# Phthalate Calibration, Reproducibility and MDL studies using an IEC Standard Method

Application Note
Electronics Industry

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Abstract
This application note presents calibration plots, RSDs and MDLs for IEC Method 62321-8 using a CDS Model 6150 Autosampler.

Materials being investigated by thermal sampling techniques such as pyrolysis are frequently polymeric, but 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 extract additives before pyrolysis. In some instances, however, analysis of the polymer structure takes a back seat to the nature and amount of additives present.

Certain phthalate additives are known to be harmful to humans, resulting in regulations regarding their use. With growing environmental awareness and perceptions, the use of phthalates has been restricted in many countries of the world, including the European Union and the United States of America. As a result, a few international standards and conformity assessment bodies such as the International Electrotechnical Commission (IEC) and the American Society for Testing and Materials (ASTM), have published standards for determining certain phthalates in polymeric materials. The recent IEC 62321-8 defines approaches to determine di-isobutyl phthalate (DIBP), di-n-butyl phthalate (DBP), benzyl butyl phthalate (BBP), bis-2-ethyl hexyl phthalate (DEHP), di-n-octyl phthalate (DNOP), di-isononyl phthalate (DINP) and di-iso-decyl phthalate (DIDP) in electronics using GC-MS and TD-GC-MS. Thermal extraction of additives is a straightforward approach involving only a few steps and therefore the possibility of greater recovery when compared to solvent extraction techniques. The sample is simply placed in a sample tube, dropped into the 6150 Pyroprobe, which then automatically thermally extracts by two sequential temperature ramps as defined in the Experimental Parameters, straight to a single quad GC-MS. Chromatograms and extracted ion chromatograms in Figure 1 match the chromatograms in Annex C.2 of the International Standard.

The statistical measures related to reproducibility depend on the 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. Five microliters of a 100ng/mcL of a phthalate solution in hexane was added to DISC tubes for replicate analysis. Figure 2 shows replicate EICs for two of the phthalates, DIBP and DBP. Eight replicates of the standard presented area RSDs around or under 3% (Table 1).

Experimental Parameters
The sample was pyrolyzed in a DISC tube, using a CDS Pyroprobe 6150 with Autosampler.

Method 1:
Pyroprobe :

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

| | |
|---|---|
| Interface: | 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: | 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<br>20°C/min to 300°C<br>hold 5 minutes |
| Ion Source: | 230°C |
| Mass Range: | 50-1000amu |

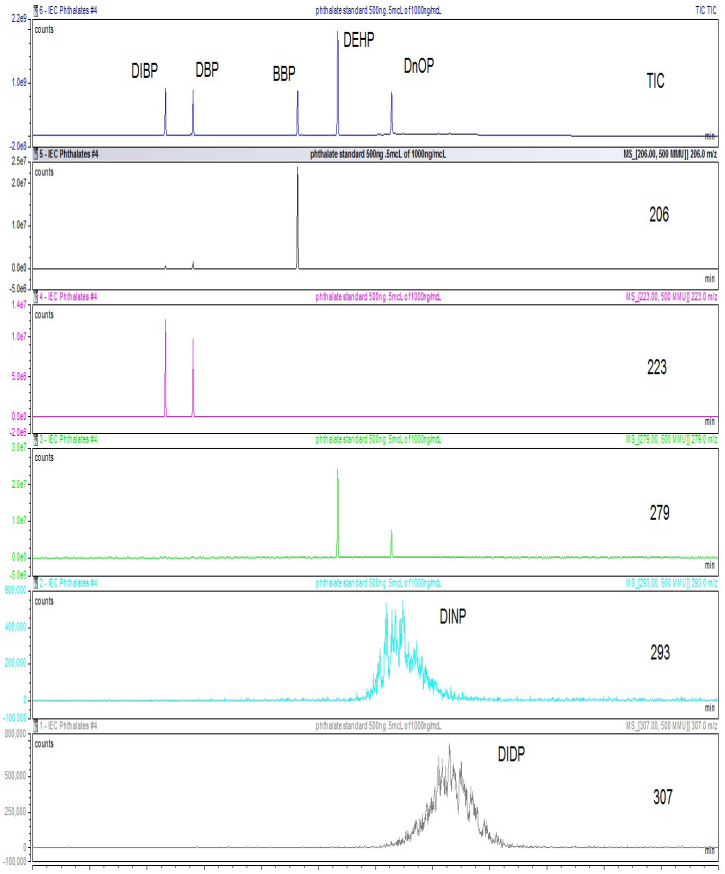


Figure 1: 500ng Phthalate Standard TIC and Extracted Ion Chromatograms.

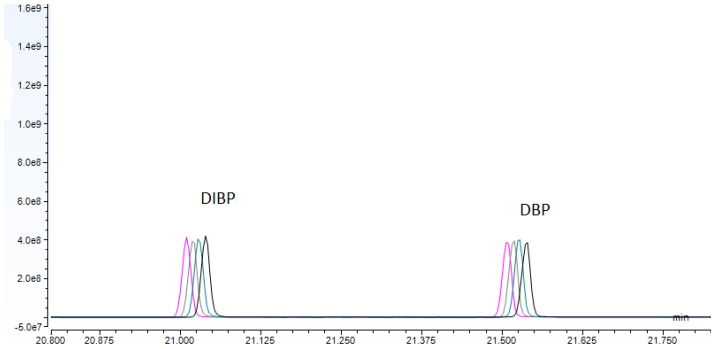


Figure 2: Extracted Ion 223 Overlap of 4 Replicates of DIBP and DBP to show similarity of peak areas.

| 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.

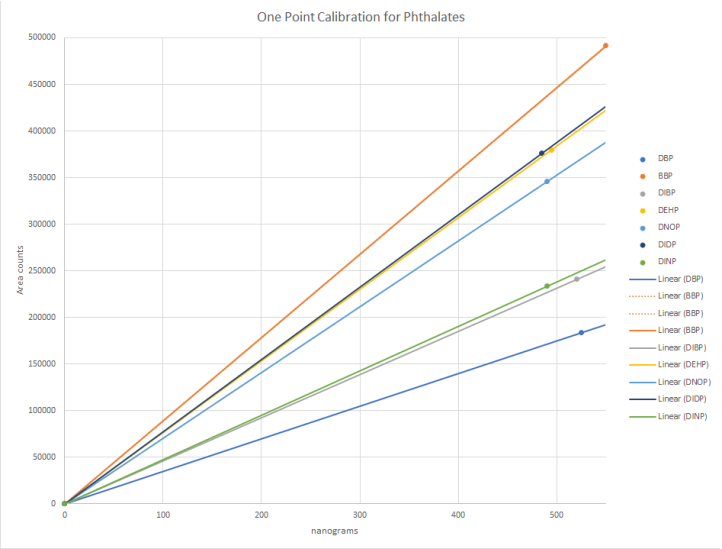

Figure 3: One Point Calibration for Phthalates.

| Phthalate | Quant Ion | MDL |
|---|---|---|
| DIBP | 223 | 21.7 mg/kg |
| DBP | 223 | 21.0 mg/kg |
| BBP | 206 | 21.0 mg/kg |
| DEHP | 279 | 14.7 mg/kg |
| DNOP | 279 | 9.4 mg/kg |
| DINP | 293 | 17.9 mg/kg |
| DIDP | 307 | 13.6 mg/kg |

Table 2: Calculated MDLs of 7 regulated 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 plots are shown in Figure 3.

In a Method Detection Limit Study, 0.5 microliters of 100ng/mcL phthalate standard solution was added to about 0.5mg PVC in DISC tubes. Seven replicates produced calculated MDLs ranging from 9.4 to 21.7 mg/kg, 78-91% lower than the 100mg/kg requirement (Table1).

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