Polymer and Phthalate Analysis with FTIR Spectroscopy

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Fourier transform infrared (FTIR) spectroscopy is a versatile tool used to characterize various type of samples by differentiating origins, quantifying additives, detecting contaminants, monitoring degradation byproducts, fighting adulteration and so on.

FTIR spectroscopy has become a widely used technique for quick, economic and multiplex characteristics, and yet many people don’t fully understand how it works and how to make it more efficient.

Polymeric material characterization is an important fields of FTIR spectroscopy. Some particular interests are on the rapid and economic quantitation of the phthalate plasticizer to screen the polymers.
Polymer

- A polymer is a large molecule, or macromolecule, composed of many repeated subunits.

- Both natural and synthetic polymers are created via polymerization of many small molecules, known as monomers. Single or multiple monomers may be used to yield different polymer material.

- Polymers are formulated with a large number of additives that enable polymers to perform important functions over a wide range of conditions, such as **plasticizers**, stabilizers (UV, heat, chemical), fillers, colorants, actives, stiffeners (fibers, cross linkers)
Principles of IR Spectroscopy

➢ Most organic molecules absorb light in the infrared region of the electromagnetic spectrum

➢ Absorption at certain frequencies or wavenumbers corresponds specifically to the bonds present

➢ Absorbance of the infrared light versus the frequency is the spectrum

➢ IR spectroscopy is for both qualification and quantification analysis
Why use FTIR in Chemical Analysis

FTIR spectroscopy is one of the most widely used laboratory tools for chemical analysis

- **Multiplex**: capable of detecting and quantifying multiple components and parameters simultaneously • e.g. moisture, alcohol, carbohydrate, protein...

- **Easy to use**: No cumbersome sample preparation

- **Inexpensive**: No reagents or wet chemistry required to reduce per measurement cost

- **Fast**: replaces tedious and time-consuming physical and chemical methods

- **High-throughput**: specified automation analyzer are available to handle massive amount of samples
FTIR Spectrometer

Key components of an FTIR spectrometer.

- **IR Source**
- **Reference Laser**
- **Moving Mirror**
- **Fixed Mirror**
- **Detector**
- **Sample Cell**
- **IR Detector**

**Formula:**

\[ \nu_{\text{harm}} = \frac{1}{2} \left( \nu_0 \right)^n \]

**Images:**
- Stretching
- Bending
- Twisting
- Rocking

**Graphs:**
- Constructive Interference
- Destructive Interference
Types of FTIR Sampling Techniques

Type of Analysis MODE:

Transmission/Absorbance
(liquids, gases, powders, films)

* Reflectance
(liquids, thins films, bulk materials)

*ATR
(all, except gases)

SAMPLE

CRystal (IRE)

d_p

*Diffuse Reflectance
(or DRIFT - mainly powders)

(liquids, thins films, bulk materials)
IR Transmission

➢ Transmission techniques offer many advantages and should be used whenever possible, unless reliable sample preparation becomes too difficult, too time consuming or impractical.

➢ Transmission spectra are of the highest quality and are often used as references for the purpose of quantitative analysis. The basic measurements adhere to the Beer-Lambert law.

\[
A = a \cdot b \cdot c
\]

A = absorbance
a = absorptivity
b = pathlength
c = component concentration

* The longer the pathlength, the stronger the Absorbance
IR Transmission Devices

➢ Gas cell and liquid cell with different pathlength and operating process for transmission measurements.
Attenuated Total Reflectance (ATR) is today’s most widely used FTIR sampling tool. The main feature of ATR sampling is the small depth of penetration (i.e. pathlength) of the IR beam into the sample (i.e. usually less than 1um), making it a virtually “surface” analysis.

ATR generally allows qualitative or quantitative analysis of samples with little or no sample preparation, which greatly speeds sample analysis. The “open” sample interface allows easy sample cleaning. For liquid samples, simple rinsing and wiping would recover the crystal surface for new measurements.

However, the advantage of small penetration depth could be a problem if larger pathlength is critical (e.g. high sensitivity quantitation). One solution is to increase the reflecting (bouncing) numbers.

While.............
# ATR – Penetration Depth

- Diamond-ATR vs. Ge-ATR
  - Refractive Index
  - Hardness
  - Cost
  - Different applications

### Table: Penetration Depth for Different Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>$n_1$</th>
<th>$d_p$, for $n_2 = 1.5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMTIR</td>
<td>2.5</td>
<td>1.70</td>
</tr>
<tr>
<td>Diamond/ZnSe</td>
<td>2.4</td>
<td>2.01</td>
</tr>
<tr>
<td>Germanium</td>
<td>4.0</td>
<td>0.66</td>
</tr>
</tbody>
</table>
Specular Reflectance

Specular reflectance sampling in FTIR is a very important technique for measurement of thin layer substance on reflective substrates and analysis of bulk materials and measurement of monomolecular layers on a substrate material. The greatest advantage is that it provides a means of sample analysis with NO sample destruction---which is especially critical for fragile samples.

Types of specular reflectance experiments

- Reflection-Absorption of relatively thin films on reflective substrates measured at near normal angle of incidence
- Specular Reflectance measurements of relatively thick substances measured at near normal angle of incidence
- Grazing Angle Reflection-Absorption of ultra-thin films or monolayers deposited on surfaces measured at high angle of incidence
Diffuse Reflectance

➢ Diffuse reflectance is an excellent sampling tool for powdered or crystalline materials.

➢ Diffuse reflectance is an excellent sampling technique as it eliminates the time-consuming process of pressing pellets for transmission measurements.

➢ Diffuse reflectance can also be used to study the effects of temperature and catalysis by configuring the accessory with a heating or cooling environmental chamber.

➢ one of the greatest additional benefits of diffuse reflectance sampling is that it is ideally amenable to automation.
Agilent FTIR Portfolio

Cary 630 Entry-level FTIR

5500 Series

Cary 610/620 FTIR Microscopes

4500 Series Portable FTIR

4200 FlexScan FTIR

4100 ExoScan

4300 TopScan
Choosing Proper FTIR Technology

➢ Sample Properties
   States (Liquid, Solid, Powder, Gels, Grease or …. )
   Safety (Poisonous, Contamination)
   Homogeneity, Viscosity, Adhesion, Volatility, Moisture Level
   ……….

➢ Operation Consideration
   Sample Treatments (Grinding, Extraction, Filtration …..)
   Availability (Volume)
   Cleaning
   In-lab or in-Field
   Numbers of samples (High-throughput, automation?)

➢ Analytical Expectation
   Quantify or Qualify
   Sensitivity (LOD, LOQ)
   Reproducibility
   Validation
ATR: An Universal Approach

➢ ATR is usually the 1st option as an “universal” technique for all type of samples except for gas.

➢ Minimum or no sample preparation are needed. Require firm physical contact (pressure for solids)

➢ Easy cleaning to recover the crystal

➢ A surface technique for both qualification and quantitation, but sensitivity is restricted due to penetration depth (i.e. 1-2um for single-bounce Diamond-ATR)

➢ Less interfered by moisture.

➢ Used both in-lab and in-field
Combining FTIR with other Polymer Testing

➢ FTIR can be combined with many other polymer analytical techniques to generate molecular-level information during mechanical, thermal and decomposing process.

- DMA-FTIR
- TMA-FTIR
- DSC-FTIR
- TGA-FTIR
- .......

![Image of FTIR equipment and diagram showing various testing procedures.](image-url)
Phthalates or phthalate esters, are mainly used as plasticizers for plastics such as PVC to increase their flexibility, transparency, durability and longevity.

The plasticizer acts as a lubricant which enhances chain mobility --- the polymer molecules are more easily able to move and slip past each other in response to an applied load.
Phthalate Impact

➢ Lower molecular weight ortho-phthalate plasticizers have serious health effects and are restricted or banned in many countries for use in children’s products.

• Prohibited Phthalates
  - DEHP – di (2-ethylhexyl) phthalate
  - DBP – dibutyl phthalate
  - BBP – benzyl butyl phthalate

• Interim - Prohibited Phthalates
  - DINP – diisononyl phthalate
  - DIDP – diisodecyl phthalate
  - DNOP – di-n-octyl phthalate

➢ One of the most common plastics liable to plasticizer issue is polyvinyl chloride (PVC).
Detection of Phthalates

➢ Direct FT/IR – limited sensitivity, selectivity, but rapid and economical

➢ ASTM D2124 extraction then FT/IR – time consuming, not portable

➢ Pyrolysis GC/MS – possible breakdown of long chain phthalates such as DINP and DIDP, difficult quantification, not portable

➢ DART-MS – Direct Analysis Real Time Mass Spectrometry – difficult quantification, not portable
FTIR as Pre-screening for Phthalates

➢ There are substantial benefits gained by pre-screening plastic materials for phthalates with Agilent portable FTIR spectrometers. Examples include:

– Rapid measurement of total phthalate concentration to a 0.1% limit of quantitation (LOQ) with little or no sample preparation.

– Non-destructive identification of higher level phthalate-containing parts.

– Quick identification of plastic parts that are unlikely to contain plasticizers, such as polyethylene, polypropylene, polystyrene, nylon, polyester, cardboard/paper, or silicone rubber.

– Quick screening and detection of cross contamination between a non-phthalate and a phthalate factory part.
Agilent 4500 3B-ATR System

- 4500 is a portable FTIR system
- Optimized for ATR measurements
- Methods established and validated

- 3B ATR has 3X pathlength than single bounce ATR
- Durable diamond ATR Crystal
- No sample preparation needed
- Easy cleaning
The package has had substantial traction with the following industries:
- Toy and child products
- Electronics and electronic components
- Shoes and other apparel
- Food packaging
- Medical product

The following types of customers have shown substantial interest
- Polymer producers
- Manufacturers of polymer based products
- Importers of these products
- Distributors of polymer products
- Compliance and law firms
- Governmental agencies
- Contract labs
Features of the 4500 Polymer Analyzer

➢ The 4500 portable spectrometer is designed to deliver lab-quality results in the field.

➢ The three reflection diamond ATR provides greater pathlength for more accurate quantitative measurements and lower detection limits. Diamond ensures that sample does not abrade or otherwise compromise the sensor surface.

➢ Agilent Mobile MicroLab software is highly intuitive and requires little training. Push button methods enhance ease-of-use and speedy results.

➢ Results are presented in custom report style and offer color-coded alerts to warn you if a sample is out of specification.
## Polymers Included in the Package

### Polymers included in the 4500 Phthalate Analysis Method

<table>
<thead>
<tr>
<th>No.</th>
<th>Polymer material</th>
<th>No.</th>
<th>Polymer material</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Polyvinyl chloride (PVC)</td>
<td>13</td>
<td>Polyethylene terephthalate (PET)</td>
</tr>
<tr>
<td></td>
<td>PVC with replacement plasticizers (DINCH, DOA, ATBC, DOTM, DINA, phosphate esters, monoglycerides)</td>
<td>14</td>
<td>Polypropylene</td>
</tr>
<tr>
<td></td>
<td>Rigid PVC</td>
<td>15</td>
<td>Polyacrylates</td>
</tr>
<tr>
<td>2</td>
<td>Polyurethanes (TPU)</td>
<td>16</td>
<td>Polyimide</td>
</tr>
<tr>
<td>3</td>
<td>Thermoplastic urethane (TPU)</td>
<td>17</td>
<td>Acetal (POM)</td>
</tr>
<tr>
<td>4</td>
<td>Poly styrene-butadiene-styrene (SBS) rubber</td>
<td>18</td>
<td>Polycarbonate</td>
</tr>
<tr>
<td>5</td>
<td>Styrene Ethylene Butylene Styrene (SEBS) rubber</td>
<td>19</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>6</td>
<td>Natural rubber</td>
<td>20</td>
<td>Acrylonitrile butadiene styrene (ABS)</td>
</tr>
<tr>
<td>7</td>
<td>Butyl rubber</td>
<td>21</td>
<td>Polyvinyl acetate (PVA)</td>
</tr>
<tr>
<td>8</td>
<td>Ethylene propylene diene monomer (EPDM)</td>
<td>22</td>
<td>Nylon cellulose</td>
</tr>
<tr>
<td>9</td>
<td>Silicone (PDMS)</td>
<td>23</td>
<td>Cellulose</td>
</tr>
<tr>
<td>10</td>
<td>Nitrile</td>
<td>24</td>
<td>Leather</td>
</tr>
<tr>
<td>11</td>
<td>Polyethylene</td>
<td>25</td>
<td>Cotton</td>
</tr>
<tr>
<td>12</td>
<td>Nitrocellulose</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The package affords highly accurate measurement of total phthalates in PVC to 0.1% LOQ (even in PVC that contains fillers or carbon particles).

The speed, accuracy, portability, and ease of analysis of the 4500 Polymer Package enable the system to rapidly screen large numbers of samples for phthalates so as to reduce the demand on GC/MS equipment.

The package provides positive identification of polymers, which helps you properly prepare samples for GC/MS analysis, protecting sensitive columns and injectors from contamination by unknown materials.
IR Spectral Quantitation

- PVC samples plasticized with DINCH and phthalates, 0.00% (orange), 0.60% (pink), 1.76% (green), and 3.29% total phthalates (blue).

- Phthalate component can be associated with certain absorption bands in the spectra. The shapes can be used to reveal the type and the intensity can be used to quantify concentration.
Phthalate Quantitation

- Prediction Curve of phthalate. The correlation coefficient, LOD and LOQ are shown.

- Phthalate component can be associated with certain absorption bands in the spectra. The shapes can be used to reveal the type and the intensity can be used to quantify concentration.

Table 1. The correlation coefficient’s ($R^2$), limit of detection (LOD) and limit of quantitation (LOQ) are shown for each full range calibration of phthalates (DEHP) in plasticized PVC.

<table>
<thead>
<tr>
<th>Calibration</th>
<th>$R^2$</th>
<th>LOD</th>
<th>LOQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEHP in DINCH</td>
<td>0.9992</td>
<td>0.020</td>
<td>0.06</td>
</tr>
<tr>
<td>DEHP in DOTP</td>
<td>0.9972</td>
<td>0.050</td>
<td>0.15</td>
</tr>
<tr>
<td>DEHP in ATBC</td>
<td>0.9998</td>
<td>0.024</td>
<td>0.07</td>
</tr>
<tr>
<td>DEHP in DOA</td>
<td>0.9992</td>
<td>0.02*</td>
<td>0.06*</td>
</tr>
<tr>
<td>DEHP in TOTM</td>
<td>0.9995</td>
<td>0.05*</td>
<td>0.015*</td>
</tr>
</tbody>
</table>

App Note : 5991-3649EN
Heterogenous Samples

➢ An important difference between GC-MS and FTIR-ATR is that ATR is a surface technique. In the above example, a billfold tested for phthalates, 4.462% DEHP by GC-MS and 8.99% by FTIR.

➢ The key is that the billfold it has two layers, PET and PVC. Only the PVC layer contains phthalate.
Youtube Link

https://www.youtube.com/watch?v=jKSTygsUSfE
Summary

➢ FTIR is powerful tool to identify polymers and quantify phthalate plasticizer components

➢ ATR is convenient, economical and accurate approach to achieve phthalate type and concentration information

➢ FTIR results act as the **screening tool** to reduce the sample testing requirement for GC-MS analysis, the golden standard but more expensive.

➢ Agilent 4500 3B-ATR portable spectrometer equipped with polymer package with analysis of phthalate is an excellent solution to conduct polymer identification and phthalate quantitation task in the field.
QUESTIONS?