



Phthalate Calibration and Reproducibility with a Reference Polymer Material using an IEC Standard Method

Application Note

Electronics Industry

Abstract

This application note presents RSDs of phthalates with a reference polymer material for IEC 62321-8 method using a CDS 6000 Series Pyroprobe Autosampler.

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Introduction

RoHS, or Restriction of Hazardous Substances restricts the use of specific hazardous materials found in electrical and electronic products. This includes the following 4 phthalates: Bis(2-Ethylhexyl) phthalate (DEHP), Benzyl butyl phthalate (BBP), di-n-butyl phthalate (DBP), Diisobutyl phthalate (DIBP). Additionally, 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 di-n-octyl phthalate (DNOP), di-isononyl phthalate (DINP) and di-iso-decyl phthalate (DIDP) in electronics using TD-GC-MS as a quick screening technique before applying unnecessary solvent extractions for GC-MS analysis. CDS Analytical provides a reference polymer material, CDS P/N 6203-5094, containing the previously mentioned phthalates as well as di-n-hexyl phthalate (DNHP) to facilitate the TD screening technique. Concentrations of the phthalates in the reference material are found in Table 1. This application note investigates IEC method 62321-8 using this reference polymer material.



Table 1. Concentration of phthalates in Reference Polymer Material
CDS P/N 6203-5094 batch number RM(004a).

Phthalate	Concentration (mg/kg)
DEHP	1389
DIBP	1156
BBP	1297
DBP	1151
DNOP	1229
DINP	555
DIDP	1410

Experimental Parameters

The reference polymer material, CDS P/N 6203-5094 batch number RM(004a), was trimmed to around 0.5mg sizes with exact weights recorded, then added to a DISC tubes for TD-GC-MS analyses using a CDS Pyroprobe 6150 with Autosampler interfaced to a GC-MS.

Method 1:

DISC :

Initial:	200°C	GC Signal:	
Ramp:	20°C/minute	GC ready:	ON
Final:	300°C	GC start:	ON

Interface:	300°C
Transfer Line:	325°C
Valve Oven:	300°C



Method 2:

DISC:

Initial: 300°C

Ramp: 5°C/minute

Final: 340°C hold 1 min

GC Signal:

GC ready

GC start

OFF

OFF

Interface: 300°C

Transfer Line: 325°C

Valve Oven: 300°C

GC-MS

Column: 5% phenyl (30m x 0.25mm)

Carrier: Helium, 50:1 split

Injector: 320°C; Gas Saver ON at 13 minutes

Oven: 80°C for 13 minutes

20°C/min to 300°C

hold 5 minutes

Ion Source: 230°C

Mass Range: 50-1000amu

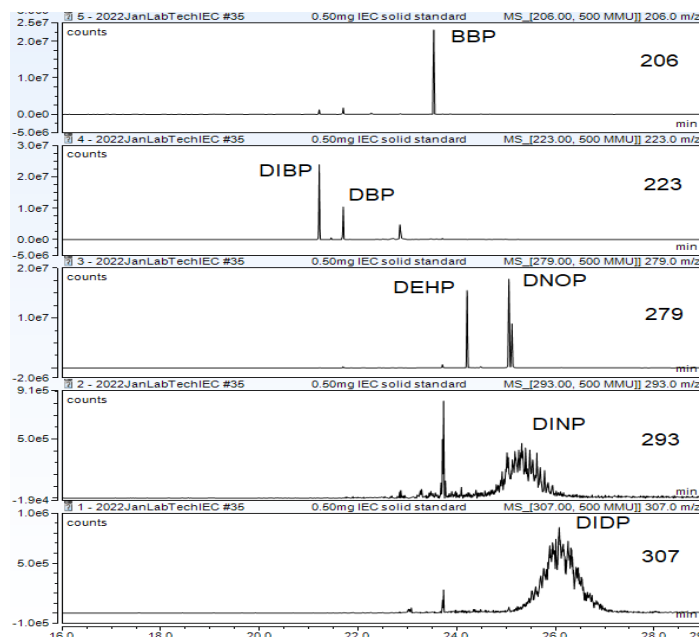


Figure 2. Reference Polymer Material Extracted Ion Chromatograms.

Results and Discussion

A TD-GC-MS chromatogram of the reference polymer material is shown in Figure 1. The chromatogram shows DNHP, DIBP, BBP, DEHP, DNOP, and many other compounds like hexadecanoic acid, octadecanoic acid, and non-phthalate plasticizers Tributyl aconitate and Tributyl acetyl citrate. Extracted ion chromatograms shown in Figure 2 shows the phthalates, which is similar to the chromatograms in Annex C.2 of the International Standard.

Figure 3 shows 9 replicate time-offset EICs of DEHP to show the similarity of peak areas. Nine replicates of the solid standard presented RSDs for all 7 the IEC regulated phthalates average 5% (Table 2).

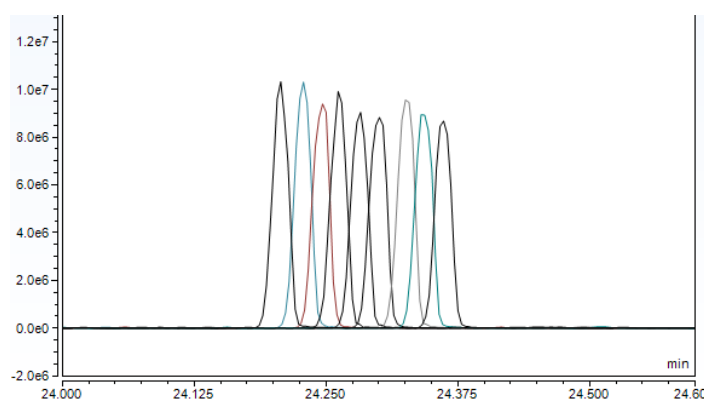
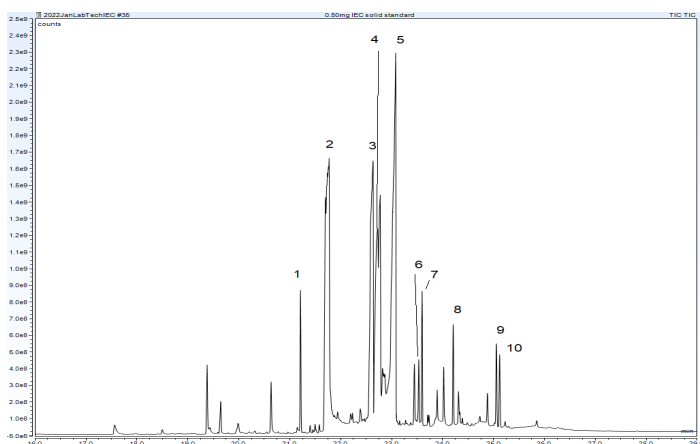


Figure 3. Extracted Ion 279 Overlap of 9 Replicates of DEHP, time offset by 10%, to show similarity of peak areas.



Peak	Identification
1	DIBP
2	n-Hexadecanoic acid
3	Tributyl aconitate
4	Octadecanoic acid
5	Tributyl acetyl citrate
6	BBP
7	Isobutyl stearate
8	DEHP
9	DNOP
10	DNHP

Figure 1. 0.5mg reference polymer Material TIC.

Calibration and determination of phthalate concentration is based on a one-point calibration; the area count of each phthalate plotted against amount in nanograms. The area count vs. nanograms of each of the 7 phthalates and in an unknown sample are shown in the calibration plot (Figure 4).

Table 2. Area/mg RSDs of 7 IEC regulated phthalates in Reference Polymer Material.

Phthalate	Quant Ion	Area/mg RSD
DIBP	223	8.0 %
DBP	223	4.4 %
BBP	206	7.7 %
DEHP	279	2.9 %
DNOP	279	2.8 %
DINP	293	5.0 %
DIDP	307	3.3 %

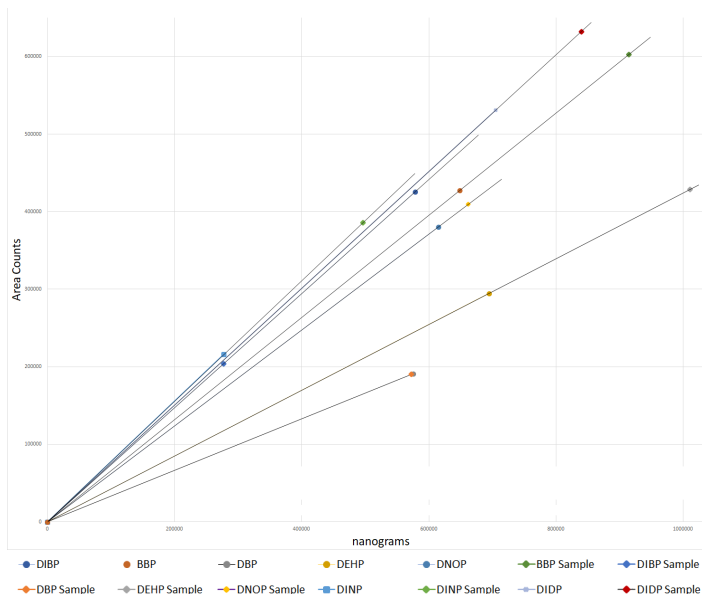


Figure 4. One Point Calibration for Phthalates with unknown sample plugged in.

The concentration each phthalate in the unknown sample was calculated by using the equation $c_{\text{final}} = y \times \left(\frac{1}{a}\right) \times \left(\frac{1}{m}\right)$ where

c_{final} is the concentration of each phthalate in the sample in mg/kg;

y is the peak area of each phthalate in the sample;

a is the slope of the calibration curve;

m is the mass of the sample (mg).

A screening judgement was made in accordance with the flow chart in Annex N of the IEC 62321-8 Method when the acceptability threshold concentrations are set at 1000 mg/kg. Where 500 mg/kg and under is “below limit”, 1500 or over is “over limit” and between 500 and 1500 mg/kg is inconclusive. The calculated concentrations and screening results of the unknown sample are shown in Table 3.

Table 3. Concentration and Screening Result of 7 IEC regulated phthalates in an unknown sample.

Phthalate	concentration (mg/kg)	Screening Result
DIBP	554	INC
DBP	1144	INC
BBP	1829	OL
DEHP	2020	OL
DNOP	1324	INC
DINP	993	INC
DIDP	1679	OL

“BL” is “below limit” or passing

“OL” is “over limit” or failing

“INC” is “inconclusive” requiring GC-MS referee testing.

The screening results in Table 3 indicate that the sample is over the limit for BBP, DEHP, and DIDP, and requires GC-MS referee testing for DIBP, DBP, DNOP, and DINP to determine if the threshold of under 1000mg/kg was achieved for these phthalates.

Conclusion

The Pyroprobe 6150 together with the reference polymer material for added convenience provides repeatable, reliable results for thermal desorption of phthalates in accordance with standard regulations and methods, like IEC 6321-8 for determination of phthalates in electrotechnical products.