Phthalate Analysis in Accordance with an IEC Standard Method

Application Note
Electronics Industry

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Abstract

This application note demonstrates compliance of IEC 62321-8 standard method for phthalates using a CDS 6000 Series Pyroprobe Autosampler.

Introduction

Materials being investigated by thermal sampling techniques are frequently polymeric in nature, but may contain a variety of volatile and semi-volatile contaminants and additives. When using gas chromatography, these non-polymeric constituents may produce some of the most significant peaks in the chromatogram. Figure 1, for example, shows the pyrolysis of a piece of clear food wrap containing a plasticizer. The peak for the plasticizer is considerably larger than the peaks for the aromatics coming from the polymer itself. In analyzing polymers using pyrolysis-GC/MS, the additives can also degrade to produce smaller molecules. Peaks for these compounds may interfere with the pyrolysis results, so it has become common to perform two or more analyses on the sample at increasing temperatures, to remove the additives before pyrolysis. The packaging material in Figure 2 was heated first to 300°C to remove the plasticizer, then analyzed for polymer content at 700°C.

This step-wise approach is also applicable to analyses in which the interest lies in the additives or contaminants more than in the polymer matrix. Certain items are known to cause health hazards and impact the environment in electrotechnical products, like some phthalates. Because of this, these items are now a cause of concern in government legislations. In March of 2017, the International Electrotechnical Commission (IEC) published a new standard for hazardous substances in electronic equipment for determining phthalates in polymeric materials. IEC 62321-8 defines approaches to determine certain phthalates, di-isobutyl phthalate (DIBP), di-n-butyl phthalate (DBP), benzylbutyl isononyl phthalate (DINP) and di-iso-decyl phthalate in electronics, by GC-MS, and Py-TD-GC-MS.

The specified Py/TD method involves two separate heating ramps during the course of one GC run. This requires the TD accessory to heat the sample starting at a setpoint of 200°C, increasing to 20°C per minute to 300°C, then continue heating to a setpoint of 340°C at 5°C per minute to 340°C.

The above method was performed using a CDS 6000 Series Pyroprobe Autosampler. A standard solution of phthalates prepared in hexane was added to quartz wool in a quartz tube. The Pyroprobe was used to desorb the standard to a GC/MS in accordance with the IEC test standard. The autosampler was programmed using a sequence of two methods for one GC run. The first method waits for the GC ready signal, starts the GC and heats while heating the sample chamber from 200°C to 300°C at 20°C per minute. The second method is programmed to ignore the GC ready signal, and heats the chamber from 300°C to 340°C at 5°C per minute during the same GC run. Methods and sequences are shown in Figure 4. TIC and extracted ion chromatograms in Figure 4 closely matches the chromatograms in Annex C.2 of the International Standard.

Experimental Parameters

The sample was pyrolyzed in a quartz 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 2 minutes 20°C/min to 300°C hold 5 minutes
Ion Source:	230°C
Mass Range:	35-550

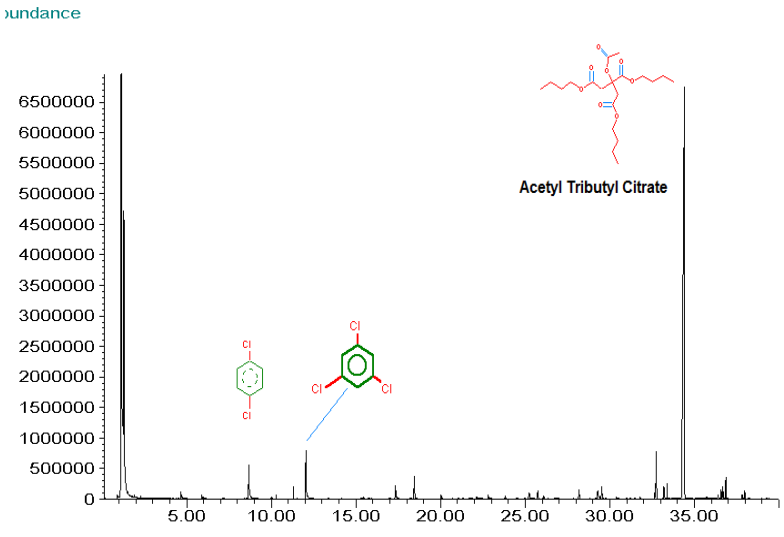


Figure 1. Food wrap containing citrate plasticizer, 750°C.

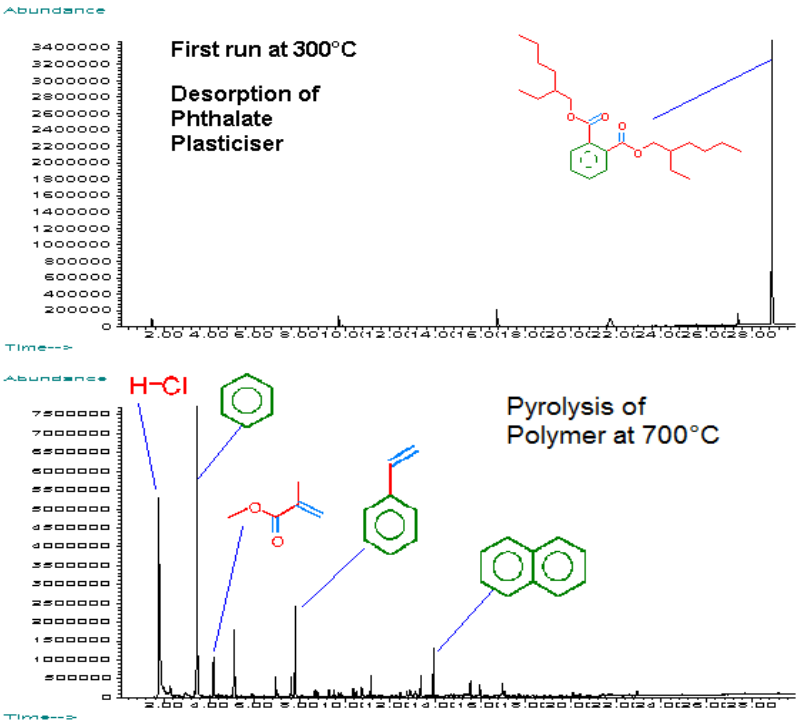
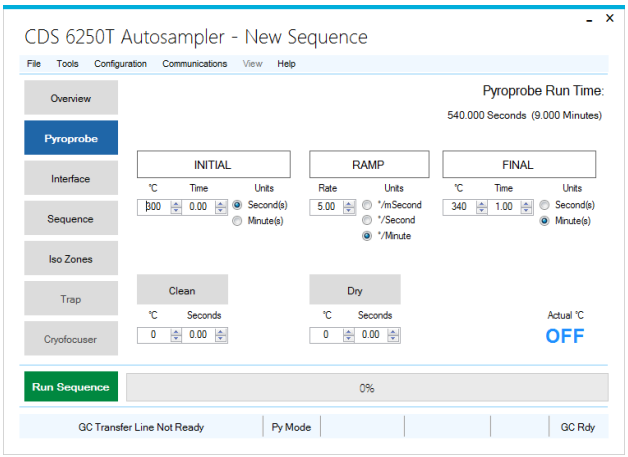
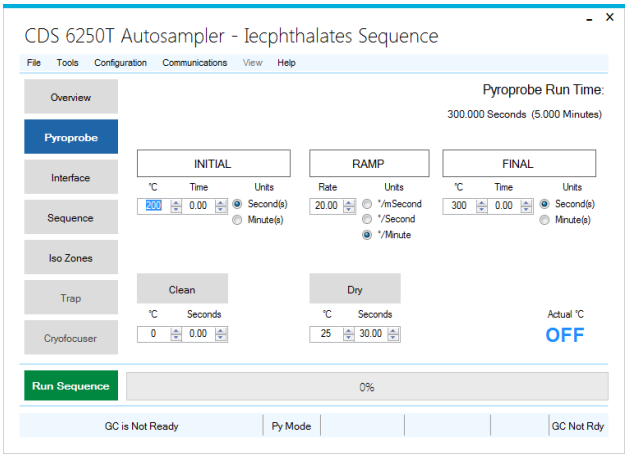
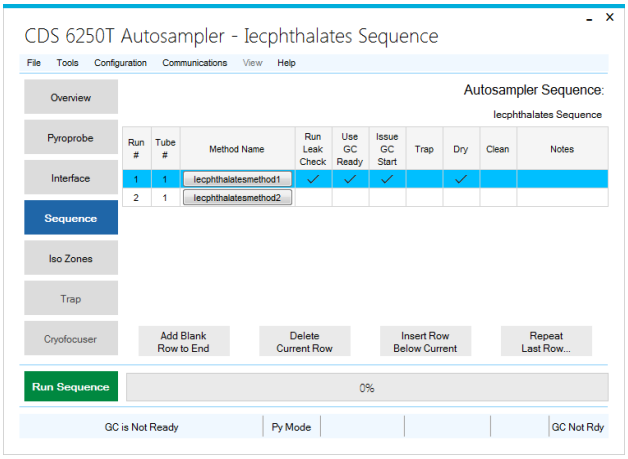


Figure 2. Packaging polymer analyzed at 300°C, then 700°C.







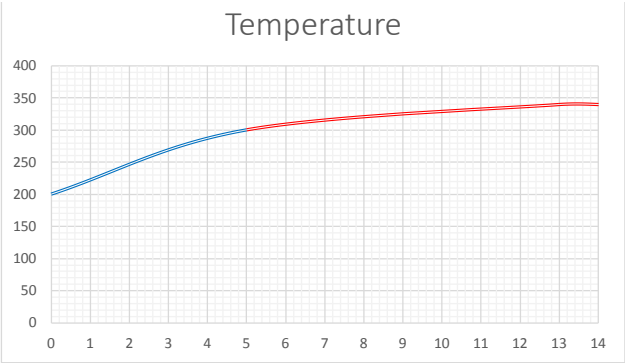


Figure 3: Pyroprobe setup: From top: Method 1 parameters, Method 2 parameters, Autosampler Sequence Table and example temperature profile.

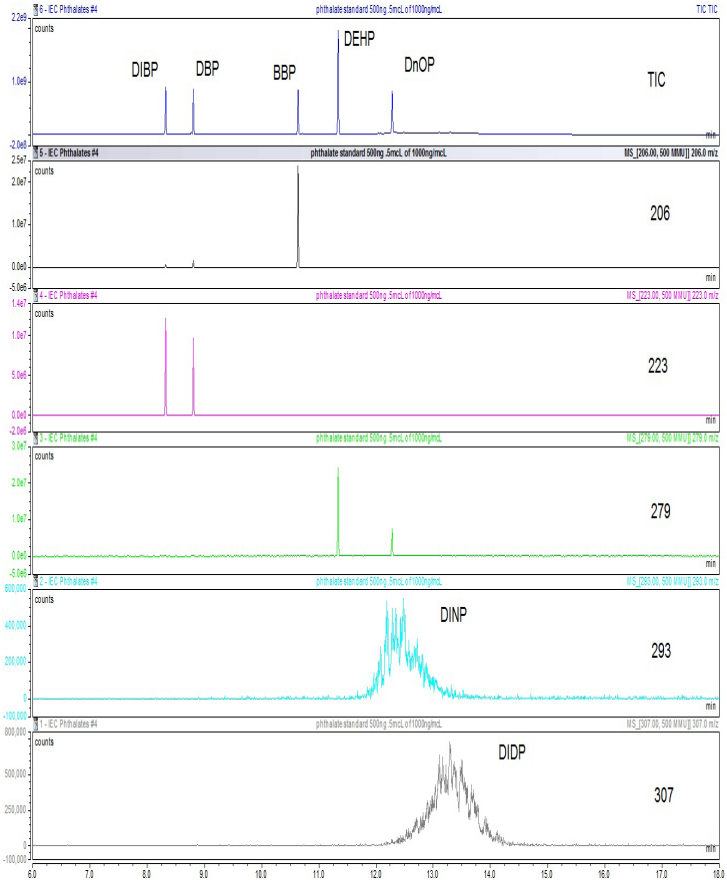


Figure 4: 500ng Phthalate Standard TIC and Extracted Ion Chromatograms.