Sensitive and Reproducible Phthalate Analysis Using the Agilent 5977A Series GC/MSD

Application Note

Environmental

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Abstract

A method has been developed on the Agilent 5977A Series GC/MSD that enables minimum detection limits (MDLs) less than 0.01 mg/mL and relative standard deviations (RSDs) less than 5% for six phthalates using the Etune setting and electron ionization (EI) mode. A second Positive Chemical Ionization (PCI) method using either methane or ammonia has also been developed to allow better spectral differentiation of phthalate compounds.

Introduction

Phthalates are esters of phthalic acid and are used as plasticizers to increase the flexibility, transparency, durability, and longevity of plastics. They can be found in a wide range of products, including adhesives and glues, electronics, personal-care products, medical devices and tubing, packaging, and children's toys. These compounds are easily released into the environment as they are not covalently bound to the plastics in which they are mixed. Studies have implicated phthalates in a number of health problems, including asthma, endocrine disruption, reproductive abnormalities, cancer, low birth weight, autism, and ADHD.

As a result, the European Union (EU), the United States (USA) and several other countries have begun to regulate phthalate exposure. The use of six phthalates in children's toys and child care articles has been restricted in the EU (2005/84/EC) since 2007, and in the USA since 2009 (Table 1).

This application note demonstrates the ability of the 5977A Series GC/MSD to enable linear and reproducible detection of the six regulated phthalates using both EI and PCI, with relative standard deviations (RSDs) below 2% for five of the six phthalates at 0.05 mg/L (50 ppb), and below 5% for the sixth one.

Table 1. The Six Phthalates Regulated in Toys by the USA and the EU

Compound name	Acronym	CAS no.
Dibutyl phthalate	DBP	84-74-2
Benzylbutyl phthalate	BBP	85-68-7
Bis-(2-ethylhexyl) phthalate	DEHP	117-81-7
Di-n-octyl phthalate	DNOP	117-84-0
Diisononyl phthalate	DINP	28553-12-0
Diisodecyl phthalate	DIDP	26761-40-0

Experimental

Standards and Reagents

Phthalate standards were commercially obtained and calibration working solutions were prepared in dichloromethane using the Agilent 7696A Sample Prep WorkBench.

Instruments

The study was performed on an Agilent 7890B Series GC equipped with a Split/Splitless Inlet and coupled to an Agilent 5977A Series GC/MSD, using Synchronous SIM/SCAN as well as both EI and PCI acquisition modes. Table 2 lists the instrument conditions.

Table 2. Agilent 7890B/5977A Gas Chromatograph and Mass Spectrometer Conditions

GC run conditions	
Analytical column	Agilent HP-5ms 30m × 0.25 mm, 0.25 µm (p/n 19191S-433UI)
Injection volume	1 µL
Injection mode	Splitless
Inlet temperature	290 °C
Liner	Ultra inert liner, single taper, wool (p/n 5190-2293)
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 and Etune
Gain factor	1
Extractor source temperature	230 °C
Quadrupole temperature	150 °C
MS conditions PCI	
Solvent delay	5 minutes
Acquisition mode	SCAN
Gain factor	1
CI gas flow	Methane 29%; Ammonia 20%
Extractor Source temperature	300 °C
Quadrupole temperature	150 °C

Acquisition Parameters

Table 3 shows the SIM ions used for acquisition.

Table 3. Acquisition Parameters

SIM group	Compound	Retention time (min)	Quantifier ion	Qualifier ion(s)
1 (5–9.2 minutes)	DBP	8.46	223	149, 167, 205
2 (9.2–10.7 minutes)	BBP	9.77	206	91, 149
	DEHP	10.358	279	149, 167
3 (10.7 minutes - End)	DNOP	11.01	279	149, 167, 261
	DINP	11.3	293	149, 167
	DIDP	12.05	307	149, 167

Results and Discussion

Synchronous SIM/SCAN Analysis

The synchronous Scan and SIM total ion current (TIC) traces in electron ionization (EI) mode for a mixture of the six phthalates are shown in Figure 1, and the quantitative ion traces for DINP and DIDP, which coelute, are shown in Figure 2.

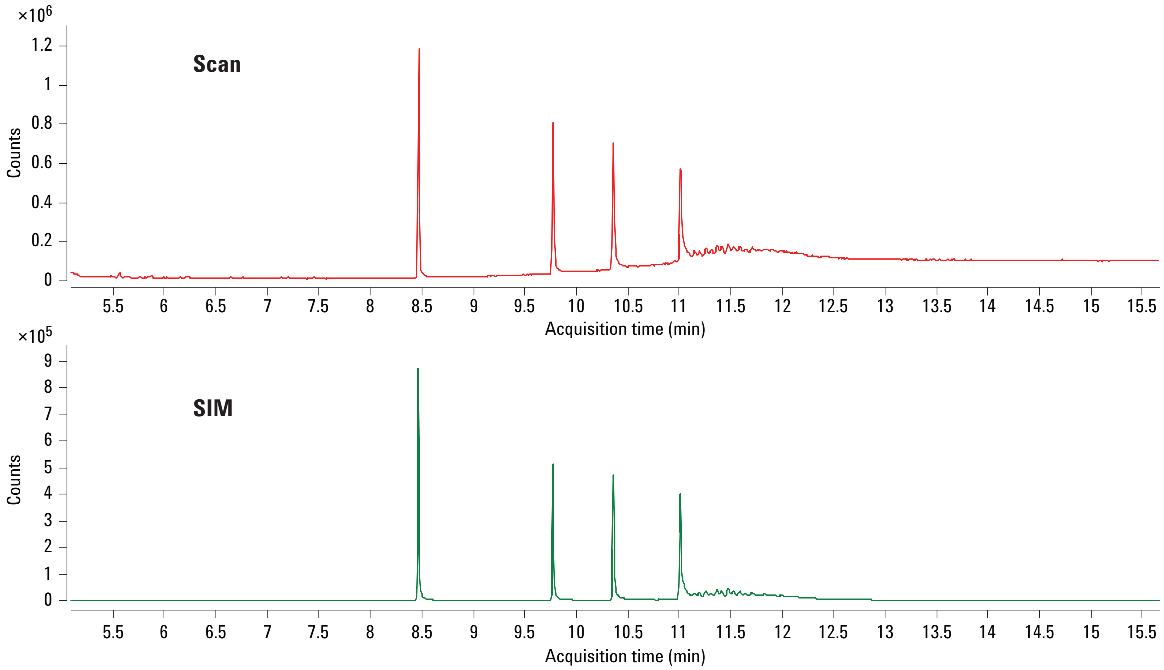

Figure 1. Synchronous Scan (above) and SIM (below) TIC traces of the six phthalate standards in EI mode at 1 mg/L.

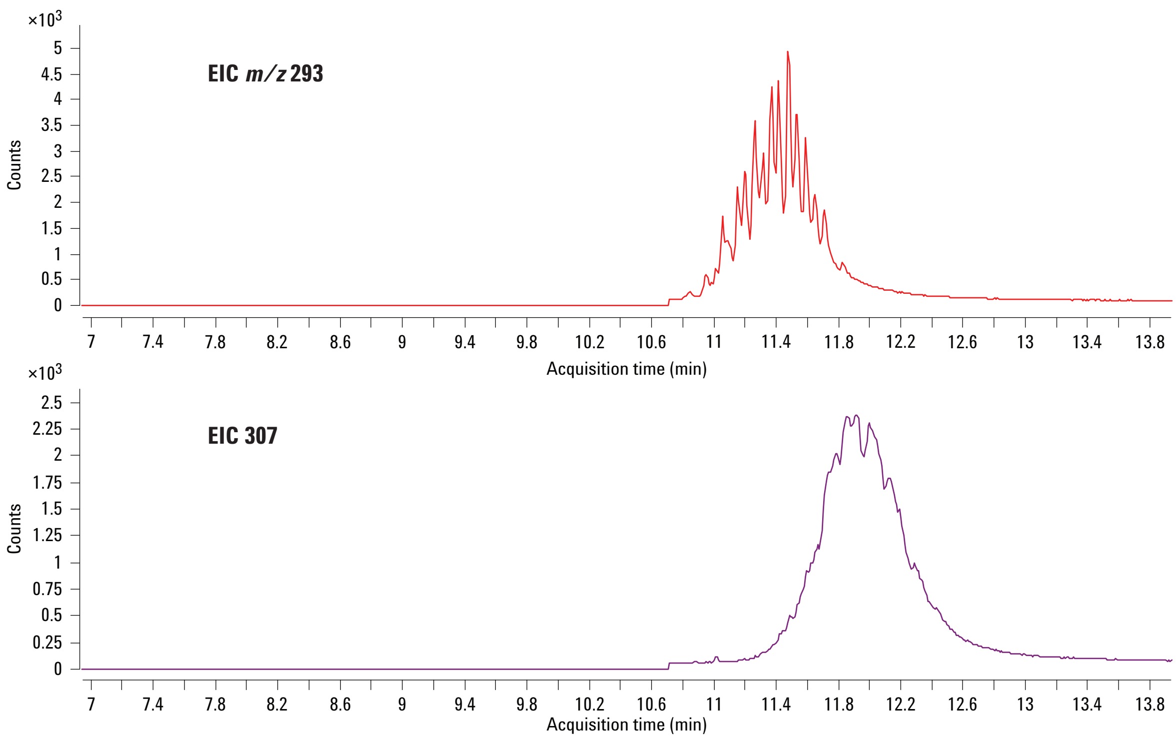

Figure 2. SIM traces in EI mode of the quantitative ions for DINP (upper, m/z 293) and DIDP (lower, m/z 307) at 2 mg/L.

Linearity Sensitivity

Calibration curves were constructed from 0.05 to 1 mg/L in EI mode. Both Etune and Atune settings gave calibration curves with very high R^2 values (Table 4). The Etune setting produced 2–3 times more ions as compared to the Atune setting (Figure 3), which potentially allows for lower minimum detection limits (MDLs, Table 5).

Table 4. Calibration Coefficient (R^2) Values in EI Mode Using Etune or Atune

Compound	Etune	Atune
DBP	0.9988	0.9986
BBP	0.9976	0.9956
DEHP	0.9971	0.9950
DNOP	0.9937	0.9954
DINP	0.9950	0.9920
DIDP	0.9942	0.9918

Five calibration solutions at 0.05, 0.1, 0.25, 0.5 and 1 mg/L.

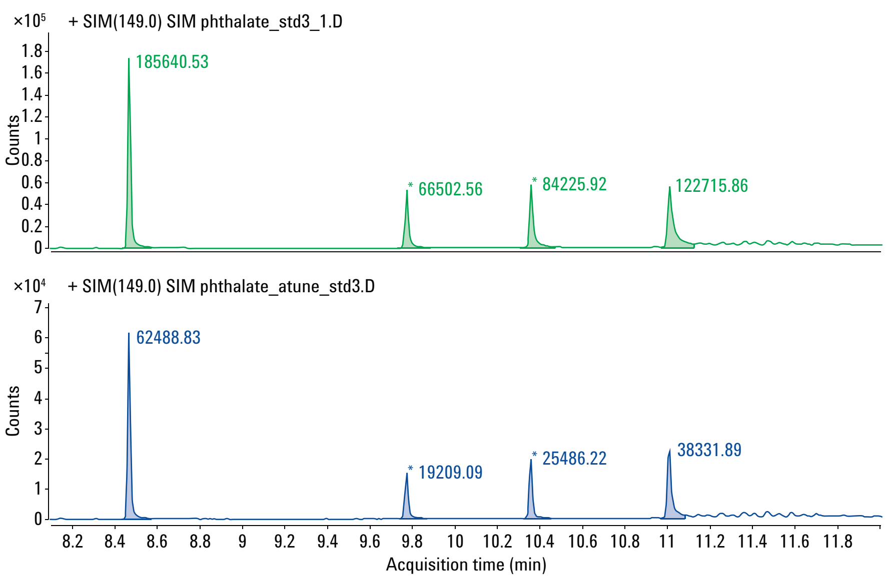

Figure 3. Comparison of peak areas for Etune and Atune. DBP, BBP, DEHP, and DNOP, 0.25 mg/L (ppm) each; DINP and DIDP, 0.5 mg/L each.

Table 5. Minimum Detection Limits (mg/L) for Etune and Atune Settings

Compound	Etune	Atune
DBP	0.009	0.004
BBP	0.003	0.005
DEHP	0.002	0.003
DNOP	0.003	0.005
DINP	0.008	0.016
DIDP	0.006	0.012

Reproducibility

Figures 4 and 5 illustrate the excellent reproducibility obtainable in EI mode with the 5977A GC/MSD, even at low concentrations. Using Etune, the RSD values for 10 injections at 0.05 mg/L of each of the six phthalates were all under 2% except for DBP, which was under 5% (Table 6). Etune gave lower RSDs than Atune for all six phthalates except for DBP.

Table 6. Relative Standard Deviation Values (RSDs, %) for Etune and Atune Settings

Compound	Etune	Atune
DBP	4.6%	2.1%
BBP	1.3	2.4
DEHP	1.0	1.6
DNOP	1.3	2.6
DINP	1.8	3.5
DIDP	1.2	2.6

10 Injections of 0.05 mg/L phthalate standard mix

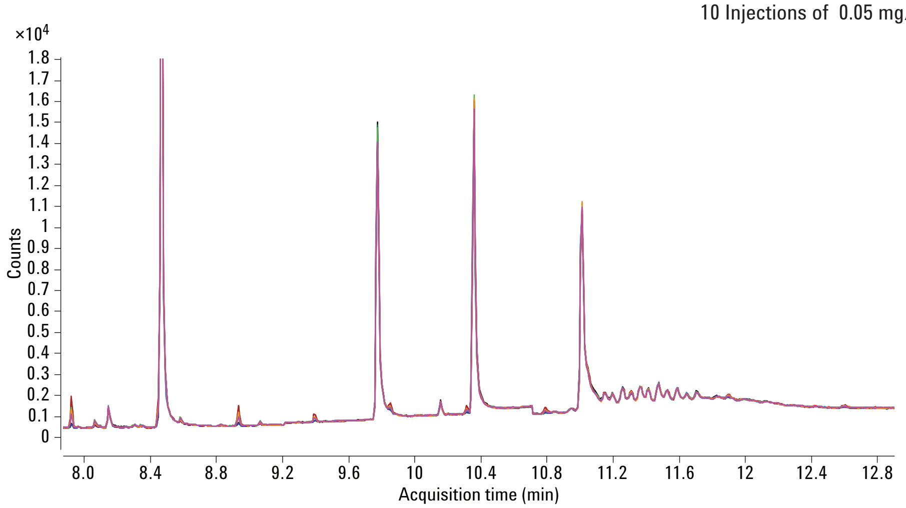

Figure 4. TIC trace overlay in EI mode of 10 successive injections of the standard mix of six phthalates. DBP, BBP, DEHP, and DNOP, 0.05 mg/L each; DINP and DIDP, 0.1 mg/L each.

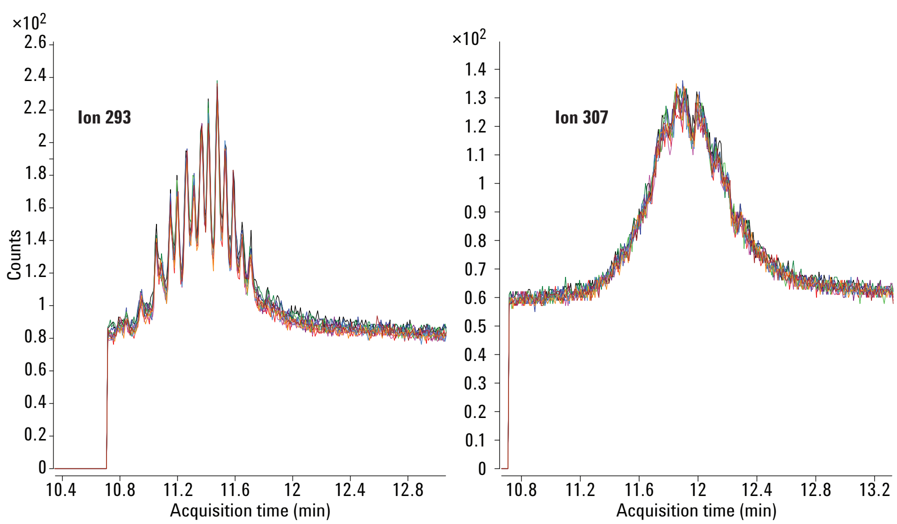

Figure 5. SIM trace overlay of 10 successive injections of DINP (left) and DIDP (right), at 0.1 mg/L.

Advantages of PCI Ammonia

GC/MS analysis of most phthalates in EI mode generates the same base peak for all of the phthalates (*m/z* 149), making it difficult to assign identity based on library searches. This can be made even more difficult in matrices that may generate interferences that can obscure the less abundant ions.

Applying PCI increases the specificity of the ionization, and can be used to overcome the problem presented by EI analysis, if the right gas is used. While PCI generally is a less sensitive technique, more molecular/pseudo-molecular ions are formed. Methane CI generates the same base peak for most phthalates as EI (m/z 149), but also produces additional peaks, which reveal information on the alkyl side chains and higher mass fragments representing protonated and adduct molecular species. Ammonia gas produces a spectrum that is nearly entirely made up of the protonated molecular species which can be useful in clearly differentiating phthalates with similar retention times (Figure 6).

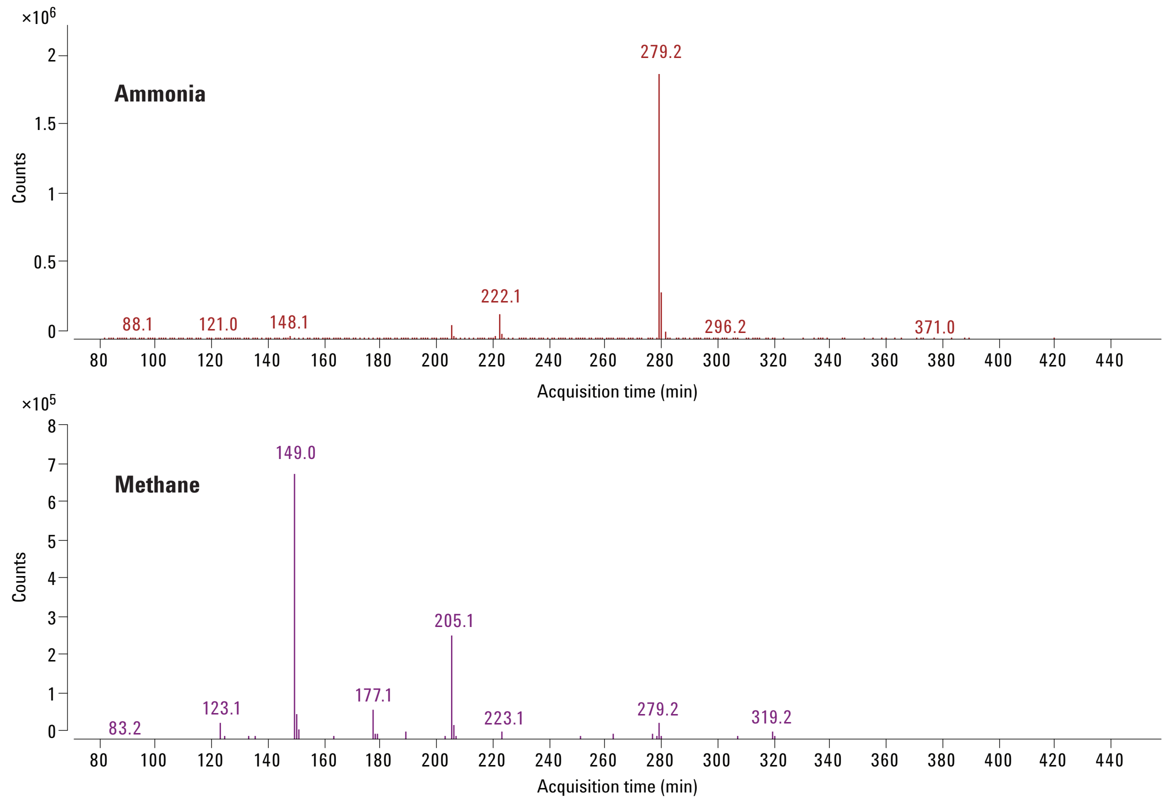

Figure 6. Ammonia and Methane PCI spectra for DBP at 5 mg/L.

Conclusion

The Agilent 5977A Series GC/MSD can deliver sensitive, accurate and reproducible analysis of phthalates at levels as low as 0.05 mg/L in EI mode. Use of the new Extractor EI source can provide higher peak areas and lower MDLs and RSDs for phthalate determinations. The 5977A Series GC/MSD also supports the use of PCI, which can provide superior differentiation between the phthalate compounds by producing spectra with the molecular species as the predominant ion. The use of automation like the 7696A Sample Prep WorkBench to prepare standards can provide reproducible calibration coefficient (R^2) values.

For More Information

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