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Analysis of Phthalate with Hydrogen Carrier Gas

Using the Agilent HydroInert source on a challenging cable sample in gas chromatography/mass spectrometry

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Abstract

Gas chromatography/mass spectrometry (GC/MS) plays a pivotal role in the analysis of phthalates in consumer products. In light of the recent helium supply challenges, the adoption of hydrogen (H_2) as a carrier gas has gained prominence. However, using hydrogen as carrier gas in many GC/MS analyses may cause hydrogenation or dechlorination problems in the ion sources that use helium gas as carrier gas. The Agilent GC 8890, coupled with the Agilent 5977C GC/MSD and using the Agilent HydroInert source with hydrogen as the carrier gas with the backflush technique, provides an effective solution to these challenges. It not only meets International Electrotechnical Commission (IEC) requirements but also successfully addresses the issue of instability when dealing with complex sample matrices.

Introduction

Phthalates are a group of chemical compounds that are synthesized from phthalic acid. They are widely used as plasticizers in many products, including children's toys and electrical and electronic equipment. Unfortunately, phthalates can leach out of plastic materials and enter the environment. This exposure can have adverse effects on human health.

The prevalence of phthalates in various products and the associated health risks have led to the implementation of regulations governing their use. Relevant policies include the European Union's updated directive under the Restriction of Hazardous Substances (RoHS) framework, designated as 2015/863/EU[1], and its 2007 Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) framework.[2]

Traditionally, helium has been the preferred carrier gas for GC/MS analysis. However, due to recurring helium shortages and rising costs, hydrogen is emerging as a viable alternative. Hydrogen is more cost-effective and efficient than helium, making it a promising prospect for phthalate analyses.

This application note centers on the analysis of phthalates using a GC/MS system in Selected Ion Monitoring (SIM) mode with hydrogen serving as the GC carrier gas. When transitioning to hydrogen for GC/MS analysis, several critical factors must be considered.

Hydrogen, being a chemically reactive gas, can induce chemical reactions within various components of the GC/MS system, including the inlet, column, and sometimes the mass spectrometer Electron Ionization (MS EI) source. These reactions can alter the mass spectra of peaks in the total ion chromatogram (TIC), potentially leading to the misidentification of compounds in the analysis results.

The Agilent HydroInert source was developed to mitigate these concerns related to the MS source. The HydroInert source, when used with hydrogen as the carrier gas, preserves mass spectral accuracy and allows users to continue using existing helium-based mass spectral libraries and quantitative methods.

This application note uses the solvent extraction method, which is in accordance with the analytical methodology outlined in IEC standard 62321-8:2017.[3] The presence of residual sample matrix components in this method can contaminate essential column components, such as the inlet, column, and ionization source. This contamination can adversely affect the accuracy and reliability of the instrument during analysis.

The self-cleaning capability of the hydrogen gas ionization source, combined with the backflush technique, helps address issues related to sample background effects, reduces maintenance frequency, and ensures precision and accuracy throughout the analysis process.

Experimental

Reagents and chemicals
- Tetrahydrofuran (THF) 99.9% was purchased from Sigma-Aldrich.
- HPLC-grade acetonitrile (ACN) was obtained from Supelco.
- Benzyl benzoate (BB) 98%, benzyl butyl phthalate (BBP) 98%, dibutyl phthalate (DBP) 98%, di-isobutyl phthalate (DIBP) 98%, di-n-pentyl phthalate (DPENP) 2,500 mg/L, di-n-hexyl phthalate (DHEXP), dicyclohexyl phthalate (DCHP) > 98%, di(2-ethylhexyl) phthalate (DEHP) > 98%, dinoctyl phthalate (DNOP) > 98%, di-isononyl phthalate (DINP) > 98%, and di-isodecyl phthalate (DIDP) were obtained from Sigma-Aldrich.

Standards solution and standards preparation
Phthalate ester standard solutions were prepared by diluting a mixture of phthalate ester standards at a concentration of 100 mg/L in a mixture of THF:ACN (1:1) to create a series of standards with concentrations of 0.2, 0.5, 1, 2, and 5 µg/mL, respectively. Also, each of the standard solutions was supplemented with an internal standard, BB, at a concentration of 1 µg/mL.

Sample preparation
1. Weigh 300 mg of the sample and transfer it to a 40 mL vial. Record the mass to the nearest 0.1 mg.
2. Add 10 mL of THF and 30 µL of internal standard BB (1,000 µg/mL) to the vial.
3. Seal the vial tightly and place it in an ultrasonic bath. Sonicate for 30 to 60 minutes until the sample dissolves.
4. After the sample has completely dissolved, let the vial cool to room temperature.
5. Carefully add 20 mL of ACN drop by drop into the vial to precipitate the sample matrix.
6. Let the resulting solution stand at room temperature for 30 minutes.
7. Allow the polymer to settle or filter the mixture through a 0.45 µm polytetrafluoroethylene membrane.
8. Inject on GC/MS.

Instrumentation

The experimental system used in this study was configured (Figure 1) to address and reduce potential challenges arising from the use of hydrogen as the carrier gas and the complexity of the sample matrix in phthalates analysis. The system comprised an 8890 GC configured with an Agilent 7693A automatic liquid sampler (G4513A) and a split/splitless inlet coupled to a 5977C gas chromatography/mass selective detector (GC/MSD) configured with a HydroInert source.

Tables 1 and 2 show the GC and MS conditions for phthalate analysis and the SIM ion parameters used for data acquisition.
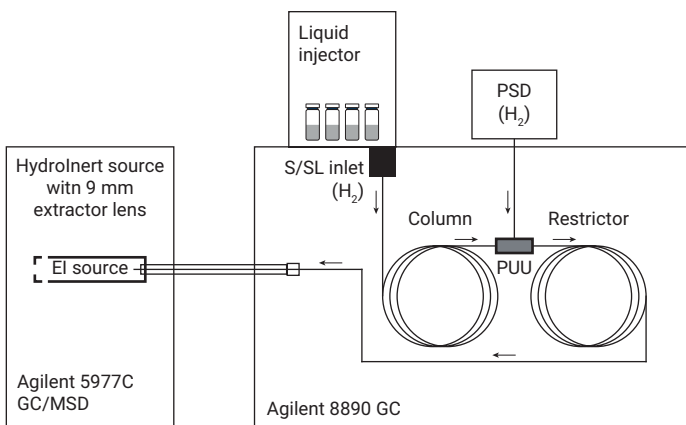

Figure 1. System configuration. S/SL Inlet = split/splitless inlet, PUU = purged ultimate union.

Table 1. GC and MS conditions for phthalate analysis.

Parameter	Value
Agilent 8890 GC	
SSL Inlet	250 °C, Mode: split (5:1)
Liner	Inlet liner, Ultra Inert, split, low pressure drop, glass wool (p/n 5190-2295)
Injection Volume	1 µL
Column	0.7 mL/min, constant flow mode (H$_2$) Agilent DB-5ms Ultra Inert, 30 m × 0.18 mm, 0.18 µm (p/n 121-5522UI)
Restrictor	1.1 mL/min, constant flow mode (H$_2$) Purge flow: 3 mL/min Agilent DB-5ms Ultra Inert 5 m × 0.15 mm, 0.15 µm (p/n 165-6626)
Oven Program	110 °C (0.5 min) 30.5 °C/min to 280 °C (0.5 min) 30.5 °C/min to 320 °C (2 min)
Agilent 8890 GC Backflush Parameters	
Inlet Pressure (Backflushing)	2 psi
Backflush Pressure	20 psi
Void Volumes	5.1715
Backflush Time	4 min
Agilent 5977C GC/MSD	
Source Temperature	280 °C
MS Quadrupole	150 °C
MS Transfer Line	280 °C
Acquisition Type	SIM mode
Gain Factor	1.0

Table 2. SIM ion parameters used for data acquisition (same with helium as carrier gas).

Compound	RT (min)	Quantifier Ion (*m/z*)	Qualifier Ions (*m/z*)
BB	5.133	194	105, 212
DIBP	5.395	149	150, 167
DPP	5.724	150	149, 223
DPENP	6.347	149	150, 237
BBP	7.002	149	150, 251
DBP	7.071	149	91, 150
DCHP	7.632	149	150, 167
DEHP	7.666	149	150, 167
DNOP	8.23	149	150, 249
DINP	8.554	293	127, 149
DIDP	8.898	307	149, 167

Results and discussion

Chromatographic performance

IEC 62321-8 describes a 17-minute GC method for the determination of phthalates in polymers by GC/MS. When using hydrogen as the carrier gas, an elution profile similar to previous studies conducted with helium was observed. The combination of hydrogen as the carrier gas and a smaller diameter column resulted in a faster run time compared to helium. The SIM chromatogram of the 1 µg/mL standard solution containing the phthalate is shown in Figure 2. Good chromatographic peak shapes and signal-to-noise ratio (S/N) were obtained for 10 phthalates (excluding the internal standard) in 15 minutes (including backflushing time).
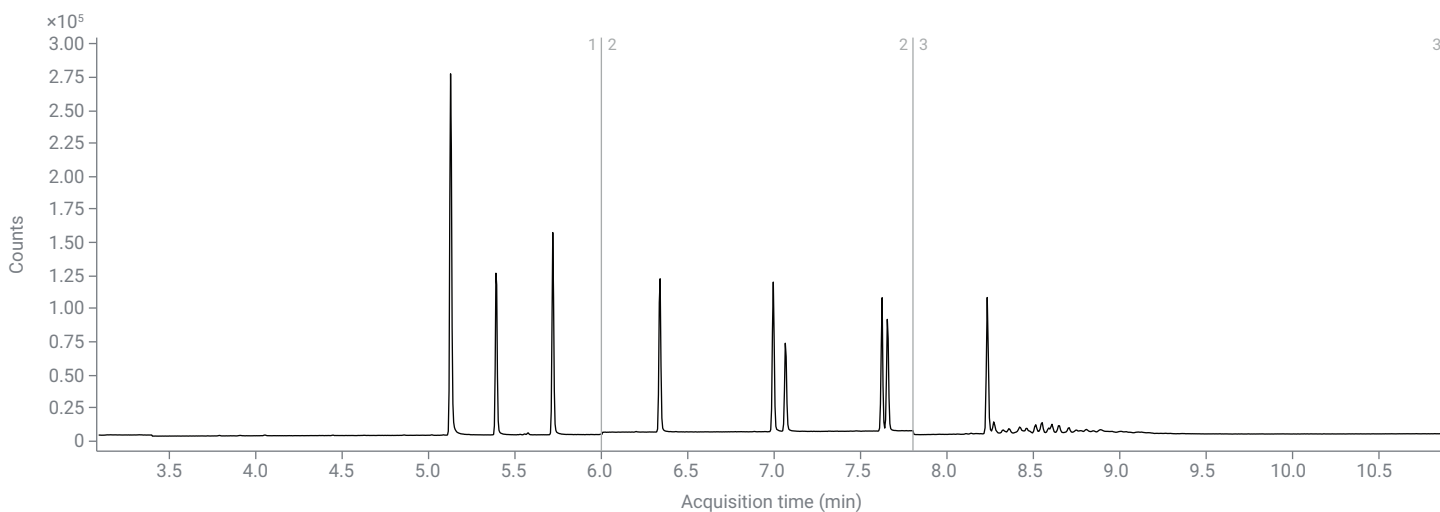
Linearity and range

The linearity and range of the analysis were determined by constructing solvent and standard addition calibration curves for all phthalate compounds within the concentration range of 0.2 to 5 mg/L. Internal standard (BB) concentration was 1 mg/L. The linearity was confirmed by observing R^2 values exceeding 0.996. Figure 3 displays representative calibration plots for four phthalate compounds. Also, the bias percentage for all phthalate compounds at the lowest concentration standard fell within the acceptable range of 80 to 120% of the actual concentration (Table 3).

Table 3. Linear least-squares regression weighted calibration data for 10 phthalates.

Chemicals	Type	Origin	Weight	R^2	%Bias STD 1
BBP	Linear	Include	1/x	0.99921	106.4
DIBP	Linear	Include	1/x	0.99849	104.9
DBP	Linear	Include	1/x	0.99841	111.3
DCHP	Linear	Include	1/x	0.99889	112.1
DEHP	Linear	Include	1/x	0.99902	108.0
DIDP	Linear	Include	1/x	0.99912	996.9
DPENP	Linear	Include	1/x	0.99931	104.9
DNOP	Linear	Include	1/x	0.99802	115.8
DINP	Linear	Include	1/x	0.99935	100.1
DPP	Linear	Include	1/x	0.99920	106.3

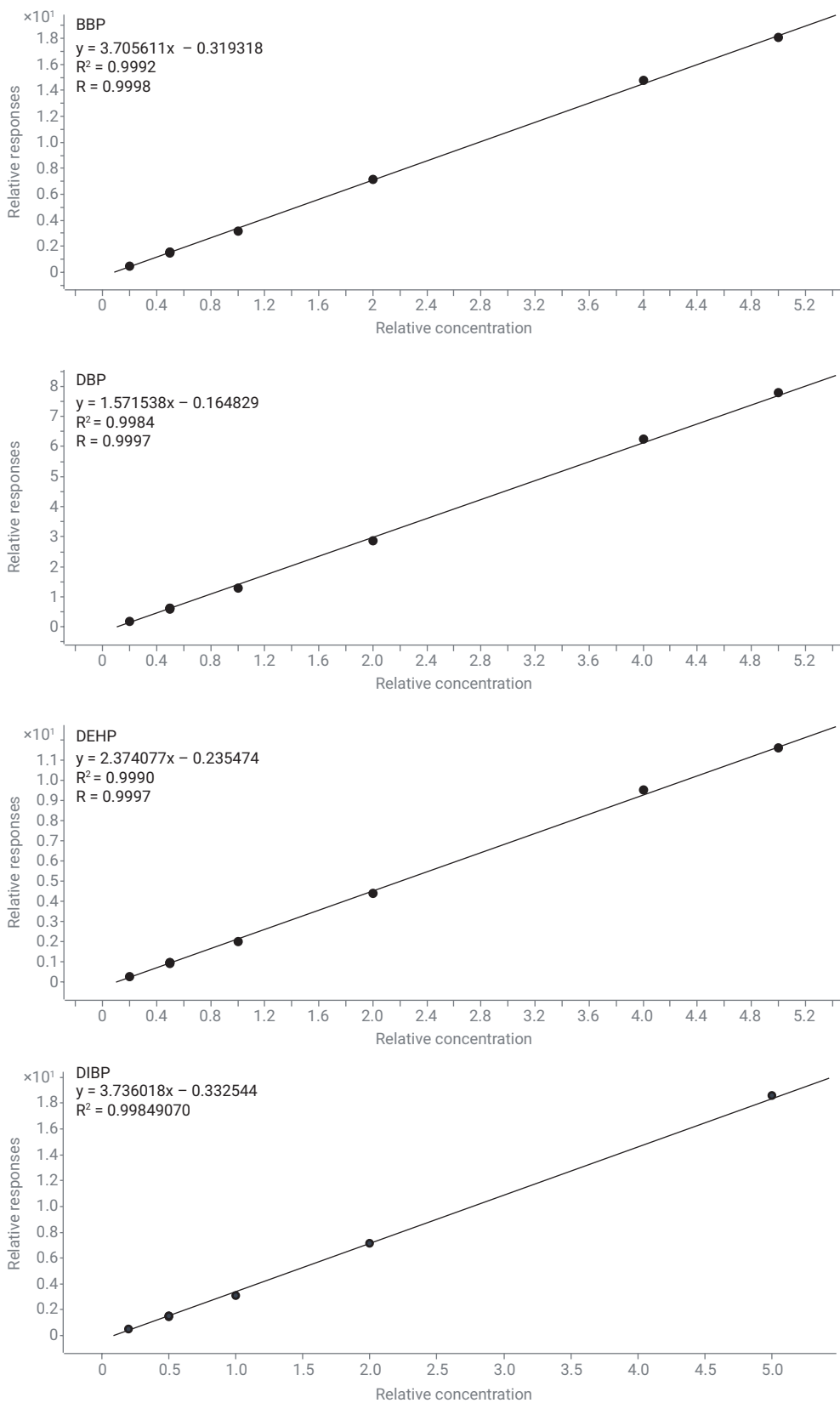**Figure 2.** SIM TIC of 10 phthalates at 1 mg/L and BB as internal standard (ISTD) at 1 mg/L.

Figure 3. Calibration curves of four phthalates in ROSH 3 from 0.2 to 5 mg/L.

Method detection limit (MDL)

The MDL was estimated based on the standard deviation (SD) of the analysis results of nine spiked polymer samples on two different days at 50 mg/kg. Note that phthalates were not detected in the original polymer samples.

The MDLs for phthalate in the polymer matrix ranged from 1.80 to 3.74 mg/kg, as illustrated in Figure 4. For all 10 phthalate compounds, the calculated relative standard deviations (RSDs) were below 20%. These MDL values meet the low detection limits required for phthalate analysis in electrotechnical products.

Recovery, repeatability, and reproducibility

The recovery, repeatability, and reproducibility were evaluated based on the results of the analysis of 14 spiked samples on two different days. The samples were spiked at concentrations of 50 and 500 mg/kg. The average values of recovery obtained for the spiked samples at different concentrations ranged from 89.6 to 101.1%, as shown in Figure 5. Recovery between 70 and 120% is considered satisfactory based on the limits specified in IEC 62321-8. In addition, the %RSD of the recovery values calculated from 14 spiked samples on three days for each concentration was less than 20%, which satisfies the requirements of IEC 62321-8.
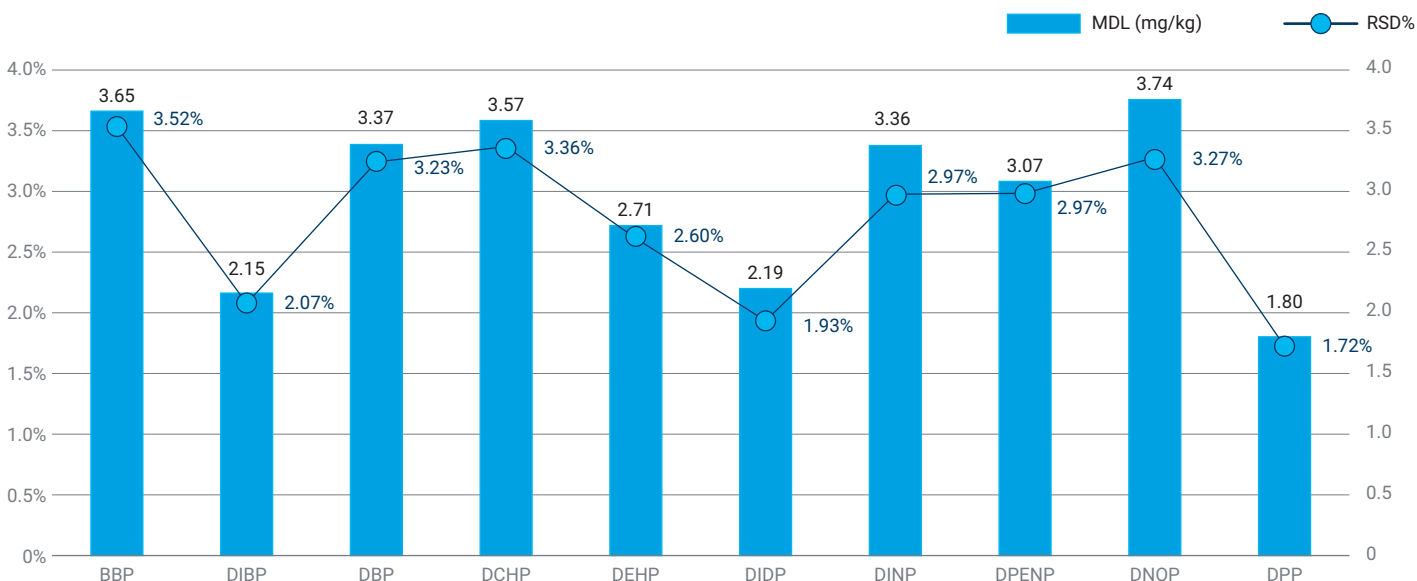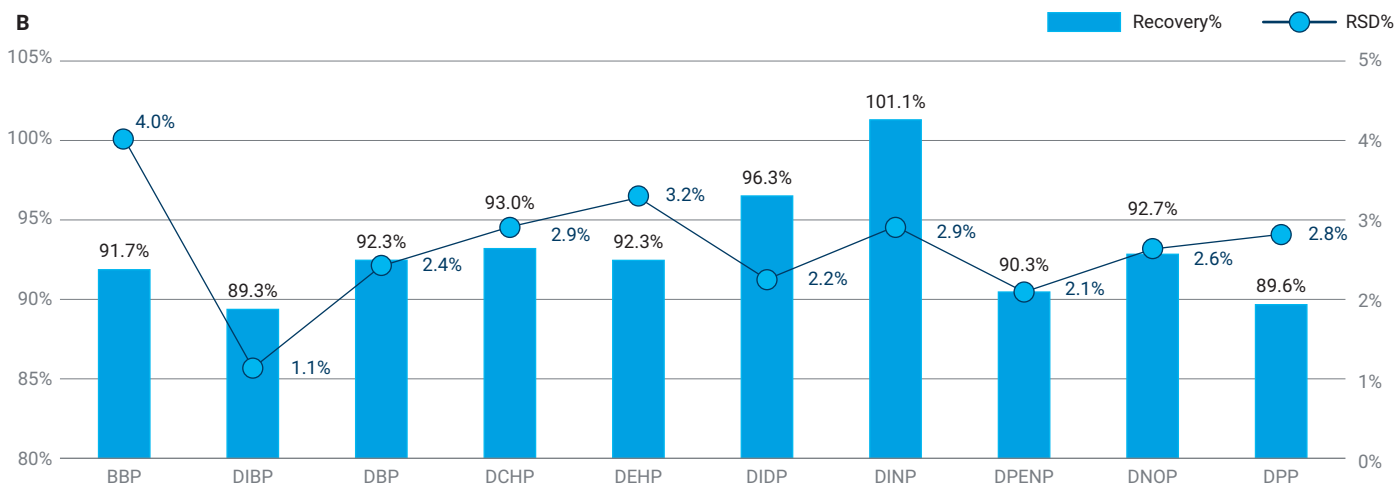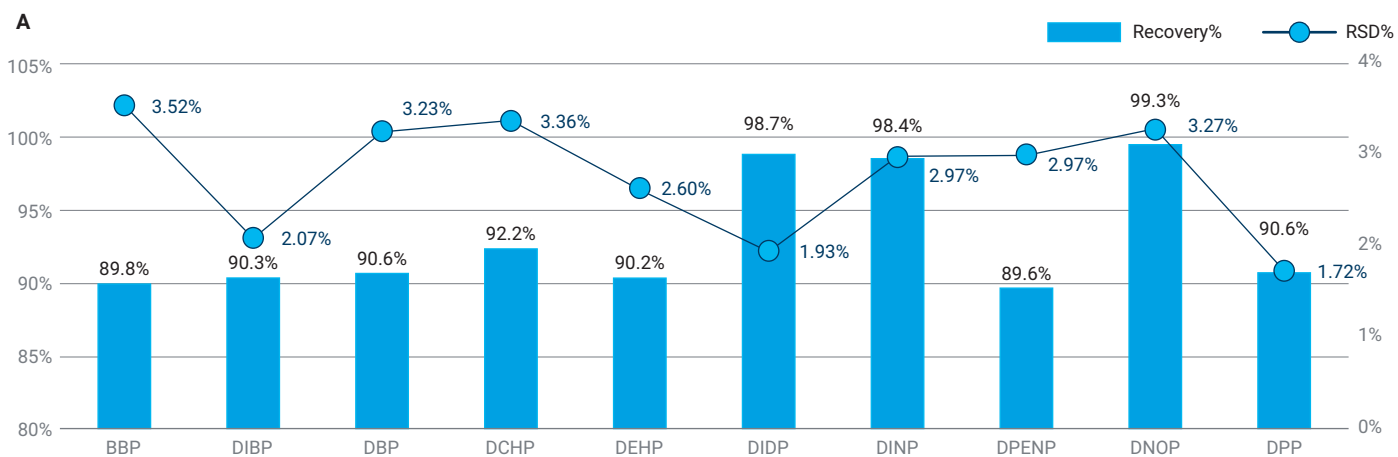

Figure 4. MDLs of phthalates in polymer samples.

Figure 5. (A) Recovery% at 50 mg/kg of phthalate in polymer samples. (B) Recovery% at 500 mg/kg of phthalate in polymer samples.

Analysis of various cable samples

All MDLs and limits of quantification (LOQs ≈ 3MDLs) were below the lowest calibration point for all compounds. Therefore, the reporting limits for this study were defined as any value greater than or equal to the lowest calibration point for the respective compound. Three real-world cable samples were assessed for the presence of phthalate. The chromatogram and result of three cable samples are presented in Figure 6 and Table 4.

Table 4. Phthalate result analysis of three cable samples.

Compound	Cable 1	Cable 2	Cable 3
DIBP	Detected	Detected	Not detected
DPP	Detected	Detected	Not detected
DPENP	Not detected	Not detected	Not detected
BBP	Not detected	Not detected	Not detected
DBP	Not detected	Not detected	Not detected
DCHP	Not detected	Not detected	Detected
DEHP	Significant level detected	Significant level detected	Not detected
DNOP	Not detected	Not detected	Significant level detected
DINP	Significant level detected	Detected	Not detected
DIDP	Significant level detected	Detected	Not detected

Not detected: below the calibration range tested
Detected: within the calibration range
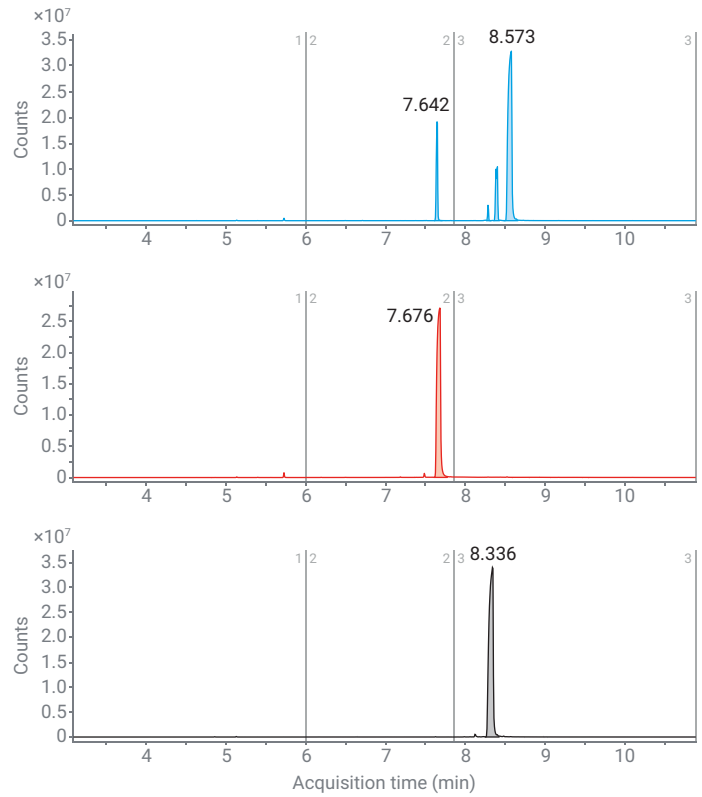Significant level detected: above the calibration range

Figure 6. TIC SIM of phthalates in three cable samples.

Method robustness in cable matrix

When using helium gas for phthalate analysis on cable samples, a common issue is a significant reduction on compound responses, which cause high %RSD for certain types of cable matrices. The method robustness when using Agilent HydroInert source with hydrogen carrier gas, in combination with the backflush technique, was assessed through continuous analysis of standards and three different cable sample matrices. The %RSD values for the response of 1 mg/L standard points of phthalates analyzed throughout the analysis of the three cable sample matrices are presented in Table 5.

The %RSD of the response, calculated from the 1 mg/L standard without any maintenance (inlet, ion source), remained below 7% for all compounds across the three cable sample matrices. Also, the %RSD was consistently below 20% for all compounds, showcasing outstanding quantitation stability even when continuously subjected to a complex extract (Figure 7).

Table 5. The %RSD values for the response at 1 mg/L in the method robustness test.

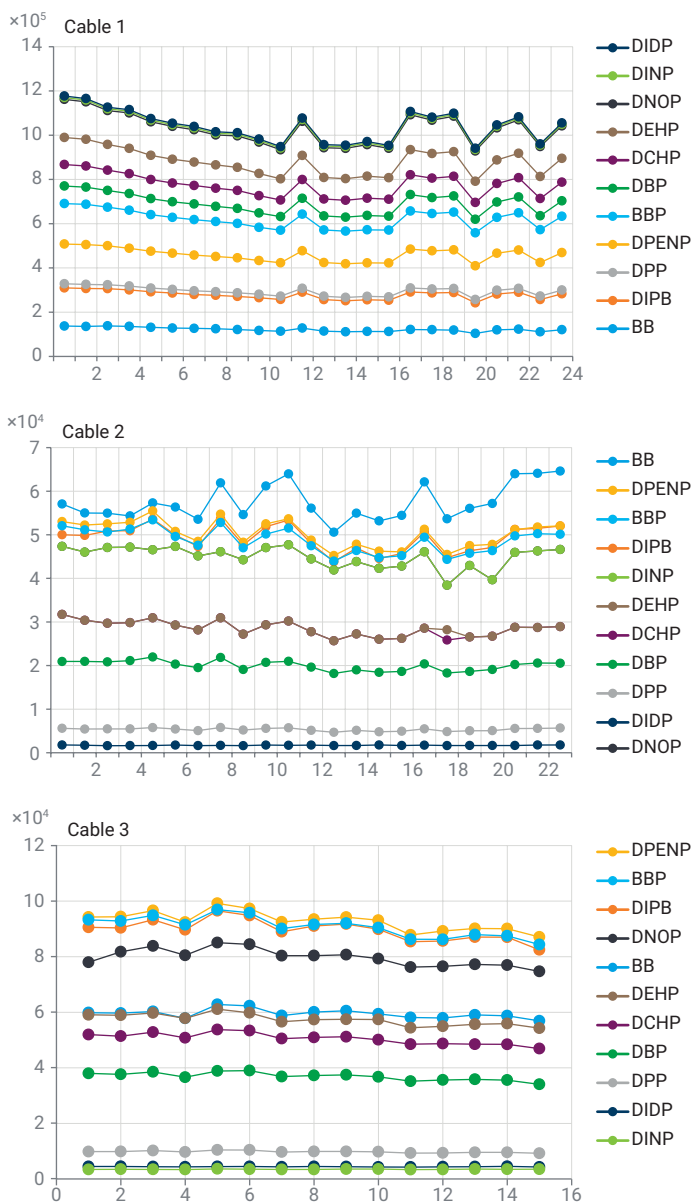| Sample	N (Standard Injection)	RSD Area									
		DIBP	DPP	DPENP	BBP	DBP	DCHP	DEHP	DNOP	DINP	DIDP
Cable 1 (80 injections)	24.000	7.00	6.62	5.74	5.68	6.35	5.85	5.68	5.96	5.67	6.35
Cable 2 (30 injections)	24.000	6.11	6.16	6.08	5.83	5.72	6.30	5.96	5.66	2.41	3.44
Cable 3 (30 injections)	15.000	4.16	3.75	3.73	4.11	3.89	3.98	3.64	3.95	1.96	2.08

Figure 7. The response values at 1 mg/L in the method robustness test.

Conclusion

This application note demonstrates the configuration of the Agilent 8890 GC coupled with the Agilent 5977C, using an Agilent HydroInert source with hydrogen as the carrier gas in combination with the backflush technique. In addition to fulfilling the requirements of the International Electrotechnical Commission 62321 standard for the analysis of phthalates in electrical products, it also highlights the method's robustness and addresses the issue of instability when analyzing samples with complex components. This is achieved through the self-cleaning properties of hydrogen gas within the ion source and the use of the backflush technique to remove components that are difficult to evaporate.

References

1. European Union (EU) Commission Delegated Directive 2015/863 of 31 March 2015 Amending Annex II to Directive 2011/65/EU of the European Parliament and of the Council Concerning the List of Restricted Substances, C/2015/2067, OJ L 137, 4.6.2015, p. 10–12, http://data.europa.eu/eli/dir_del/2015/863/oj

2. European Union Regulation No. 1907/2006. Registration, Evaluation, Authorisation, and Restriction of Chemicals (REACH), Establishing a European Chemicals Agency. Annex XIV. https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:02006R1907-20231201

3. International Electrotechnical Commission (IEC) 62321-8, Determination of Certain Substances in Electrotechnical Products—Part 8: Phthalates in Polymers by Gas Chromatography/Mass Spectrometry (GC-MS), Gas Chromatography/Mass Spectrometry Using a Pyrolyzer/Thermal Desorption Accessory (Py/TD-GC-MS) *Int. Electrotech. Commission* **2017**, pp. 1–70.

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