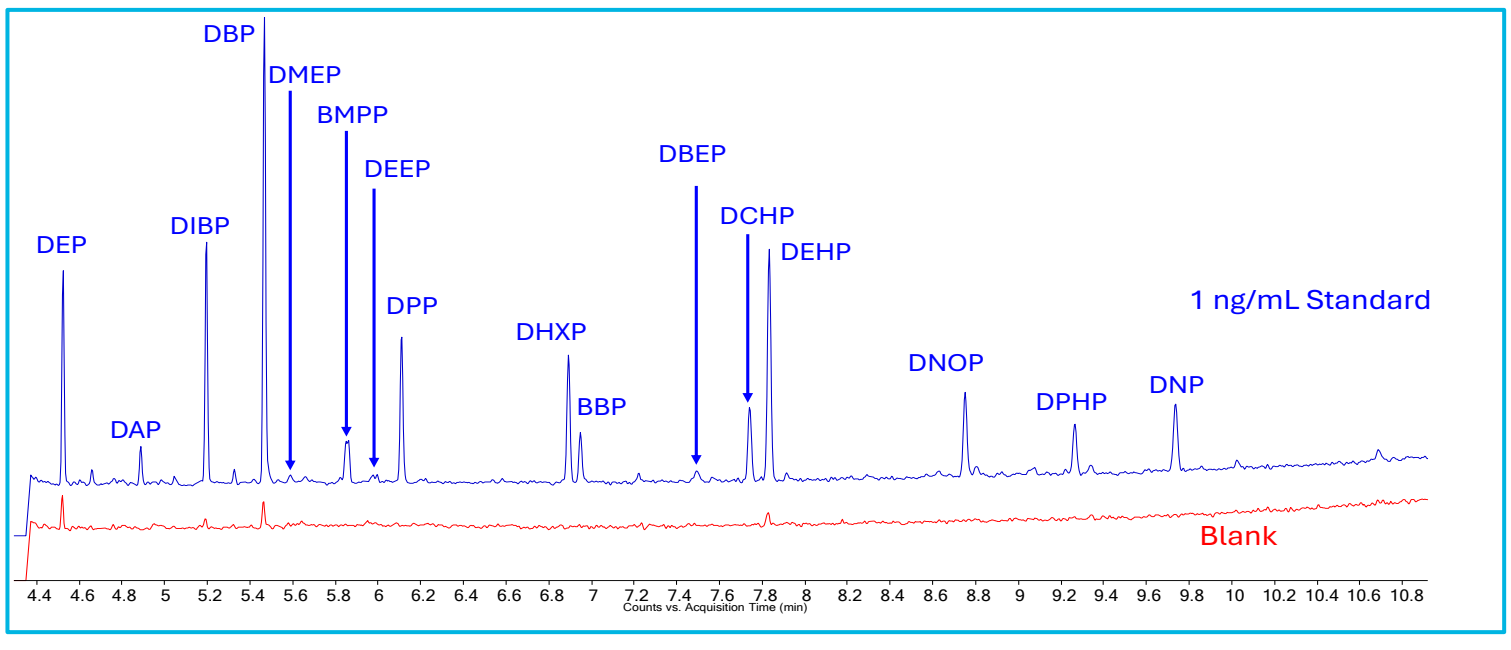


Figure 4. SIM 149 chromatograms of 1 ng/mL calibration standard and blank using the baked consumables, polyurethane caps, and new washed needle support.



Phthalate Standards

Calibration standards were prepared for 17 phthalates at 11 concentration levels: 1, 2.5, 5, 10, 20, 50, 100, 250, 500, 800, and 1000 ng/mL in isooctane.

Calibration standards for the DIDP and DINP isomers were dissolved in isooctane at 11 concentration levels: 50, 100, 250, 500, 750, 1000, 2500, 5000, 7500, 10000, and 20000 ng/mL.

Figure 1 shows the target ion chromatogram for the 17 component 50 ppb phthalate standard.

Figure 2 shows the target ion chromatogram for the 1000 ppb DINP and DIDP standard.

Interferences and Contaminants

The sensitivity of the GC/MS method employed here is sufficient to see the 17 individual phthalates at low pg levels (ng/mL). However, interferences and contamination initially limited calibration at the lowest concentrations. The interferences were identified as silicone peaks, and the contamination resulted from low levels of common phthalates found in the consumables and glassware used.

Figure 3 shows an example of the problems encountered when first running isooctane solvent blanks.

The blank problem was greatly reduced by baking the vials, vial inserts, and the disposable Pasteur pipettes (used for aliquoting) overnight at 130 °C in a glassware oven.

The siloxane interference problem was addressed by changing to non-silicone vial septa. Both polyurethane snap caps (PN: 5181-1512) and PTFE crimp caps (PN: 5182-0871) were found to eliminate the siloxane interferences.

Replacing or washing the autosampler needle support insert (PN: G4513-40525) in methanol after extended use may also help reduce interferences.

Results and Discussion

Figure 4 shows the SIM m/z 149 chromatograms of the 1 ng/mL (1 pg) calibration standard and blank using the baked consumables, polyurethane caps, and new washed needle support. Note that the scale is the same for both chromatograms, but the blank has been offset for clarity. While there are still some small amounts of contamination evident, they are much lower and thus permit calibration down to low ppb concentrations. The use of the PTFE crimp caps gave similar results. Note that the polyurethane caps worked well with isooctane but are incompatible with some solvents like DCM. Check solvent compatibility before using them.

Table 3. Results for 11 level SIM mode calibration over a range of 1 to 1,000 pg for 17 phthalates and 50 to 20,000 pg for DINP and DIDP

RT	Name	CF	CF Limit Low	CF Limit High	CF Weight	RSE	CF R2	Conc IDL	IDL (ppb)
4.175	DMP	Linear	1	1,000	1/x	9.5	1.000	1	0.20
4.524	DEP	Linear	1	1,000	1/x	9.9	0.999	1	0.21
4.892	DAP	Linear	1	1,000	1/x	11.6	0.999	1	0.23
5.200	DIBP	Linear	1	1,000	1/x	7.3	0.999	1	0.60
5.471	DBP	Linear	1	1,000	1/x	5.4	1.000	1	0.60
5.594	DMEP	Quadratic	2.5	1,000	1/x	14.1	0.999	2.5	0.40
5.865	BMPP	Linear	1	1,000	1/x	7.7	0.999	1	0.17
5.985	DEEP	Linear	1	1,000	1/x	14.9	0.998	2.5	0.56
6.119	DPP	Linear	1	1,000	1/x	10	0.999	1	0.16
6.899	DHXP	Linear	1	1,000	1/x	11.1	0.999	1	0.19
6.955	BBP	Linear	1	1,000	1/x	11.3	0.999	1	0.18
7.498	DBEP	Quadratic	1	1,000	1/x	14.3	0.999	1	0.73
7.751	DCHP	Linear	1	1,000	1/x	11.7	0.999	1	0.26
7.841	DEHP	Linear	2.5	1,000	1/x	9.6	0.999	1	0.61
8.758	DNOP	Linear	1	1,000	1/x	11.3	0.999	1	0.27
9.274	DPHP	Linear	1	1,000	1/x	10.1	0.999	1	0.30
9.745	DNP	Linear	1	1,000	1/x	11.8	0.999	1	0.31
8.754	DINP	Linear	50	20,000	1/x	11.3	0.998	50	7.08
9.762	DIDP	Linear	50	20,000	1/x	11.7	0.998	50	7.13

Conclusions

- The Agilent 5977C GC/MSD and 8890 GC, when used with the method described here, provide excellent peak shape, resolution, sensitivity, and a 13 min run time..
- The combination of hydrogen carrier and the Agilent J&W HP-5ms 180 µm diameter column allowed for reduced analysis time relative to helium and a 250 µm diameter column .
- Calibration curves were linear for 14 of the phthalates from 1 to 1,000 pg. DMEP and DBEP required quadratic curve fits, and DMEP and DEHP were calibrated from 2.5 to 1,000 pg. DINP and DIDP were calibrated from 50 to 20,000 pg with a linear fit.
- Specific attention to the consumables used and their preparation before use is important for reaching the lowest calibration levels.

References

[1]Agilent EI GC/MS Instrument Helium to Hydrogen Carrier Gas Conversion. User Guide. 5994-2312EN. 2022

The authors declare no competing financial interest.

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