Gas Chromatography-Infrared Spectroscopy

Frank S. Weston
Applications Scientist

GC-IR: Separate & Identify
“Divide & Conquer”

Like GC-MS, this is a separation technique followed by an identification, in this case using infrared spectroscopy.

Before the advent of FTIR instruments (which are fast), GC-IR measurements were made by depositing the packed column effluent on to a salt window and running in the IR instrument.

FTIR instruments allow the real-time analysis of the GC effluent. Not limited to gas effluent – with different interfaces one can perform LC-IR, GPC-IR, TGA-IR, etc.

Both Qualitative and Quantitative
The electromagnetic spectrum can be divided into specific regions, including: Gamma rays, X-Rays, Ultraviolet, Visible, Infrared, Microwave, and Radio.

Frequency in cm$^{-1}$

Gamma - 4000
X-Rays - 400
UV
Visible
NIR
MID-IR
FIR
Microwave
Radio
Electric Power
The IR spectrum of a sample is a plot of the amount of IR energy (y-axis) that is absorbed at frequencies (x-axis) in IR, the region of the electromagnetic spectrum.
How is an IR Spectrum Collected?

Interferogram (raw data) of Background & Sample Collected

Ratio of Background And Sample Single Beam Spectra

Fourier Transform
Application Benefits

IR
Aromatic Substitution
Cis/Trans Isomers
Ring Junctions
Ring Isomers
Aliphatic Chains
Functional Group Selective

GC

MS
Mass Selective
Molecular Weight
Homolog Information
Elemental Composition
Substituent Information
Isotope Information

HIGH CONFIDENCE IN IDENTIFICATION
Mass Spectra: Isomers of Ethyltoluene

Benzene, 1-ethyl-2-methyl-
MASS SPECTRUM

ortho

Benzene, 1-ethyl-3-methyl-
MASS SPECTRUM

meta

Benzene, 1-ethyl-4-methyl-
MASS SPECTRUM

para
Infrared Spectra: Isomers of Ethyltoluene
Application Areas

- Chemical Applications (ex/ Organics in Water)
- Petro Chemical (Aromatics in Gasoline, Oxygenates in Gasoline)
- Environmental (Hazardous Waste ID, Soil Contamination)
- Drugs & Forensics (Amphetamine Isomers, Bath Salts)
- Pharmaceutical (Drug Development, QA/QC, Brand v Generic)
- Foods, Flavor, & Fragrances (cis/trans, reverse engineering, QA/QC)
- *Agilent (and legacy HP) 6890/7890 GC or Agilent 600-series (and legacy Varian) FTIR.*
Components of a GC-IR system

Gas Chromatograph
  - optional autoinjector

Interface Optics

Fourier Transform Infrared Spectrometer

Data Station/Instrument Control
  - Series connection to FID, PDHID, MS, etc.

*FT-IR is not a destructive technique*
Complete System

- Agilent Cary 600 Series
- Light Pipe Interface
- 7890A GC
- Temperature Controller
- G4513A Autoinjector

Data Station runs Resolutions Pro (FT-IR software); ChemStation or EZChrom; Third Party Spectral Libraries
Outlet to GC

Inlet from Column

IR Beam Out

IR Beam In

Heated Oven

IR Transparent Windows
Specifications

- Mounted on right side of FTIR via collimated beam from spectrometer (highest amount of IR energy commercially available by 4 to 10 times greater depending on the Agilent Cary FTIR coupled)

- Integrated Liquid Nitrogen Cooled MCT detector

- Light Pipe 120mm long & 1.0 mm i.d.

- IR Windows KBr or ZnSe

- Temperature Maximum 300°C

- GC Column compatibility – 0.25 to 0.52 mm i.d.

- Purged Interface
Data Obtained – Chromatogram (X and Y Axes)

Chromatogram based on changes in total infrared intensity
Data – IR Absorbance (Z Plane)

Chromatogram based on intensity of the IR band between 1760 and 1730 cm\(^{-1}\) (esters, aldehydes and ketones)

Identified as diethyl phthalate
An Unknown Organic Mixture
An Unknown Organic Mixture – Peak #1

ACETONE
An Unknown Organic Mixture – Peak #5

ETHYL PHOSPHATE
Sample – Fuel Additive
## Fuel Additive – ID of Components

### Extraction 2

<table>
<thead>
<tr>
<th>#</th>
<th>Name</th>
<th>Spectrum</th>
<th>ID by KIA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Extraction 1</td>
<td></td>
<td>2-propanol &amp; acetone</td>
</tr>
<tr>
<td>2</td>
<td>Extraction 2</td>
<td></td>
<td>toluene</td>
</tr>
<tr>
<td>3</td>
<td>Extraction 3</td>
<td></td>
<td>octane or 1-bromo docosane</td>
</tr>
<tr>
<td>4</td>
<td>Extraction 4</td>
<td></td>
<td>2-methyl heptane</td>
</tr>
<tr>
<td>5</td>
<td>Extraction 5</td>
<td></td>
<td>n-hexane</td>
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<tr>
<td>6</td>
<td>Extraction 6</td>
<td></td>
<td>octane or 1-bromo docosane</td>
</tr>
<tr>
<td>7</td>
<td>Extraction 7</td>
<td></td>
<td>heptane or 1-bromo-heptadecane</td>
</tr>
<tr>
<td>8</td>
<td>Extraction 8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Extraction 9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Extraction 10</td>
<td></td>
<td>pentyli ester nitric acid</td>
</tr>
</tbody>
</table>
Calibration curves can be generated using both linear (or classical) least squares or chemometric techniques, such as partial least squares, for quantitating the amount of analyte present.
Quantitative Analysis

A standard of C14, C15, C16 (FID GC Standard) at 33 ppm was injected onto the Cary GC-IR. Various dilutions were performed using from 33 ppm to about 3 ppm. This example illustrates the C14 spectral peaks at 2930 wavenumbers from the extraction peak eluding at 4.7 minutes on the time axis.
Quantitative Analysis

Resolutions Pro integrated quantitative analysis capability allows for one to generate a calibration curve in minutes. This curve can then be applied using a single icon click to quantitate the amount of analyte present.
Sample Injection Phase

- As previously demonstrated, the most common injection is of the **liquid** phase using an autoinjector or manual syringe.
- **Gases** can also be injected directly for GC-IR analysis. This is accomplished using an valve injection system consisting of Valco® switching valves and a sample loop of known volume.

Specialty Gas Analysis – A Practical Guidebook (Jeremiah Hogan)
Sample Injection Phase

Solid phase samples can prove to be a difficult analysis because of the sample preparation involved (extraction)

Why not inject the solid directly onto the analytical column via the Agilent GC injection system?
CDS Pyroprobe with Agilent GC-IR System making the ultimate solid phase forensic tool.

- Single Step Pyrolyzer
- Needle Connection through Injection Port
- Temperature Programmable to 1400C
Solid Sample Injection: Pyrolysis GC-IR

The solid sample (or slurry type, viscous samples that do not inject using a standard syringe) is loaded into a quartz tube which is then inserted into the pyroprobe.

The filament of the probe is heated up to 1400°C at injection.
Solid Sample Injection: Pyrolysis GC-IR

The injection is made as shown on this Agilent 7890 GC.

Because the FTIR is nondestructive the sample can be analyzed by multiple detectors – first through the lightpipe then to an FID, TCD, PDHID, MS, etc.

Using a fully functional FTIR, versus a mere infrared detector, allows one to use other techniques, like ATR, on the same instrument for a multi-technique verification and analysis.
Pyrolysis GC-IR Example: Kraton

A Piece of Kraton polymer injected on Pyrolysis GC-IR
Features

Trigger in and trigger out

Multiple types of chemistries can be monitored in the same run (Functional Group Analysis)

Search libraries are available to search for identifications and lots of peaks can be search at once.

Classical Least Squares & Chemometric calibrations for Quantitative Analysis
Advantages of Using an Agilent Research Grade FTIR

• Throughput, Throughput, Throughput (increased energy, increased sensitivity, increased signal-to-noise, increased stability → faster analyses at lower detection limits!

• True power of FTIR and versatility → ATR, PAS, Microscopy, & Focal Plane Array Imaging (extremely useful tools for forensic analyses all from one instrument)

• Field Upgradable

• Enhanced Quantitative Analysis through Chemometrics

• Powerful Library Searching and Mixture Analysis through Know-It-All® features
ATR Sampling Technique

Ease of use

• Simple and rapid cleaning
• High chemical and physical tolerance
• Improved reproducibility
Photoacoustic – Areas of Application

<table>
<thead>
<tr>
<th>Raw Materials</th>
<th>In Process Control</th>
</tr>
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<tbody>
<tr>
<td>Final Product</td>
<td>QA/QC</td>
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<tr>
<td>Decomposition</td>
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</tr>
<tr>
<td>Pyrolysis</td>
<td></td>
</tr>
<tr>
<td>Distillation Fraction</td>
<td></td>
</tr>
<tr>
<td>Forensics</td>
<td></td>
</tr>
</tbody>
</table>

| UV-Visible             | Near-Infrared      |
| Mid-Infrared           | Far-Infrared       |

- Carbons
- Coals
- Hydrocarbons
- Hydrocarbon Fuels
- Corrosion
- Clays & Clay Minerals
- Wood & Paper
- Polymers
- Gases
- Food Products
- Biology & Biochemistry
- Medical Applications
- Carbonyl Compounds
- Textiles
- Catalysts
Agilent’s Patented PAS Harmonic Spectra in 1 Scan

- First Harmonic - 100 Hz
- Third Harmonic - 300 Hz
- Fifth Harmonic - 500 Hz
- Seventh Harmonic - 700 Hz
- Ninth Harmonic - 900 Hz

- PE (1465 cm\(^{-1}\))
- PET (1725 cm\(^{-1}\))
- PP (1370 cm\(^{-1}\))
- PC (1780 cm\(^{-1}\))
Microscopy and Imaging Examples
Identification of Fibres

- **2245 cm$^{-1}$**
- **2939.4 cm$^{-1}$**
- **2875.2 cm$^{-1}$**

Acrylic

Polyester

Wool

[Graphs showing the absorbance of different wavelengths for Acrylic, Polyester, and Wool]
Detection of illicit drugs on Fingerprint

ATR FTIR imaging in forensic science, Agilent
Can see the polyethylene but there are other features present in this spectrum. To ease the spectral analysis, one can use the Mixture Analysis algorithm.
Mixture Analysis Result

- DA #10281; HUMISEAL 2A53 PART B

Mixture Analysis confirms PE & PA
Title: GC-IR with Resolutions Pro: Quantitative Analysis & Kinetics

Description: This course will focus on the tandem of technique combing the chromatographic separation of a chemical species with an Agilent 7890 (or legacy 6890/5890) and using the FT-IR (Agilent 600-series or legacy instrument) as a detector. Advantages of GC-IR over other techniques will be discussed. The course is a combination of lecture and hands-on laboratories that will cover basic FT-IR & GC theory, sample preparation, instrument maintenance, quantitative analysis (both linear least squares and partial least squares), kinetics applications, and troubleshooting.

Prerequisites: None;

Days: 2

Site: Little Falls (Wilmington, DE)
Interested in a Product Demonstration?

Samples can be submitted to one of our Application Labs – coordinated through your local Account Manager or Product Specialist.

Completed Sample Submission Form & MSDS

WebEx – very easy to demo without an onsite visit

Or we welcome you and your colleagues to visit one of our Centers of Excellence (COE) demonstration laboratories.
Summary

- The Agilent Cary GC-IR is a powerful qualitative and quantitative solution for “Divide & Conquer” Analytical Chemistry in many areas of science & research including:
  - Biochemistry & Biology
  - Pharmaceutics & Medicine
  - Forensics
  - Material Science & Polymer Chemistry
  - Foods
  - Petrochemical & Energy
  - Electronic Specialty Gases & Wafer Fabs
Summary

• The Agilent Cary GC-IR can be equipped to analyze solid, liquid, and gas phase samples

• Driven by a research grade performing spectrometer, the Cary GC-IR can be used as a multifunctional analytical tool for handling a variety of samples all on one instrument when configured:
  – Separate & Identify by GC-IR
  – Surface Analysis by ATR
  – Depth Profiling by Photoacoustic Spectroscopy (PAS)
  – Small Sample Identification (less than 10 microns) by IR-Microscopy
  – Chemical Homogeneity and Functional Group Distribution to better than 2 microns by Focal Plane Array ATR Imaging