Wrocław University of Science and Technology

Faculty of Chemistry

Sustainable Bioproducts and Bioprocess Engineering

Course: Biocomponents characterization

Class: IR and FT-IR analyses, sample preparation, calibration

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FT-IR (Fourier Transform Infrared Spectroscopy)

FT-IR technique is used to obtain an infrared spectrum of absorption of a solid, liquid and gas sample. The main goal of any absorption spectroscopy (FT-IR) is to measure how well a sample absorbs light at each wavelength. This technique shines a beam containing many frequencies (polychromatic beam, Fig. 1) of light at once and measures how much of that beam is absorbed by the sample.

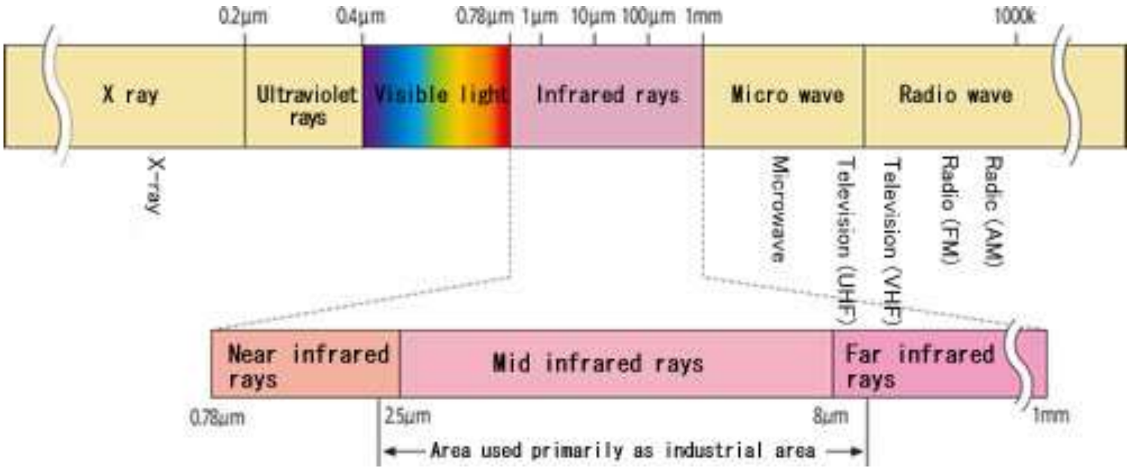


Fig. 1 The IR range on a light spectrum [1].

Next, the beam is modified to contain a different combination of frequencies, giving a second data point. This process is repeated many times. Afterward, a computer takes all this data and works backward to infer what the absorption is at each wavelength.

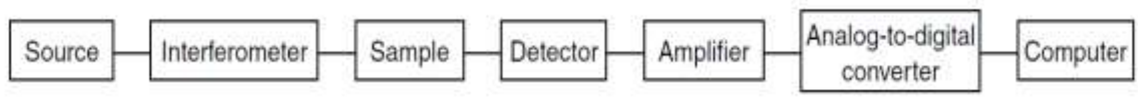


Fig. 2 Basic components of the FT-IR spectrometer.

As is presented in Fig. 2, the beam is generated by starting with a light source (globar, SiC, element heated to about 1200 K)-one containing the full spectrum of wavelengths to be measured. The light shines into a Michelson interferometer, which has two mirrors (Fig. 3), one of which is moved by a motor. As this mirror moves, each wavelength of light in the beam is periodically blocked, transmitted, blocked, transmitted, by the interferometer, due to wave interference. Different wavelengths are modulated at different rates, so that at each moment the beam coming out of the interferometer has a different spectrum.

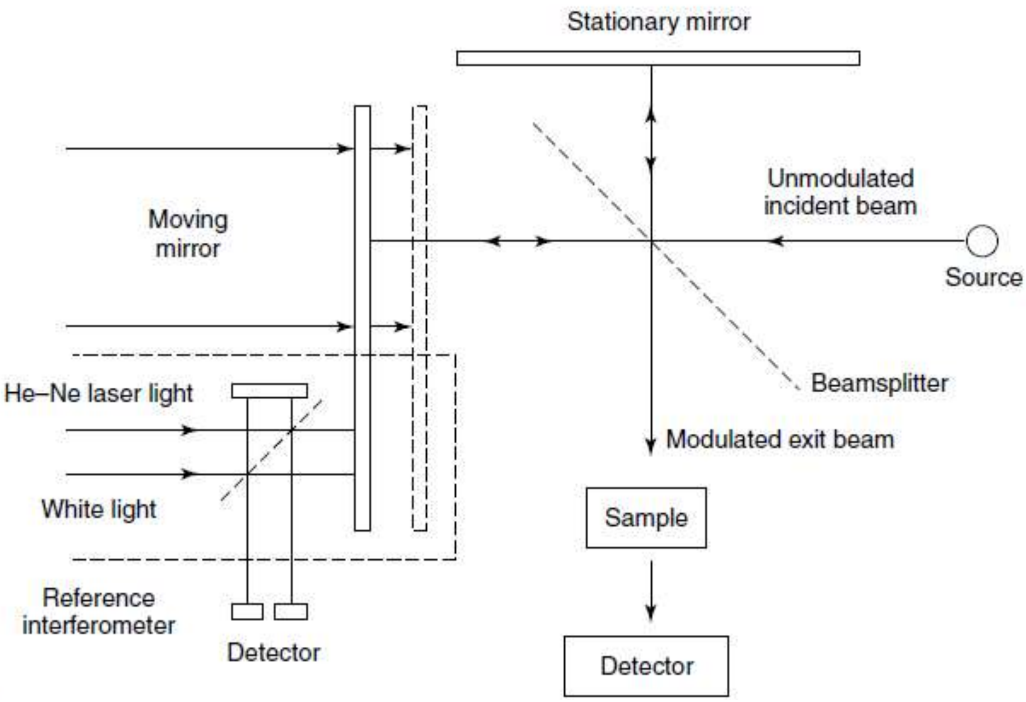


Fig. 3 Schematic of a Michelson interferometer [2].

As mentioned, computer processing is required to turn the raw data called ‘interferogram’ which is presented as the IR spectrum of the sample by means of a Fourier transform algorithm [2]. Infrared spectrophotometers record the relative amount of energy as a function of the wavelength/frequency of the infrared radiation when it passes through a sample. FT-IR spectrometers can be used in a variety of industries including environmental, pharmaceutical, and petrochemical.

We usually can obtain 2 types of IR spectrum:

-IR spectrum (where was measured the transmittance -T)
-ATR spectrum (where was measured the absorbance-Abs)

$$\mathbf{T = I / Io}$$

Because the intensity of the transmitted light (I) is never greater than the intensity of the incident light (Io), transmittance (T) is always less than 1.
In practice, one usually multiplies T by 100 to obtain the ***percent transmittance (%T)***, which ranges from 0 to 100 %.

$$\mathbf{\%T = T * 100}$$

Relation between T and Abs describes the equation

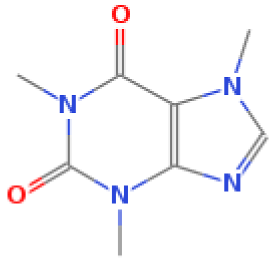
$$\mathbf{Abs = -\log_{10} T} \quad \text{or} \quad \mathbf{Abs = \log_{10} (1/T)}$$

Beer-Lambert law

$$\mathbf{Abs = -\log_{10} T} = \varepsilon lc$$

Look and compare!

The caffeine IR spectrum



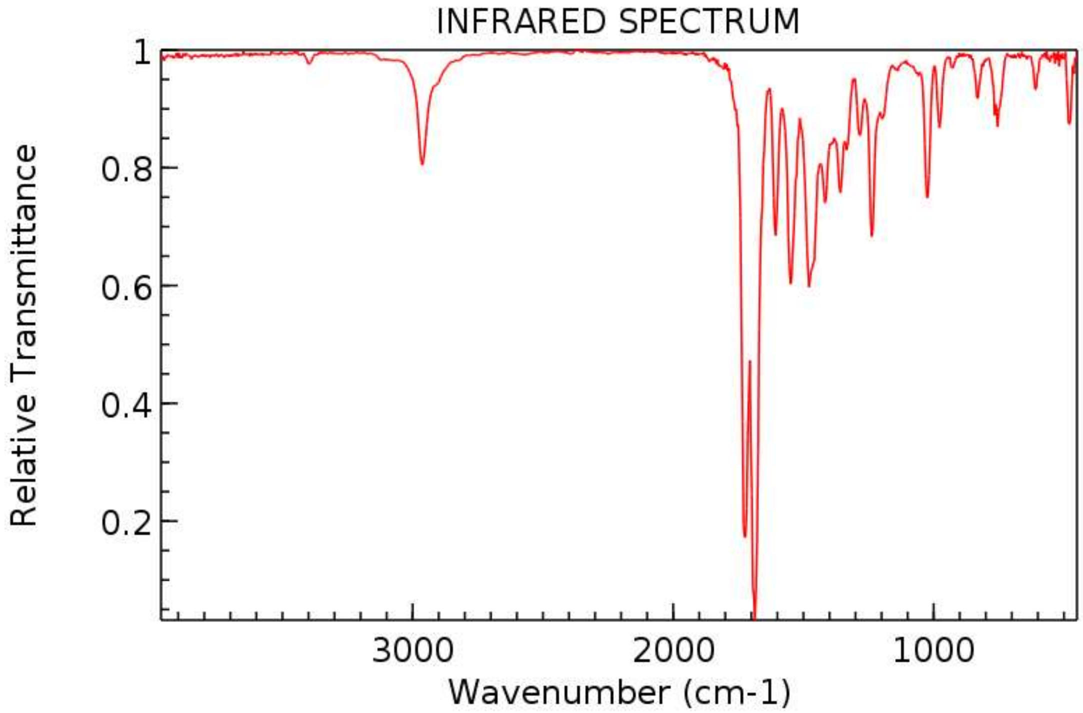


Fig. 4 FT-IR spectrum of caffeine (Transmittance is measured) [3].

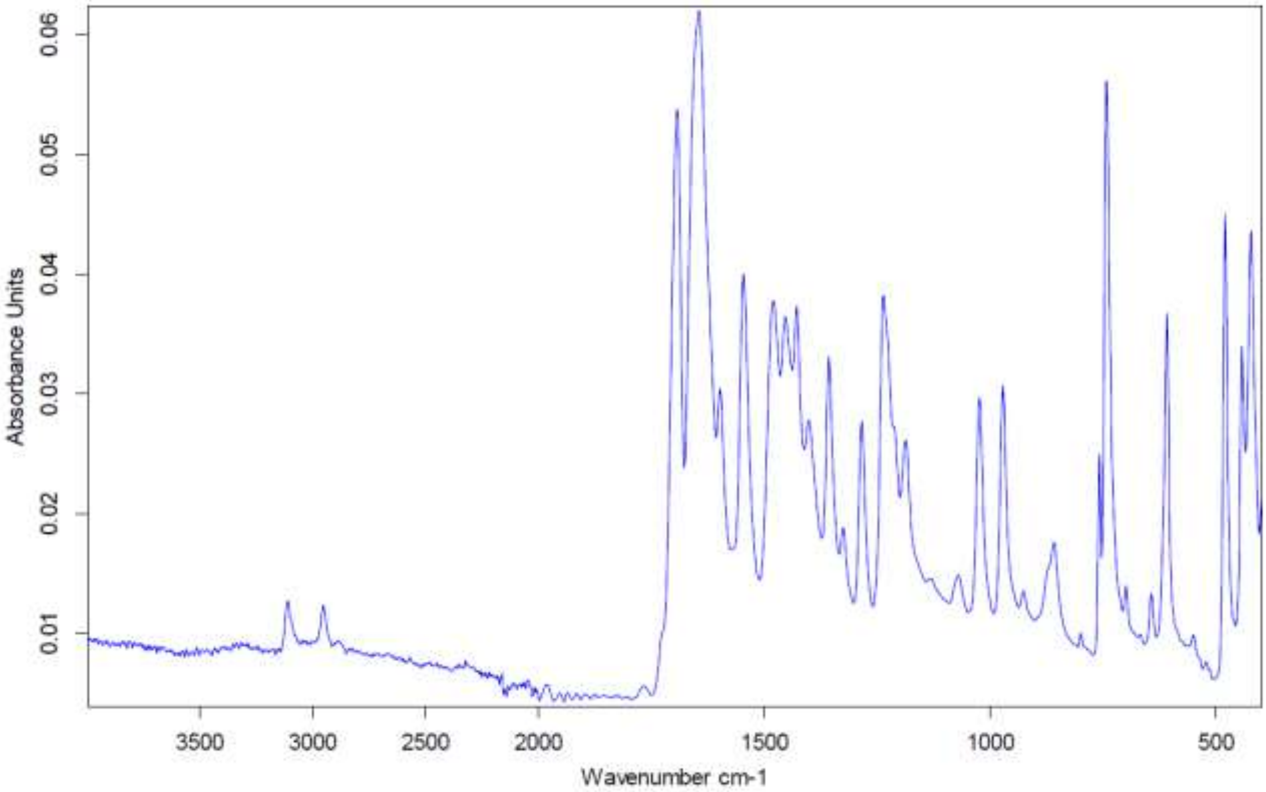


Fig. 5 FT-ATR spectrum of caffeine (Absorbance is recorded).

FT-IR rules

For the molecule to show infrared absorptions it must possess a specific feature, it means an electric dipole moment of the molecule must change during the vibration. This is the main selection rule for IR spectroscopy which is an extension of the theory about the moment of oscillatory transition ($\Delta v = \pm 1$, for harmonic oscillator model).

Figure 6 shows an ‘infrared-active heteronuclear diatomic molecule’. The dipole moment of such a molecule changes as the bond expands and contacts in comparison to ‘infrared-inactive homonuclear diatomic molecule’ where dipole moment remains zero no matter how long the bond is [4].

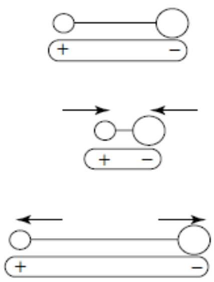
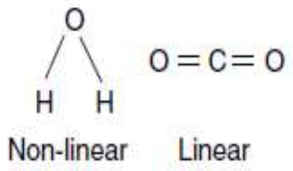


Fig. 6 Change in dipole moment of a heteronuclear diatomic molecule [2].

In case of diatomic molecule, only stretching vibration is possible. This accounts for one degree of vibrational freedom. Polyatomic molecules containing many (N) atoms will have 3N degrees of freedom. Look below for the molecules containing 3 atoms, two groups of triatomic molecules (linear or non-linear). The examples of linear and non-linear are CO_2 and H_2O respectively.



Type of degrees of freedom	Linear	Non-linear
Translational	3	3
Rotational	2	3
Vibrational	$3N-5$	$3N-6$
Total	$3N$	$3N$

Fig. 8 CO_2 and H_2O structures and degrees of freedom for polyatomic molecules (table).

Both molecules have three degrees of translational freedom, additional H_2O has 3 degrees of rational freedom, but CO_2 has only two. Subtracting these from 3N, there are 3N-5 degrees of freedom for CO_2 (or any linear molecule) and 3N-6 for any non-linear molecule (H_2O). N-is amount of atoms, in both examples is three, after calculated we can obtain four vibrational modes for CO_2 and three for water [2]. That means we observed 4 peaks (bands) in CO_2 and 3 peaks in water IR spectrum respectively.

The measuring techniques

The most popular techniques are:

1) KBr pellets (for solid state) or KBr cells (for liquid) technique

Fig. 9 IR accessory for preparing KBr pellets (left) and liquid sample (right) [5-6].

Preparing samples for a transmission measurement is a rather complex task. Liquid samples must be poured into a liquid cell with suitable path length (Fig. 9). Solids typically have to be diluted with the IR-inactive KBr and pressed to the well-known “KBr-pellet”.

Both types of measurement technique have their drawbacks:

- Liquid cells must be free of air bubbles and are not easy to clean.
- KBr is hygroscopic and therefore not easy to handle and store.
- A good KBr pellet is rather hard to make. The operation is time consuming and requires a special tool kit including a hydraulic press (Fig. 9)
- The homogenization of the sample and KBr is hard to achieve for some substances such as rubbers or elastomers. The making and measurement of suitable KBr pellets are time-consuming and only experienced operators are able to obtain good results. In many cases, the pellet is turbid and the baseline of the resulting spectrum is drifted due to the influence of the stray light [5].

2) ATR (Attenuated Total Reflection) technique

To overcome the disadvantages of KBr pellets and liquid cells, IR-measurements are mainly performed in ATR mode as this technique is simpler to use than the conventional transmission mode. All types of samples (e.g. solids, liquids, powders, pastes, pellets, slurries, fibbers etc.) are placed undiluted on the ATR crystal (Fig. 10). The measurement is typically performed within a few seconds. The infrared beam enters the ATR crystal at an angle of typically 45° (relative to the crystal surface) and is totally reflected at the crystal to sample interface. In the spectral regions where the sample absorbs energy, the evanescent wave is attenuated. After one or several internal reflections, the IR beam exits the ATR crystal and is directed to the IR-detector.

Fig. 10 ATR diamond plate [5].

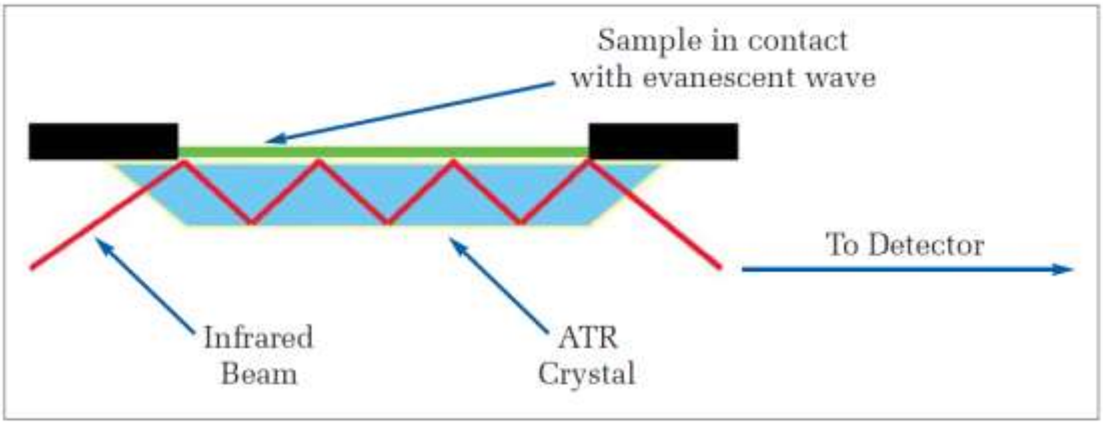


Fig. 11 The beam path in ATR tools [7].

Spectral range and use of the method

MIR, Mid-IR (4000-400 cm^{-1}) spectroscopy is used to identify structures because functional groups give rise to characteristic bands both in terms of intensity and position (frequency), especially in Finger print region.

In contrast to the Mid-IR region where spectral features arise mainly from intramolecular vibrational modes, Far-IR, FIR (400-10 cm^{-1}) spectral features can be due to a number of different types of transitions. In addition to the low frequency vibrational modes (these may involve heavy metal atoms if present, metal-ligand connections in complexes), other underlying mechanisms include torsional and ring-puckering modes, charge-transfer species. In this region can be observed complexation reaction [2].

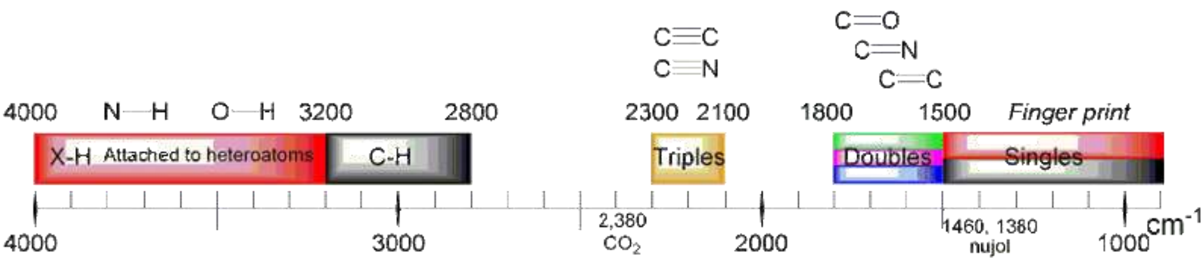


Fig. 12 MIR spectral range and Finger print region with characteristic bands.

References:

[1] http://thepredatorseye.com/

[2] B. Stuard, “Infrared spectroscopy: fundamentals and applications”, J. Wiley & Sons, 2004

[3] https://webbook.nist.gov/cgi/cbook.cgi?ID=C58082&Type=THZ-IR-SPEC&Index=0

[4] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part A., sixth ed., J. Wiley & Sons, Hoboken, 2009

[5] https://www.azom.com/article.aspx?ArticleID=5958

[6] https://www.spectral-systems.com/products/kbr-horizon-fill-liquid-cells/

[7] http://las.perkinelmer.com/content/TechnicalInfo/TCH_FTIRATR.pdf

What should you know?

1. Formation of the IR spectrum any molecules.
2. The main selection rules in IR spectroscopy.
3. Construction and mode of action of the FT-IR spectrometer.
4. Characteristic types of vibrations in the infrared spectra.

Topic of the class:

“Measurement and analysis of vibrational spectra of fluids used in the fuel industry”-part 1

Experimental part

During the lab students take the fluid samples (radiator fluid, brake fluid, engine oil, etc.) in order to recorded IR and ATR spectra. After the measurement, identify the sample using the spectral database. Next the comparison both spectra must be made. **Student will prepare the report after the next class (Raman spectroscopy, sample preparation and calibration).**