Application Note

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Phthalate Analysis Using an Agilent 8890 GC and an Agilent 5977A GC/MSD

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Abstract

Mixtures of seven phthalates were analyzed using the Agilent 8890 GC coupled to an Agilent 5977A GC/MSD with an Xtr source. Calibration coefficients greater than 0.99 were obtained across the dynamic range analyzed, and minimum detection limits (MDLs) less than 0.01 mg/L were demonstrated for each phthalate.

To demonstrate the utility of this analytical system as a screening tool for phthalate detection, three real-world samples were analyzed for their phthalate content.

Introduction

Phthalates are a class of compounds derived from the esterification of phthalic acid. They are commonly used as plasticizers in products ranging from children's toys to electrical and electronic equipment (EEE). Unfortunately, phthalates are easily released from their plastic matrices and are introduced into the environment where they can have detrimental impacts on human health.

The prevalence of phthalates and their potential health risks has led to the use of several phthalates being regulated. An updated directive for the Restriction of Hazardous Substances (RoHS) was published in 2015 (2015/863/EU) to amend Annex II to the RoHS 2 directive of 2011 (2011/65/EU). The 2015 amendment added four phthalates to the RoHS list of hazardous substances. The phthalates added are commonly used as plasticizers to soften PVC and vinyl insulation on electrical wires, including diisobutyl phthalate (DIBP), dibutyl phthalate (DBP), benzybutyl phthalate (BBP), and *bis*(2ethylhexyl) phthalate (DEHP)[1].

Phthalates are also regulated for use in children's toys and childcare articles by entry 51 of Annex XVII to REACH Regulation (EC) No. 1907/2006[2]. Registration, evaluation, authorization, and restriction of chemicals (REACH) began enforcement in 2007 with an 11-year phase-in plan with regulations that are stricter than and supersede RoHS 2 requirements. REACH regulates three of the four RoHS phthalates (DBP, BBP, and DEHP), as well as three additional phthalates: dinoctyl phthalate (DNOP), diisononyl phthalate (DINP), and diisodecyl phthalate (DIDP).

This Application Note demonstrates the ability of the 8890 GC coupled to a 5977A GC/MSD to provide linear and sensitive detection of the seven phthalates regulated under RoHS 2 and REACH (Table 1).

Experimental

Standards and test samples

Phthalate standards were purchased, and serial dilutions were made in hexane to 0.05, 0.1, 0.25, 0.5, and 1 mg/L.

Table 1. The seven phthalates regulated by RoHS 2 and REACH.

Compound	Acronym	CAS number
Diisobutyl phthalate	DIBP	84695
Dibutyl phthalate	DBP	84742
Benzyl butyl phthalate	BBP	85687
bis(2-Ethylhexyl) phthalate	DEHP	117817
Dinoctyl phthalate	DNOP	117840
Diisononyl phthalate	DINP	28553120
Diisodecyl phthalate	DIDP	26761400

Table 2. 8890 GC and 5977A GC/MSD conditions.

GC run conditions	
Analytical column	Agilent J&W HP5ms, 30 m × 0.25 mm, 0.25 µm
Injection volume	1 µL
Injection mode	Splitless Purge flow to split vent = 40 mL/min at 0.5 minutes
Inlet temperature	290 °C
Liner	Ultra Inert inlet liner, single taper, wool
Carrier gas	Helium, constant flow = 1.0 mL/min
Oven program	50 °C for 1 minute, 30 °C/min to 280 °C, 15 °C/min to 310 °C, 5 minutes hold
Transfer line temperature	290 °C
MS conditions EI	
Solvent delay	5 minutes
Acquisition mode	Synchronous SIM/Scan
Tune	Atune
Gain factor	1
Xtr source temperature	300 °C
Quadrupole temperature	150 °C

The pen cap and electrical cable samples were prepared by extracting 1 g of each material with 40 mL of methylene chloride at 35 °C for 20 minutes aided by sonication. An aliquot of the extract was filtered through an Agilent Captiva 0.45 µm syringe filter, and placed into a 2-mL vial containing a deactivated, glass 250-µL vial insert.

Instruments

The analysis was done using an 8890 GC configured with an Agilent 7693A automatic liquid sampler (G4513A) and a split/splitless inlet coupled to a 5977A GC/MSD configured with an Xtr source. To acquire EI data using the instrument conditions listed in Table 2, Agilent MassHunter GC/MS acquisition software was used to operate the system in synchronous SIM/Scan mode.

Acquisition parameters

Table 3 lists the characteristic ions used for quantitation and identification.

Agilent consumables

Table 4 lists the Agilent consumables used in this work.

Results and discussion

Phthalate standards

Figure 1 shows the total ion current (TIC) SIM trace from the EI analysis of the phthalates at the 1 mg/L level.

Table 3. SIM ion parameters used for data acquisition.

SIM group	Compound	RT (min)	Quantifier ion (*m/z*)	Qualifier ions (*m/z*)
1 (5 to 9.2 minutes)	DIBP	8.04	223	149, 167
	DBP	8.35	223	149, 167, 205
2 (9.2 to 10.7 minutes)	BBP	9.64	206	91, 149
	DEHP	10.23	279	149, 167
3 (10.7 minutes to end)	DNOP	10.88	279	149, 167, 261
	DINP	11	293	149, 167
	DIDP	11.7	307	147, 167

Table 4. Agilent consumables.

Consumable	Part number
Analytical column	19091S-433UI
Inlet liner	5190-2293
Inlet septum	5183-4757
Syringe filter	5190-5087
Liquid sample vial	5182-0716
Liquid sample vial cap	5185-5820
Vial insert	5188-8872
GC 5 µL syringe	G4513-80206
Helium purifier trap	RMSH-2

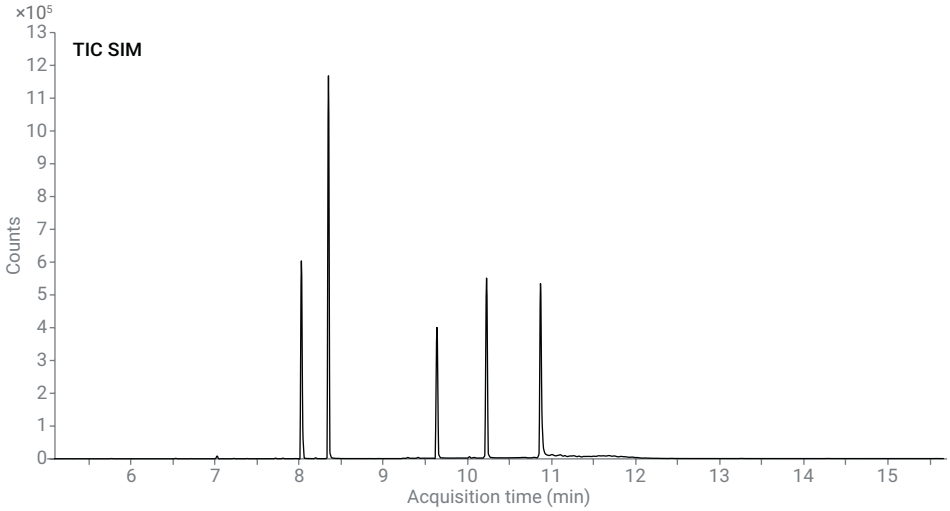

Figure 1. TIC SIM trace of the seven phthalates in EI mode at 1 mg/L.

DINP and DIDP exist as mixtures of positional isomers; Figure 2 shows their quantitative ion traces.

To create calibration curves, the phthalate standards were analyzed at 0.05, 0.1, 0.25, 0.5, and 1 mg/L. Each phthalate gave a linear response across the calibration range, where all correlation coefficient values (R^2) were greater than 0.99, as shown in Table 5.

Using the area precision for each phthalate acquired at the 0.05 mg/L level, the minimum detection limit (MDL) for each phthalate was determined to be less than 0.006 mg/L, as shown in Table 6.

Test samples

To demonstrate the utility of the 8890 GC coupled with the 5977A GC/MSD towards phthalate analysis, three real-world samples were evaluated for the presence of phthalates (Figure 3).

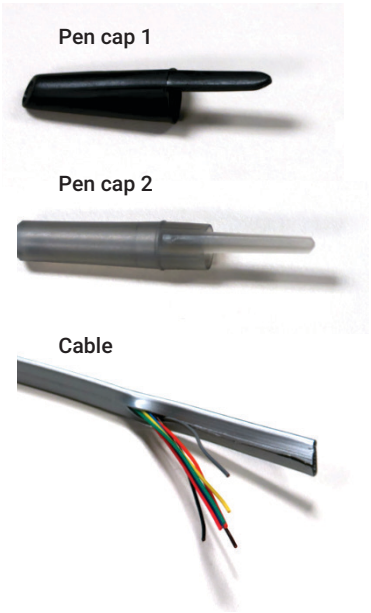

Figure 3. Photographs of the real-world samples used for phthalate extraction.

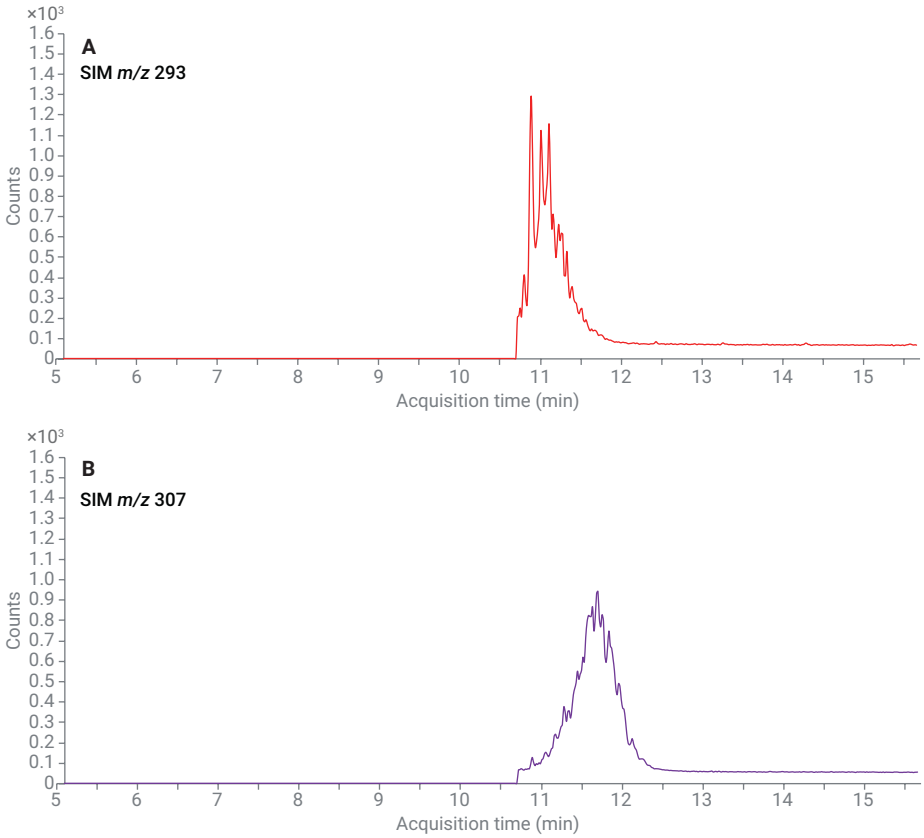

Figure 2. SIM traces of quantitative ions for DINP (*m/z* 293) and DIDP (*m/z* 307) at 1 mg/L.

Table 5. Calibration coefficients (R^2) for the seven phthalates across the five concentration ranges.

	Peak area (arbitrary units)					
Phthalate	0.05 mg/L	0.1 mg/L	0.25 mg/L	0.5 mg/L	1 mg/L	R^2
DIBP	1321	2716	6677	13778	28959	0.9993
DBP	942	1801	4380	9262	19608	0.9989
BBP	1020	2009	5516	12606	32443	0.9937
DEHP	648	1220	3037	7848	19929	0.9995
DNOP	608	1161	3734	10539	27989	0.9999
DINP	869	1821	4428	9687	23596	0.9984
DIDP	984	1933	4714	10621	27873	0.9991

Table 6. MDLs for the seven phthalates.

Compound	MDL (mg/L)
DIBP	0.005
DBP	0.006
BBP	0.006
DEHP	0.004
DNOP	0.002
DINP	0.001
DIDP	0.001

The extraction technique used in this application is sufficient to detect phthalates on the surfaces of materials. Total phthalate quantitation within a specific substance would require more complete sample pretreatment to expose greater surface area and more of the bulk material for extraction.

Care was taken to use only glass containers for sample preparation except for the PTFE syringe filters. Blank injections of the methylene chloride extraction solvent were also used to ensure accurate identification of target phthalates in the real-world samples.

Two different new pen caps were used without alteration, with pen cap 1 weighing 0.9209 g, and pen cap 2 weighing 1.13836 g. It is not mandatory for pen caps not marketed for children to follow RoHS or REACH regulations. An older piece of cable (circa 1985) that predated any RoHS requirements was spliced open so the gray, outer sheathing could be stripped from the inner wires. A section of the gray outer sheathing was cut into pieces approximately 5 mm in length, with all pieces totaling 1.02250 g. Following extraction, a filtered aliquot was analyzed using the method parameters listed in Tables 2 and 3. Figure 4 shows the SIM traces of the phthalic anhydride ion (*m/z* 149) common to phthalate species for each sample.

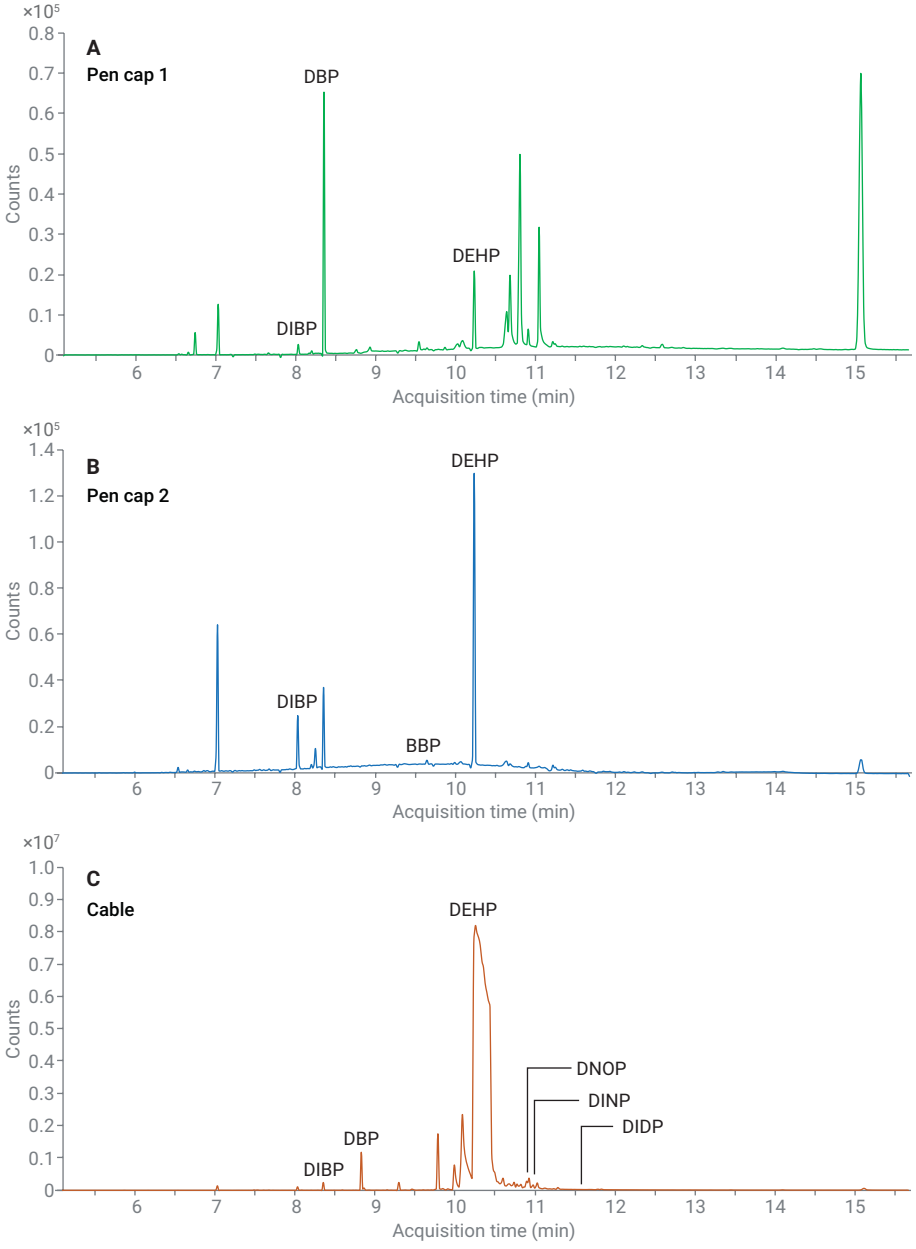

Figure 4. SIM traces of *m/z* 149 for phthalate targets from three real-world samples.

Processing the results and applying the calibration curves for each phthalate from Table 5, several phthalates were identified in the real-world samples. If their concentrations fell within the calibration range tested, they were identified as *detected*. If their concentrations were less than the calibration range, they were identified as *trace level detected*. If their concentrations were greater than the calibration range, they were identified as *significant level detected*; see Table 7.

Phthalates were detected in all three real-world assemblies. The pen caps showed only two RoHS 2 and REACH regulated phthalates, which fell within the calibration range tested in this Application Note. The other phthalates that were detected in the pen caps were below the calibration range tested here. Despite detecting RoHS 2 and REACH regulated phthalates in the pen caps, the quantities detected were well below either the RoHS 2 or REACH requirements.

All seven of the RoHS 2 and REACH regulated phthalates were detected in the cable sample. Only BBP was below the calibration range tested. DEHP, DINP, and DIDP were all above the calibration range tested, with DEHP being significantly above the calibration range. DIBP, DBP, and DNOP were within the calibration range evaluated.

Conclusion

The 8890 GC coupled with the 5977A GC/MSD provided sensitive and linear response for phthalates across the concentration range of 0.05–1 mg/L. The utility of this system as a screening tool for phthalates was demonstrated using real-world samples.

Table 7. Results from extraction and analysis of three real-world samples.

Compound	Pen cap 1	Pen cap 2	Cable
DIBP	Trace level detected	Trace level detected	Detected
DBP	Detected	Not detected	Detected
BBP	Not detected	Trace level detected	Trace level detected
DEHP	Trace level detected	Detected	Significant level detected
DNOP	Not detected	Not detected	Detected
DINP	Not detected	Not detected	Significant level detected
DIDP	Not detected	Not detected	Significant level detected

References

1. Commission Delegated Directive (EU) 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 (Text with EEA relevance), C/2015/2067, OJ L 137, 4.6.2015, p. 10–12, http://data.europa.eu/eli/dir_del/2015/863/oj
2. Corrigendum to Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December **2006** concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC (OJ L 396, 30.12.2006), OJ L 136, 29.5.2007, p. 3–280, http://data.europa.eu/eli/reg/2006/1907/corrigendum/2007-05-29/oj

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Printed in the USA, November 27, 2018
5994-0483EN

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