Application Note

Food Testing & Agriculture

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Phthalates Analysis With Method GB 5009.271-2016 Using the Agilent 8890 GC and MSD with Agilent JetClean

Author

Jie Zhang
Agilent Technologies Co. Ltd
Shanghai

Abstract

Phthalate analysis in food is vital to avoid exposing consumers to these compounds, some of which are carcinogenic. This Application Note combines the Agilent 8890 GC with an Agilent 5977B MSD for the analysis of phthalates by Chinese national food safety standard method GB 5009.271-2016. Results demonstrate the superior repeatability and sensitivity of this coupled system.

Introduction

Plastics are designed to keep our food fresher for longer periods of time. Some chemicals such as phthalates are added to plastics to make them softer and more flexible, making it easier to manufacture the plastics into different shapes. However, these additives will leach into food if the plastics are used for food packaging or containers. Some phthalates are harmful to human health. For example, di(2-ethylhexyl) phthalate (DEHP), is an endocrine disruptor, and can cause cancer. Other phthalates may affect human reproduction or development. Therefore, phthalates testing is required on foods to control the intake of these compounds, and protect consumers against phthalate-related health hazards.

Method GB 5009.271-2016[1] is the Chinese standard for phthalates analysis in food. It describes sample preparation, qualitative/quantitative analysis methods, and requirements such as method precision and detection limits. The Agilent 7890 GC system is a widely used platform in phthalates analysis[2]. With the release of the 8890 GC, the analysis of phthalates with MSD detection was performed to demonstrate its excellent performance in terms of repeatability, sensitivity, and linearity.

Experimental

Equipment

The study was performed on a 8890 GC equipped with a split/splitless inlet and an Agilent 5977B MSD with a JetClean self-cleaning ion source. An Agilent 7693A automatic liquid sampler was also used.

Chemicals

A 16-component phthalates mix (CDGG-111846-01-1 mL) was purchased from ANPEL Laboratory Technologies (Shanghai) Inc. The concentration of each component was 1,000 ng/µL in hexane.

Three single-component standards, di-isononyl phthalate (DINP), diallyl phthalate (DAP), and di-isodecyl phthalate (DIDP) were purchased from ANPEL Laboratory Technologies (Shanghai) Inc. The concentration was 1,000 ng/µL for DIDP in CH_2Cl_2, and 100 ng/µL for DINP in hexane and pure DAP. DAP was then dissolved in the 16-component mixture to 500 ng/µL in hexane.

The calibration standards are prepared according to GB 5009.271-2016 requirements, seven concentration levels for 17 phthalates: 10, 20, 50, 100, 200, 500, and 1,000 ng/mL in hexane. DIDP and DINP isomers were dissolved in hexane at eight concentration levels: 125 ng/mL, 250 ng/mL, 500 ng/mL, 1 ng/µL, 2.5 ng/µL, 5 ng/µL, 10 ng/µL, and 20 ng/µL.

Table 1. Instrument conditions.

GC System	8890A GC
S/SL Inlet	280 °C, mode: splitless; purge flow to split vent: 60 mL/min at 0.5 minutes
Liner	Splitless, Ultra Inert, no wool (p/n 5190-2292)
Oven Ramp Program	60 °C (1.5 minutes), 20 °C/min to 220 °C (1 minutes), 5 °C/min to 280 °C (4 minutes)
Carrier Gas	Helium
Column	1.2 mL/min, constant flow mode, Agilent J&W HP-5ms, 30 m × 0.25 mm, 0.25 µm (19091S-433)
MSD	**5977B GC/MSD**
JetClean Ion Source Temperature	320 °C
MS Quadrupole	180 °C
GC/MS Interface	280 °C
JetClean	Acquire and clean mode, H_2: 0.13 mL/min
Acquisition Type	SIM
Gain Factor	0.5

Results and discussion

Method GB 5009.271-2016 tests 18 phthalates. Seventeen components were tested in the same run, and DINP isomers were tested in a separate run. DIDP was added to the list because it is one of seven key phthalates analyzed by EU and EPA methods for children's toy and child care products. DIDP and DINP were analyzed in the same run. The MSD was operated in select ion monitoring (SIM) mode, and Table 2 lists the quantifier and qualifier ions for each target component.

Table 2A. Quantifier and qualifier ions, MDL, limit of quantitation (LOQ) , and retention time (RT)/area precision for phthalates 1–17.

Peak no.	Name	RT/min	RT RSD%	Quantifier	Qualifier (s)	Area RSD% of 50 ppb	Area RSD% of 1 ppm	MDL (ng/mL)	LOQ (ng/mL)	*LOQ (mg/kg) for real sample
1	DMP	8.119	0.001	163	77,194,133	4.3	2.4	6.24	21.55	0.22
2	DEP	8.984	0.001	149	177,105,222	4.3	2.3	6.24	21.53	0.22
3	DAP	9.880	0.011	149	41.132,189	4.6	2.6	6.71	23.17	0.23
4	DIBP	10.685	0.001	149	223,104,167	4.5	2.1	6.51	22.49	0.23
5	DBP	11.41	0.010	149	223,205,104	4.6	2.1	6.68	23.06	0.23
6	DMEP	11.733	0.013	149	59,104,176	3.8	2.1	5.48	18.93	0.19
7	BMPP	12.473	0.009	149	167,85,251	4.6	2.2	6.66	22.99	0.23
8	DEEP	12.783	0.008	149	72,104,193	4.3	2.2	6.35	21.92	0.22
9	DPP	13.150	0.008	149	234,219,104	4.6	1.9	6.67	23.04	0.23
10	BBP	15.392	0.006	149	104,251,233	4.3	2	6.20	21.4	0.21
11	DHXP	15.249	0.012	149	91,104,206	4.7	1.8	6.86	23.68	0.24
12	DBEP	16.834	0.010	149	85,101,193	4.7	1.9	6.76	23.35	0.23
13	DCHP	17.485	0.007	149	104,167,249	4.4	2	6.42	22.15	0.22
14	DPHP	17.829	0.009	225	77,104,153	3.8	1.8	5.44	18.79	0.19
15	DEHP	17.725	0.012	149	167,279,113	4.5	1.9	6.54	22.58	0.22
16	DNOP	20.105	0.010	149	261,104,279	4.7	1.7	6.76	23.33	0.23
17	DNP	22.595	0.011	149	275,167,293	4.3	1.7	6.17	21.29	0.21

* LOQ: this is for phthalates in real samples that can be detected by the 8890 GC with JetClean MSD detection. This does not represent instrument LOQs for each component. Please see the Results and discussion text for phthalate concentration calculations in real samples.

Table 2B. Quantifier and qualifier ions, MDL, LOQ, and RT/area precision for phthalates 18 and 19.

Peak no.	Name	RT/min	Quantifier	Qualifier (s)	Area RSD% of 250 ppb	Area RSD% of 1 ppm	MDL (ng/mL)	LOQ (ng/mL)	*LOQ (mg/kg) for real sample
18	DINP	19.00–22.8	293	149,167	8.1	2.0	60	207	2.07
19	DIDP	20.3–24.7	307	149,167	5.2	2.3	37	127.7	1.28

* LOQ: this is for phthalates in real samples that can be detected by the 8890 GC with JetClean MSD detection. This does not represent instrument LOQs for each component. Please see the Results and discussion text for phthalate concentration calculations in real samples.

Figure 1 shows the summed SIM for the 17 phthalates mixture at 100 ng/mL. Figure 2 shows the extracted chromatogram for DINP (*m/z* 293) and DIDP (*m/z* 307) at 1,000 ng/mL.

The repeatability of the 8890 GC and 5977B GC/MSD coupled system was evaluated by eight injections of 17-component calibration standards at 50 and 1,000 ng/mL. Table 2A lists the RT and area RSD%. The RT precision is below 0.013 %, and area precision is below 5 %. RT and area precision were excellent, and demonstrated the superior repeatability of the 8890 GC system. Table 2B lists the area RSD% for DINP and DIDP at 250 and 1,000 ng/mL. The concentration level of 250 ng/mL for DINP and DIDP is quite close to their instrument LOQ. At this level, the area precision for DINP and DIDP was 8.1 and 5.2 %, higher than 5 %, but still acceptable. The area precision for the isomers was much better, at 1,000 ng/mL (~2 %, as listed in Table 2B), which corresponds to 10 mg/kg in a real sample. The DINP LOQ requirement specified in method GB 5009-271.2016 is 9 mg/kg. Thus, the 2 % quantitation precision of the 8890A GC and 5977B GC/MSD coupled system at 10 mg/kg met the precision requirement of the GB method.

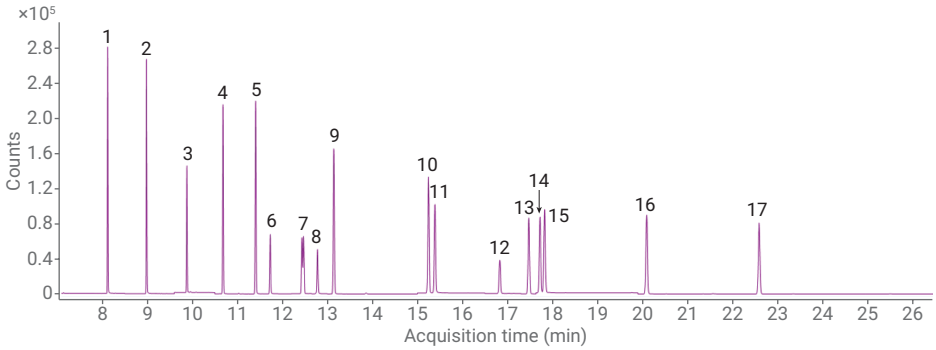

Figure 1. Summed SIM of 17 phthalates at 100 ng/mL.

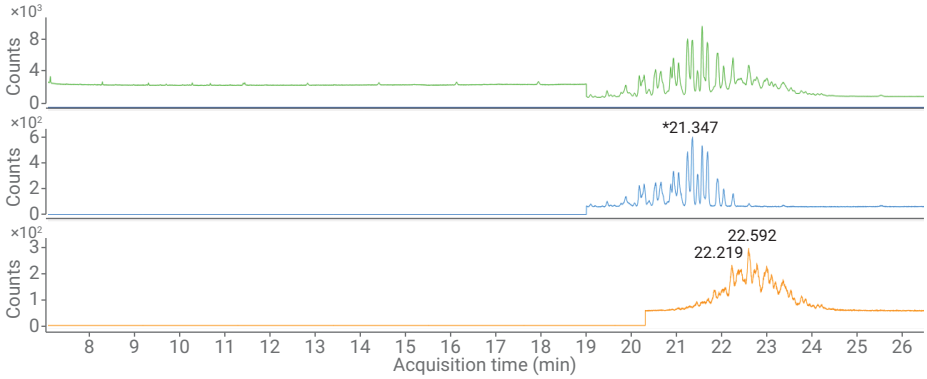

Figure 2. Summed SIM of DINP and DIDP, EIC of DINP (293), and DIDP (307) at 1,000 ng/mL.

Method GB 5009.271-2016 quantifies targeted phthalates based on the ESTD method. Calibration curves for each component in the required concentration range were developed. Table 3 lists CF formulae and regression coefficients for 19 compounds, among them 11 components with CF R^2 >0.999, and all analytes with CF R^2 >0.995. This demonstrated good system linearity, and guaranteed the accuracy of quantitation in the calibrated concentration range. Figure 3 is the representative calibration curve for DEHP, DBP, and DINP. Figure 4 shows the linearity chromatograms for 17 phthalates.

The minimum detection limit (MDL) for the 19 phthalates are calculated based on area precision at 100 ng/mL (for 17 components) and 250 ng/mL (for DINP and DIDP). As shown in Table 2A, the MDLs for 17 phthalates are below 10 ng/mL, while the MDLs for DINP and DIDP are 60 and 37 ng/mL, respectively.

Table 3. CF formula and regression coefficient for 19 phthalates.

No.	Name	CF Formula	CF R^2
1	DMP	y = 199.504382 * x + 695.067257	0.9982
2	DEP	y = 185.904431 * x + 1099.377738	0.9976
3	DAP	y = 48.068831 * x + 376.812846	0.9992
4	DIBP	y = 232.335499 * x + 3964.550726	0.9961
5	DBP	y = 266.384785 * x + 5378.384109	0.9959
6	DMEP	y = 14.884421 * x - 32.446533	0.9993
7	BMPP	y = 57.737792 * x + 173.986931	0.9983
8	DEEP	y = 25.819984 * x - 66.764028	0.9958
9	DPP	y = 266.152211 * x + 523.721885	0.9990
10	BBP	y = 93.545344 * x + 142.589035	0.9993
11	DHXP	y = 246.701295 * x + 448.673543	0.9991
12	DBEP	y = 35.263473 * x - 37.645718	0.9993
13	DCHP	y = 149.824348 * x + 338.494432	0.9990
14	DPHP	y = 152.579320 * x + 338.765271	0.9990
15	DEHP	y = 131.034535 * x + 904.491548	0.9993
16	DNOP	y = 206.143514 * x + 183.612878	0.9993
17	DNP	y = 189.772836 * x + 121.872605	0.9992
18	DINP	y = 10.362 * x + 408.24	0.9983
19	DIDP	y = 11.212* x + 733.4	0.9981

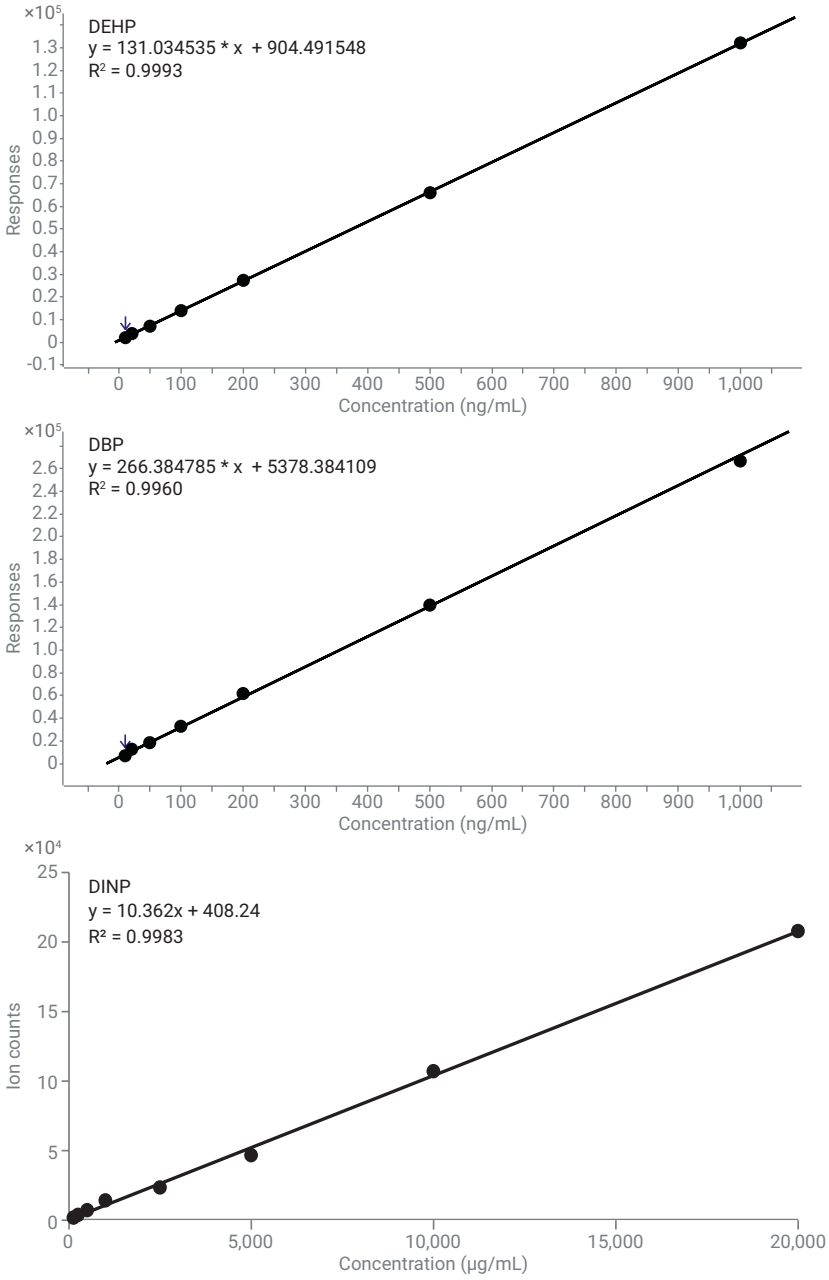

Figure 3. Calibration curve of DEHP, DBP, and DINP.

Referring to the sample preparation method described in method GB 5009.271-2016, usually 0.5 or 1 g of real-world sample is extracted by 5 or 10 mL of extraction solvent, then the cleaned extracts are injected into the GC/MS system for analysis. The concentration of phthalates in the real sample is calculated according to the formula:

$$X = \rho \times \frac{v}{m} \times \frac{1{,}000}{1{,}000}$$

X = Concentration of phthalates in real sample (mg/kg)

V = Sample final volume (mL)

m = Sample weight (g)

ρ = Concentration of phthalates calculated from calibration curve (µg/mL)

Based on instrument MDL and the above formula, the LOQs for the 18 phthalates on the 8890 GC and 5977B GC/MSD coupled system (DIDP was not included because it was not required in method GB 5009.271-2016) are well below the quantitation limit requirement in method GB 5009.271-2016.

In this Application Note, the online acquire and clean mode on the JetClean configuration was applied. To switch on this function, a trickle of hydrogen gas flowed into the ion source at 0.13 mL/min for ion source protection from real-world matrix contamination. A 9-mm drawout plate was used for better linearity in the whole calibration range. There is no real-sample analysis in this Application Note, because this work focused primarily on instrument performance. More work on real-sample analysis will be followed to further demonstrate the effectiveness and robustness of the 8890 GC and 5977B GC/MSD system in phthalates analysis.

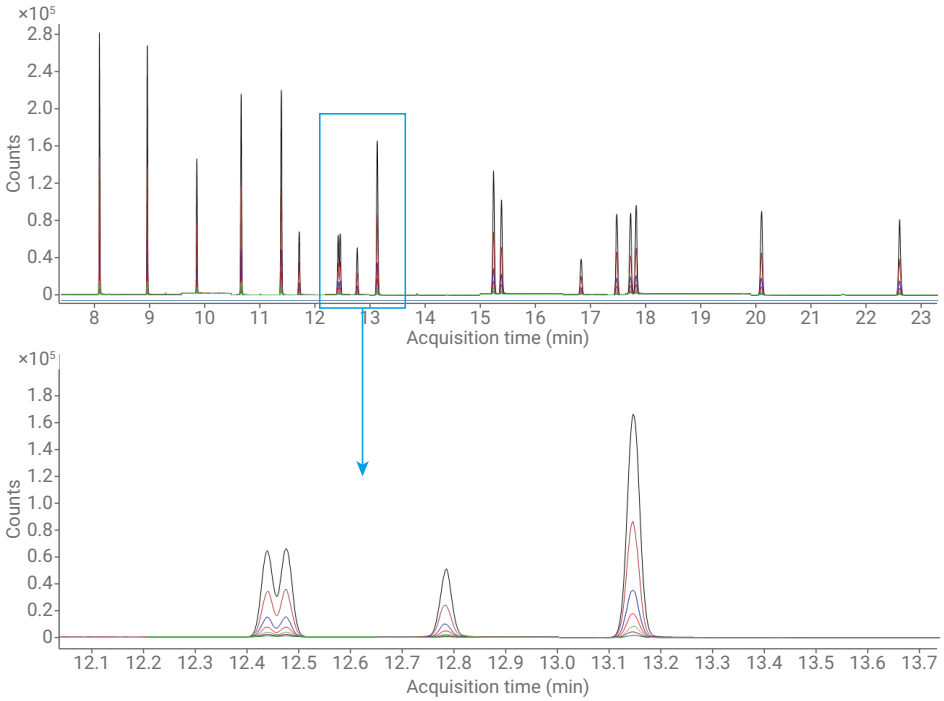

Figure 4. Linearity summed SIM of 17 phthalates from 10 to 1,000 ng/mL.

Conclusion

The 8890 GC and 5977B GC/MSD combined system provide reproducible, sensitive, and accurate identification of 19 phthalates, which was proved by excellent instrument RT/area precision and sufficiently low MDL. The linearity regression formula for 17 phthalates produces R^2 >0.995 in the range of 10 to 1,000 ppb. The linearity regression formula for DINP and DIDP in the range of 100 ppb to 20 ppm produces R^2 >0.998. This demonstrated the good linearity of the 8890 GC and 5977B GC/MSD coupled system. Using JetClean acquire and clean mode, the ion source can be protected from matrix contamination, and provide sensitive detection of phthalates to meet the method GB 5009.271-2016 detection limit requirements.

References

1. GB 5009.271-2016: Determination of Phthalates in food.
2. Feng Shuang; Hom Brian J. Sensitive and Reproducible Phthalate analysis using the Agilent 5977 series GC/MSD, *Agilent Technologies Application Note*, publication number 5991-1810EN, **2013**.

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