Application Brief

Plastics

Rapid Screening Workflow for Phthalates in Plastics by GC/MSD in Under Six Minutes

Authors

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Abstract

The Agilent Intuvo 9000/5977B GC/MSD system provides a fast screening workflow for the qualitative detection of phthalates in plastics. This method used a GC oven with direct heating technology and MS spectral deconvolution. Phthalates were extracted from two real-world plastic samples by immersing a cut piece in acetone for 30 seconds. The extract was then injected onto the GC/MSD system. The direct heating oven allowed a high-temperature program rate of 250 °C/min, enabling the completion of the GC/MS analysis in 3.4 minutes. Spectral deconvolution was coupled with the library search algorithm and time-filtering using retention indices. This workflow provided rapid identification of phthalates present in the plastic. The user-created library of pesticides and environmental pollutants and the NIST 17 spectral library were used for compound identification. The entire analysis from sample collection to reporting took under six minutes. This approach is particularly useful for prioritizing samples for more in-depth analysis.

Results and discussion

Among phthalates used as plasticizers, there are several that are currently regulated. An updated directive for the Restriction of Hazardous Substances (RoHS) published in 2015 (2015/863/EU) includes four phthalates as hazardous substances. Among those substances are diisobutyl phthalate (DIBP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), and bis(2ethylhexyl) phthalate (DEHP).[1,2] Six phthalates are also regulated for use in children's toys and childcare articles by entry 51 of Annex XVII to REACH (Registration, evaluation, authorization, and restriction of chemicals) Regulation (EC) No. 1907/20062. REACH regulates three of the four RoHS phthalates (DBP, BBP, and DEHP), as well as three extra phthalates: di-*n*-octyl phthalate (DNOP), diisononyl phthalate (DINP), and diisodecyl phthalate (DIDP).[1,3]

This application brief demonstrates the detection of several of the seven phthalates regulated under RoHS 2 and REACH. These phthalates include DIBP, DBP, DEHP, and DNOP, and were detected in a piece of ribbon cable and a plastic tube screened with the Agilent Intuvo 9000 coupled to an Agilent 5977B GC/MSD. A detailed configuration of the GC/MSD system used for this fast screening is provided in the Agilent application note 5994-2077EN.[4] An analysis time of 3.4 minutes with a one-minute post run was achieved with the use of the Intuvo Guard Chip, temperature-programmed MMI inlet, column backflushing, and oven temperature program rate of 250 °C/min.

Figure 1A shows an old piece of ribbon cable, manufactured before the RoHS updated directive, immersed in acetone for a simple and rapid extraction. The chromatogram of the extract is shown in Figure 1B with the peaks corresponding to the identified phthalates highlighted in blue. The largest peak in the chromatogram at 1.9422 minutes was confirmed to be bisphenol A. Figure 1B also shows the results of the ribbon cable sample analysis against a custom library of pesticides and common pollutants that included 14 phthalates among its 1,081 entries. Compound identification was achieved with MassHunter Unknowns Analysis software by library searching of deconvoluted spectra coupled with time-filtering using retention indices (RIs). The phthalates qualitatively identified in the sample during the fast screening are highlighted in blue in the table in Figure 1B. Among these phthalates, four are regulated under RoHS 2 and REACH, including DIBP, DBP, DEHP, and DNOP. Figures 1C and 1D illustrate the alignment of characteristic ions (left), the deconvoluted spectrum (on the top) compared with the library spectrum as a mirror plot, and the extracted spectrum before deconvolution (on the bottom) for DBP and DEHP, respectively.

Component RT	Compound Name	Match Factor	Formula	Component Area	Component RI	Library RI	Delta RI	Delta RT
1.6352	Diethyl phthalate	92.1	C12H14O4	9228.4	1627	1599	-28	-0.0147
1.6650	Benzophenone	64.7	C13H10O	1457.6	1685	1636	-49	-0.0253
1.7291	4-Nonylphenol	63.8	C15H24O	309.6	1814	1869	55	0.0281
1.7306	Benzyl benzoate	64.4	C14H12O2	5652.6	1817	1768	-49	-0.0243
1.7416	Bensulide	73.4	C14H24N...	2432.6	1838	1911	73	0.0368
1.7580	Anthracene	58.6	C14H10	1915.4	1871	1793	-78	-0.0394
1.7702	Diisobutyl phthalate	94.8	C16H22O4	42257.3	1895	1869	-26	-0.0130
1.8166	Di-n-butylphthalate	97.2	C16H22O4	118415.8	1989	1964	-25	-0.0122
1.8744	Bisphenol A	58.1	C15H16O2	2156.9	2108	2179	71	0.0374
1.9131	Pyrene	73.5	C16H10	4642.2	2181	2118	-63	-0.0336
1.9422	Bisphenol A	97.0	C15H16O2	824624.0	2236	2179	-57	-0.0303
1.9486	Fluoranthene	58.7	C16H10	1856.7	2247	2065	-182	-0.0954
2.0784	Triphenyl phosphate	56.9	C18H15O4P	3411.7	2474	2404	-70	-0.0439
2.1448	Bis(2-ethylhexyl)phthalate	95.4	C24H38O4	515194.6	2574	2550	-24	-0.0163
2.2948	Di-n-octyl phthalate	70.3	C24H38O4	31544.8	2770	2737	-33	-0.0277
2.3450	Di-n-nonyl phthalate	57.4	C26H42O4	76035.5	2826	2938	112	0.1132

Figure 1. (A) Ribbon cable extraction with acetone; (B) Unknowns Analysis results for the ribbon cable analyzed against the custom spectral library; (C) DBP identification with the extracted characteristic ions, the deconvoluted spectrum compared to the library spectrum as a mirror plot and the extracted spectrum before deconvolution shown on the bottom right; (D) DEHP identification.

Due to the spectral nature of phthalates with few characteristic ions, it was essential to confirm phthalate identification against the NIST spectral library in case a better hit could be found with NIST. Diethyl phthalate, DBP, and DEHP were confirmed as the best hits with the highest library match score (LMS) and the smallest delta RI/delta RT when reprocessing the sample against NIST (Figure 2A). Both DIBP and DNOP were among the top hits when searching against the NIST library, however, there were not enough principal ions to unambiguously confirm the identity of these two phthalates. For example, the best hit for the component eluting at 1.7702 minutes was suggested to be phthalic acid, hept-4-yl isobutyl ester instead of DIBP when searching against the NIST spectral library with an LMS of 95.5 (highlighted in blue in Figure 2A). However, the relatively high delta RI of 190 suggested that alternate hits should be inspected. Unknowns Analysis provides a convenient function for inspecting alternate hits as shown in Figure 2B. DIBP was among the top alternate hits with a high LMS of 93.9 (highlighted in blue in Figure 2B) and had the closest RI match with a delta RI of –24. This is a good example of where inspecting alternate hits and the RI match helps in choosing between hits with similar spectra.

A

Components

Component RT	Compound Name	Match Factor	Formula	Component Area	Component RI	Library RI	Delta RI	Delta RT
1.6352	Diethyl Phthalate	90.3	C12H14O4	9228.4	1627	1594	-33	-0.0174
1.7702	Phthalic acid, hept-4-yl isobutyl ester	95.5	C19H28O4	42257.3	1895	2085	190	0.0926
1.8166	Dibutyl phthalate	94.7	C16H22O4	118415.8	1989	1965	-24	-0.0117
2.1449	Bis(2-ethylhexyl) phthalate	98.0	C24H38O4	512725.2	2574	2529	-45	-0.0304
2.2945	1,3-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester	87.6	C24H38O4	35970.4	2770	2707	-63	-0.0526
2.2956	Di-n-octyl phthalate	68.9	C24H38O4	11363.6	2771	2690	-81	-0.0670

B

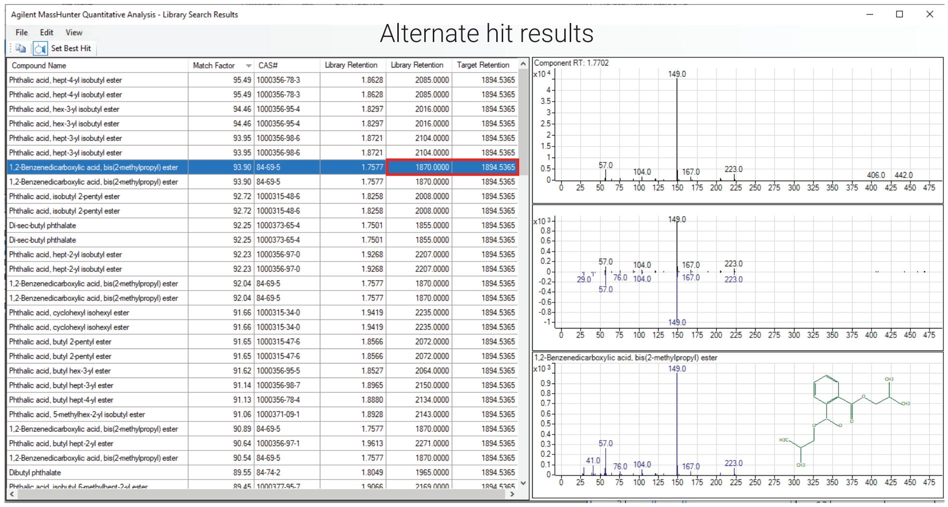


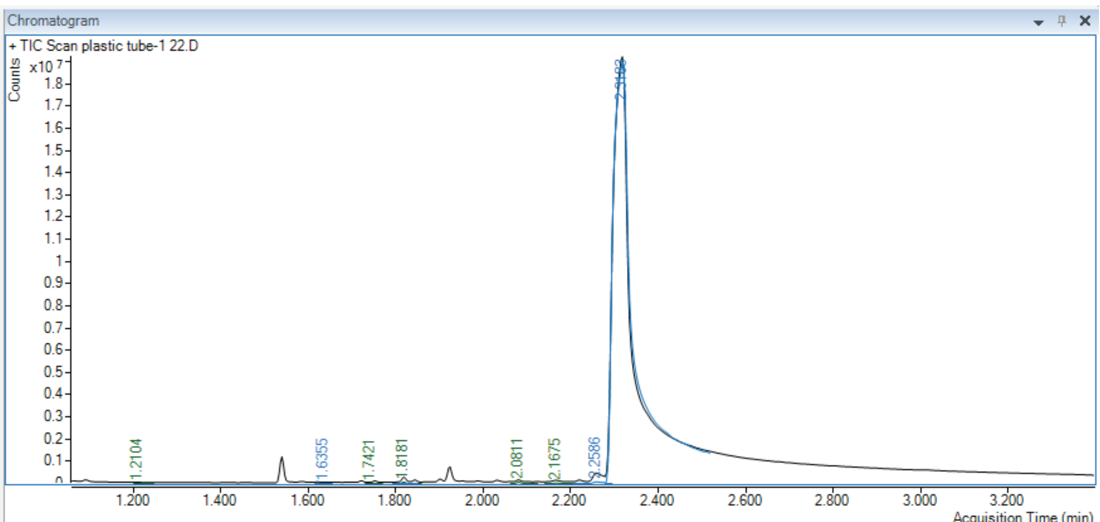
Figure 2. (A) Selected Unknowns Analysis results for the ribbon cable analyzed against the NIST spectral library; (B) Alternate hit results for the component at 1.7702 minutes found in the ribbon cable with DIBP highlighted in blue.

To increase the confidence in phthalate identification, the number of coeluting components causing chromatographic and spectral interference can be minimized using a slower oven ramp. This approach leads to longer chromatographic analysis times, an increase in chromatographic resolution, and less coelution, which can be used for confirmation purposes. This approach is described in more detail elsewhere.[4]

A sample of the plastic tube was also screened using this technique (Figure 3A). The phthalates qualitatively identified in the sample during a fast screening are highlighted in blue in the table in Figure 3B. Among four identified phthalates, three are regulated under RoHS 2 and REACH, including DBP, DNOP, and DEHP. A confirmatory analysis of the plastic tube sample against the NIST spectral library confirmed the identification of diethyl phthalate, DBP, and DNOP (Figure 3C). A better hit was found for the component eluting at 2.3183 minutes with a higher LMS and lower delta RI/delta RT when searching against the NIST spectral library, suggesting that DEHP was not present in the plastic tube sample. Two identified regulated phthalates appeared to be at very low levels as indicated by their component areas. Since the technique described here is only for qualitative screening, if the compounds identified are of concern, further quantitative analyses would need to be performed.

A

B



Components

Component RT	Compound Name	Match Factor	Formula	Component Area	Component RI	Library RI	Delta RI	Delta RT
1.2104	Phenol	73.5	C6H6O	3823.7	978	1010	32	0.0245
1.6355	Diethyl phthalate	82.5	C12H14O4	3970.3	1628	1599	-29	-0.0151
1.7421	Bensulide	56.6	C14H24N...	603.9	1839	1911	72	0.0363
1.8166	Di-n-butylphthalate	88.9	C16H22O4	9592.2	1989	1964	-25	-0.0123
1.8181	Binapacryl	61.2	C15H18N...	47622.8	1992	2244	252	0.1287
2.0811	2-Ethylhexyl diphenylphosphate	75.8	C20H27O4P	50463.3	2478	2434	-44	-0.0276
2.1675	Bis(2-ethylhexyl)phthalate	62.8	C24H38O4	21196.8	2607	2550	-57	-0.0390
2.2586	Di-n-octyl phthalate	57.8	C24H38O4	115774.9	2727	2737	10	0.0085
2.3183	Bis(2-ethylhexyl)phthalate	70.6	C24H38O4	70363243.4	2798	2550	-248	-0.1898

C

Components

Component RT	Compound Name	Match Factor	Formula	Component Area	Component RI	Library RI	Delta RI	Delta RT
1.6355	Diethyl Phthalate	80.0	C12H14O4	3970.3	1628	1594	-34	-0.0178
1.8166	Dibutyl phthalate	86.7	C16H22O4	9592.2	1989	1965	-24	-0.0118
2.2586	Di-n-octyl phthalate	68.4	C24H38O4	115774.9	2727	2690	-37	-0.0300
2.3183	1,4-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester	98.4	C24H38O4	70418766.1	2798	2766	-32	-0.0269

Figure 3. (A) Plastic tube extraction with acetone; (b) Unknowns Analysis results for the plastic tube analyzed against the custom spectral library; (C) selected Unknowns Analysis results for the plastic tube analyzed against the NIST spectral library.

Conclusion

A rapid qualitative screening workflow for phthalates in plastic was achieved using the Intuvo 9000/5977B GC/MSD system, enabling a 3.4-minute chromatographic analysis. The total workflow time was under six minutes, including sample preparation, GC/MSD analysis with backflush, data processing, and reporting.

Five phthalates, four of which are regulated under RoHS 2 and REACH, were identified in the ribbon cable sample against the custom spectral library of pesticides and environmental pollutants. Three of these phthalates were further confirmed when processing the results against the NIST spectral library.

Three phthalates, two of which are regulated under RoHS 2 and REACH, were identified in the plastic tube sample when processing the analysis against the custom spectral library and confirmed with the NIST spectral library.

References

1. Bushey, J. Phthalate Analysis Using an Agilent 8890 GC and an Agilent 5977A GC/MSD. *Agilent Technologies application note*, publication number 5994-0483EN, **2018**.
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3. 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/o
4. Andrianova, A.; Quimby, B. Rapid Rinse and Shoot: Screening Workflow for Pesticides in Fruit by GC/MSD in Under Six Minutes. *Agilent Technologies application note*, publication number 5994-2077EN, **2020**.

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