RoHS 3 Phthalate Calibration and Reproducibility Study by IEC 62321-8 Standard Method

Application Note
Electronics Industry

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Abstract
This application note presents RoHS 3 phthalate compliance, and RSDs of phthalates for IEC 62321-8 method using a CDS 6000 Series Pyroprobe Autosampler.

Materials being investigated by thermal sampling techniques such as pyrolysis are frequently polymeric, but they may also have volatile and semi-volatile contaminants and additives. When using pyrolysis- gas chromatography, these non-polymeric constituents produce some of the most significant peaks in the chromatogram. It has become common to perform two or more analyses on the sample at increasing temperatures, to remove the additives before pyrolysis. Often, analysis of the polymer structure is less important than the nature and amount of additives present, especially those additives known to be hazardous.

Restriction of Hazardous Substances, or RoHS, began in the European Union and restricts the use of specific hazardous materials found in electrical and electronic products. Businesses which sell these products may be subjected to RoHS requirements if they use restricted substances. The RoHS 3 with a deadline of July 22, 2019 requires the disclosure of the following 4 phthalates: Bis(2-Ethylhexyl) phthalate (DEHP), Benzyl butyl phthalate (BBP), di-n-butyl phthalate (DBP), Diisobutyl phthalate (DIBP). These phthalates are typically used as insulation plasticizers and are on the European Chemicals Agency REACH list of SVHC (Substances of Very High Concern).

In addition, the International Electrotechnical Commission (IEC) published a standard method for determining phthalates in electronic equipment. IEC 62321-8 defines approaches to determine previously mentioned DEHP, DIBP, BBP, DBP, as well as additional phthalates, di-n-octyl phthalate (DNOP), di-isononyl phthalate (DINP) and di-iso-decyl phthalate (DIDP) in electronics, by GC-MS and TD-GC-MS. The TD-GC-MS method involves two separate thermal desorption heating ramps for one GC run. This can be performed using a CDS 6000 Series Pyroprobe Autosampler. TIC and extracted ion chromatograms in Figure 1 match the chromatograms in Annex C.2 of the International Standard.

The diagnostic worth of the results depends on the reproducibility, and reproducibility for thermal desorption depends greatly on temperature precision, along with sample related issues like homogeneity and sample preparation. Like all analytical instrumentation, the Pyroprobe is designed to perform with optimum precision. This reproducibility is not only seen in peak area ratios with pyrolysis of polymers, but also in thermal desorption of phthalate standards. Here, five microliters of a 100ng/mL of a phthalate solution in hexane was added to DISC (Drop-In-Sample Chamber) tubes for replicate analysis in accordance with the IEC method for Phthalates. Figure 2 shows replicate TICs for two of the phthalates, DIBP and DBP. Eight replicates of the standard presented area RSDs for most of the phthalates around or under 3% (Table 1).

Experimental Parameters

The sample was pyrolyzed in a DISC tube, using a CDS Pyroprobe 6200 with Autosampler.

Method 1:
Pyroprobe :

Initial:	200°C
Ramp:	20°C/minute
Final:	300°C

Interface:

Rest:	300°C
Initial:	300°C
Transfer Line:	300°C
Valve Oven:	300°C

GC Signal:

GC ready:	ON
GC start:	ON

Method 2:
Pyroprobe :

Initial:	300°C
Ramp:	5°C/minute
Final:	340°C hold 1 min

Interface:

Rest:	300°C
Initial:	300°C
Transfer Line:	300°C
Valve Oven:	300°C

GC Signal:

GC ready	OFF
GC start	OFF

These two methods were run in sequence during one GC run.

GC/MS

Column:	5% phenyl (30m x 0.25mm)
Carrier:	Helium, 50:1 split
Injector:	320°C
Oven:	80°C for 13 minutes
	20°C/min to 300°C
	hold 5 minutes
Ion Source:	230°C
Mass Range:	50-1000amu

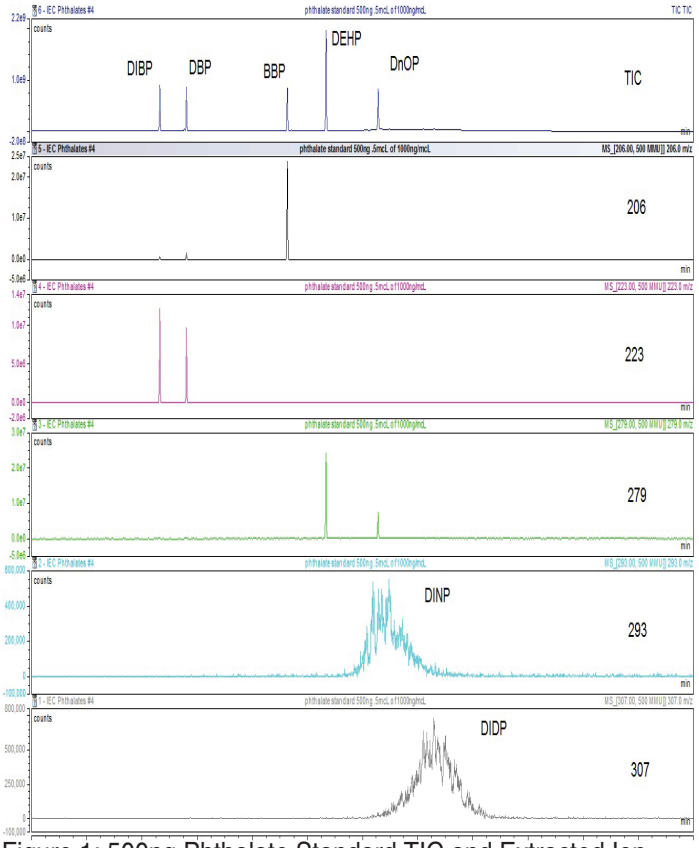

Figure 1: 500ng Phthalate Standard TIC and Extracted Ion Chromatograms.

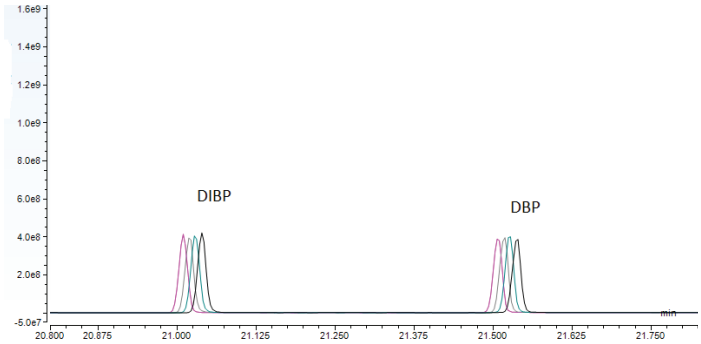

Figure 2: Extracted Ion 223 Overlap of 4 Replicates of DIBP and DBP to show similarity of peak areas.

Phthalate	Quant Ion	Area RSD
DIBP	223	3.2 %
DBP	223	2.3 %
BBP	206	4.3 %
DEHP	279	2.9 %
DNOP	279	3.2 %
DINP	293	3.0 %
DIDP	307	3.2 %

Table 1: Area RSDs of 7 regulated phthalates.

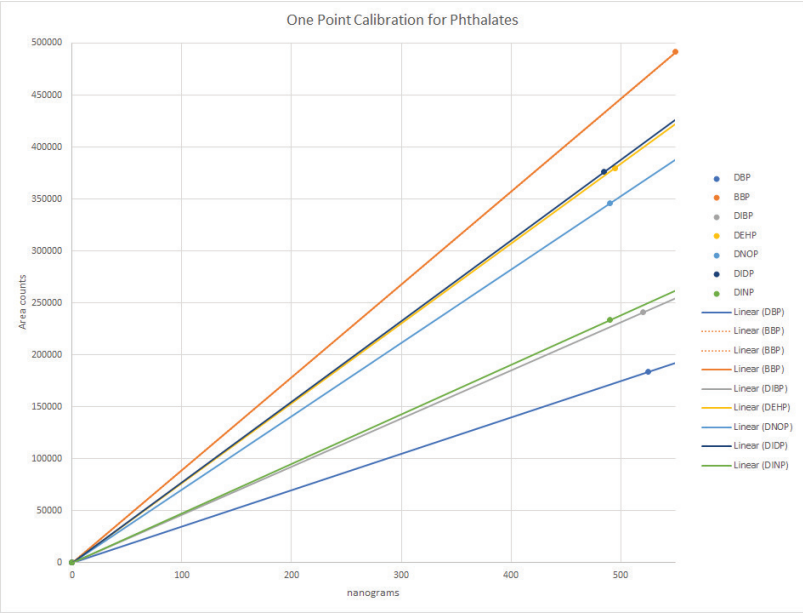

Figure 3: One Point Calibration for Phthalates.

Calibration and determination of phthalate concentration is based on a one-point calibration, the area count of each phthalate plotted against its amount. This calibration plot is shown in Figure 3.

The latest version of the Pyroprobe from CDS Analytical ensures repeatable, reliable results for thermal desorption of phthalates in accordance with standard regulations and methods, like RoHS and IEC 6321-8 for determination of phthalates in electromechanical products.