Phthalates Analysis in Fruit Juice Using an Agilent 5977E GC/MSD

Application Note

Food

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Abstract

This application note demonstrates an effective solution of phthalates using an Agilent 5977E GC/MSD. The 5977E GC/MSD, in synchronous full scan/selected ion monitoring (Scan/SIM) acquisition mode, provides high sensitivity to detect 16 phthalate esters. All of the phthalates show excellent linearity and relative standard deviations (RSD%).

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Introduction

Phthalate esters are the main plasticizers used as softening agents in the production of PVC. These compounds are reported to act as endocrine disruptors, and exposure to high levels can cause harmful effects in the human reproductive system. There have been reports from the U.S. Food and Drug Administration that certain foods and beverages, particularly fruit juices, contain high levels of phthalates.

China published a methodology with an extraction method for 16 phthalates in foods [1]. This application note focuses on the 16 phthalates including 15 compounds included in GB/T 21911-2008 with one exception. Hexyl-2-ethylhexyl phthalate was used to replace diphenyl phthalate because of the standards ordered. This application note demonstrates an analytical procedure for the quantitative analysis of 16 phthalate esters in fruit juice between the concentrations of 0.5 and 8.0 mg/L. The sample preparation of the phthalate esters was based on liquid-liquid extraction.

Experiment

Reagents and chemicals

All reagents were analytical or HPLC grade. The Phthalates standard was purchased from J&K (phthalate esters-Analyze Mix 3, 08060300). *n*-hexane was purchased from ANPEL, Shanghai. Table 1 lists the phthalates compounds. In the standard solution, *bis*(4-methyl-2-pentyl) phthalate (BMPP) is a mixture of two diastereomers, and dinonyl phthalate (DNP) is a mixture of isomers.

Equipment and materials

This experiment was performed on an Agilent 5977E GC/MSD equipped with an Agilent 7650A Automatic Liquid Sampler (G4567a). Separation of the compounds was achieved on an Agilent HP-5ms UI column 30 m × 0.25 mm, 0.25 µm (p/n 19091S-433UI). Table 2 lists the instrumental conditions.

Sample preparation

Because fruit juice is a non-fatty sample, we used the GB/T 21911-2008 sample preparation method. Place 5 mL of juice into one vial and add into it 2 mL *n*-hexane; vortex for 1 minute and let stand for 10 minutes. Remove 1 mL of the top *n*-hexane layer for GC/MS use.

Table 1. Phthalate Compounds

Name	Cas.
dimethyl phthalate (DMP)	131-11-3
diethyl phthalate (DEP)	84-66-2
di iso butyl phthalate (DIBP)	84-69-5
di butyl phthalate (DBP)	84-74-2
bis(2-methoxy ethyl) phthalate (DMEP)	117-82-8
bis(4-methyl-2-pentyl) phthalate (BMPP)	146-50-9
bis(2-ethoxy ethyl) phthalate (DEEP)	605-54-9
bis(*n*-pentyl) phthalate (DPP)	131-18-0
dihexyl phthalate (DHXP)	84-75-3
benzyl butyl phthalate (BBP)	85-68-7
hexyl-2-ethylhexyl phthalate (HEHP)	75673-16-4
bis(2-*n*-butoxyethyl) phthalate (DBEP)	117-83-9
dicyclohexyl phthalate (DCHP)	84-61-7
bis(2-ethylhexyl) phthalate (DEHP)	117-81-7
di-*n*-octyl phthalate (DNOP)	117-84-0
dinonyl phthalate (DNP)	84-76-4

Instrument conditions

Table 2. Instrumentation and Conditions of Analysis

Instrumentation	
ALS	Agilent 7650A Automatic Liquid Sampler, 50 vials
GC/MS system	Agilent 5977E GC/MSD
Inlet	Split/splitless
Liner	Ultra inert, p/n 5190-2293, splitless
Column	Agilent HP-5ms UI LTM, 30 m × 0.25 mm, 0.25 µm (p/n 19091S-433UI)
ALS experimental conditions	
Injection mode	Fast
Inlet temperature	250 °C
Injection volume	1 µL
Injection mode	Splitless
Carrier gas	Helium
Constant flow	1.0 mL/min
Oven temperature	60 °C (1 minute), 20 °C/min, 220 °C (1 minute), 5 °C/min, 280 °C (4 minutes)
MSD interface	280 °C
Ion source	300 °C
Quad. temperature	150 °C
Ionization mode	EI
Scan mode	Scan/SIM, 50–550 u; SIM ions are listed in Table 2
EMV mode	Gain factor
Gain factor	5
EMV voltage	1,625 V
Solvent delay	5.0 minutes

Calibration levels

The Chinese GB/T 21911-2008 describes five calibration solutions made by dilution in *n*-hexane. The concentration levels were: 0.5, 1.0, 2.0, 4.0, and 8.0 mg/L.

To prepare the spiked samples, add 250 µL of 8.0 mg/L solution to 5 mL of juice liquid to get a 0.4 mg/L spiked sample. Then add 2 mL of *n*-hexane to extract the targets from the juice. Remove 1 mL of the top *n*-hexane layer for GC/MS injection.

Results and Discussion

Qualitative and quantitative results

This application note used the synchronous Scan/SIM acquisition mode, as required by GB/T 21911-2008. Table 3 describes the SIM information of phthalates. Typical total ion chromatograms (TIC) of the phthalates are shown in Figure 1 with a 1.0 mg/L calibration level.

*Table 3. Calibration of Phthalates (*Indicates Quantitative Ions)*

Name	R.T (min)	SIM groups (start time min)	SIM ions (dell time = 100ms)
dimethyl phthalate (DMP)	7.901	1 from 5.0	77; 163*; 194
diethyl phthalate (DEP)	8.766	2 from 8.30	149*; 177;222
di-iso-butyl phthalate (DIBP)	10.564	3 from 9.30	149*; 205; 223
di-butyl phthalate (DBP)	11.326	4 from 10.96	149*; 205; 223
bis(2-methoxy ethyl) phthalate (DMEP)	11.661	5 from 11.49	59; 149*; 193
bis(4-methyl-2-pentyl) phthalate (BMPP)	12.433	6 from 12.0	149*; 167; 251
bis(2-ethoxy ethyl) phthalate (DEEP)	12.758	7 from 12.60	72; 149*; 221
bis(*n*-pentyl) phthalate (DPP)	13.147	8 from 12.95	149*; 219; 237
dihexyl phthalate (DHXP)	15.318	9 from 14.50	76; 104; 149*
benzyl butyl phthalate (BBP)	15.469	10 from 15.39	91; 149*; 206
hexyl-2-ethylhexyl phthalate (HEHP)	16.582	11 from 16.00	149*; 167; 251
bis(2-*n*-butoxyethyl) phthalate (DBEP)	16.928	12 from 16.77	149; 205; 223
dicyclohexyl phthalate (DCHP)	17.608	13 from 17.30	149*; 167; 249
bis(2-ethylhexyl) phthalate (DEHP)	17.835	14 from 17.72	149; 167; 279*
di-*n*-octyl phthalate (DNOP)	20.240	15 from 19.00	149; 167; 279*
dinonyl phthalate (DNP)	From 20.05 ~ 21.915	16 from 19.00	149; 167; 293*

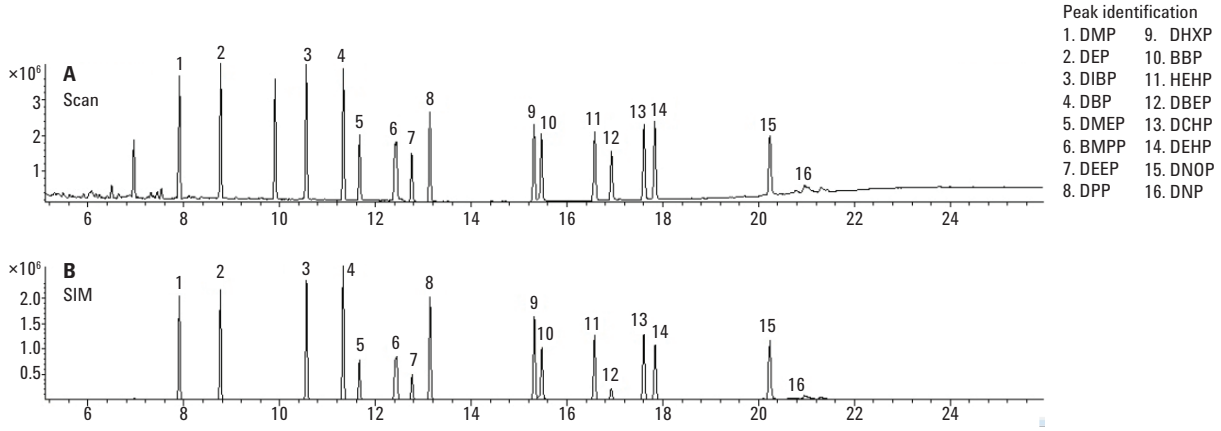

Figure 1. TIC of 16 phthalates at 1.0 mg/L. A) Scan; B) SIM.

Linearity

Table 4 describes the linearity of the 16 phthalates, and all of the compounds have excellent coefficients from 0.5 to 8.0 mg/L calibration levels.

Figures 2 to 5 show the linearity curve of some phthalates. Good linearity can provide reliable quantitative results.

Real sample

Orange juice from a local supermarket was prepared according to the sample preparation step. A phthalates standard was added to a juice blank extraction to get a 0.4 mg/L spiked sample solution. A 2.0 mL amount of *n*-hexane was added to extract the targets. Six injections were made to test the stability of the *n*-hexane extraction. Figure 6 is an overlay chromatogram of SIM mode. The RSD% of 16 phthalates was from 0.295 to 1.573. This data shows that the 5977E GC/MSD has excellent stability and reliability for fruit juice.

Table 4. Linearity of 16 Phthalates (SIM Mode)

Name	Coefficient (R^2)
dimethyl phthalate (DMP)	0.9997
diethyl phthalate (DEP)	0.9999
di-iso-butyl phthalate (DIBP)	0.9996
di-butyl phthalate (DBP)	0.9989
bis(2-methoxy ethyl) phthalate (DMEP)	0.9996
bis(4-methyl-2-pentyl) phthalate (BMPP)	0.9996
bis(2-ethoxy ethyl) phthalate (DEEP)	0.9997
bis(*n*-pentyl) phthalate (DPP)	0.9993
dihexyl phthalate (DHXP)	0.9990
benzyl butyl phthalate (BBP)	0.9992
hexyl-2-ethylhexyl phthalate (HEHP)	0.9997
bis(2-*n*-butoxyethyl) phthalate (DBEP)	0.9992
dicyclohexyl phthalate (DCHP)	0.9981
bis(2-ethylhexyl) phthalate (DEHP)	0.9998
di-*n*-octyl phthalate (DNOP)	0.9993
dinonyl phthalate (DNP)	0.9983

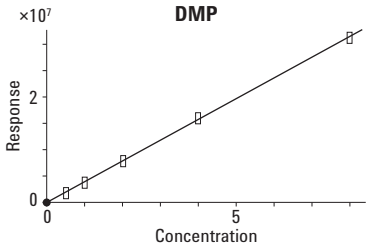

Figure 2. DMP R^2 = 0.9997.

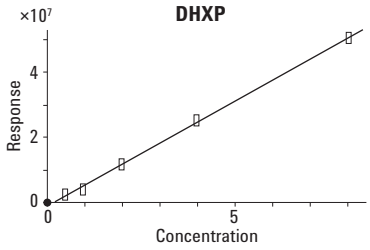

Figure 3. DHXP R^2 = 0.9990.

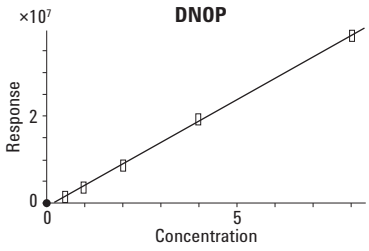

Figure 4. DNOP R^2 = 0.9993.

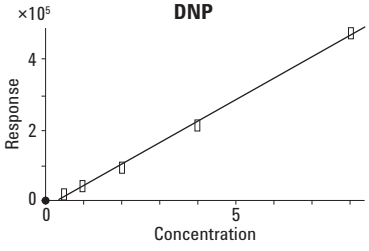

Figure 5. DNP R^2 = 0.9983.

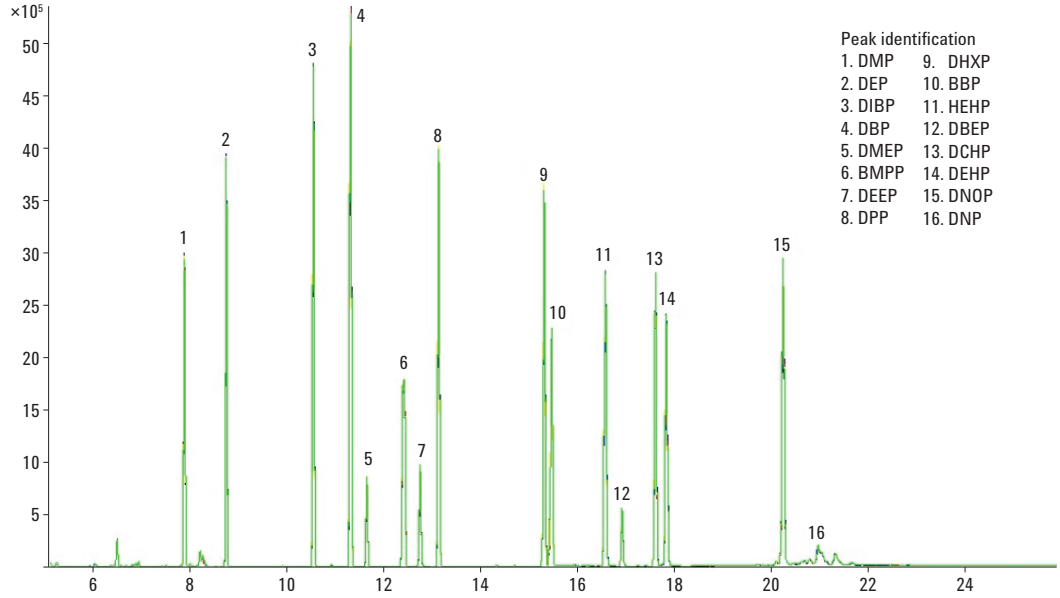

Figure 6. The overlay SIM chromatogram of six injections of spiked sample solution.

Conclusions

The method developed on the Agilent 5977E GC/MSD indicates that it is a good tool for the determination of phthalates in fruit juice. The results are very promising for both linearity and repeatability. The 5977E GC/MSD is a reliable instrument for the phthalates analysis in fruit juice.

Reference

1. GB/T 21911-2008 Determination of phthalate esters in foods.

For More Information

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