



Type of the Paper (Review Article)

## Tools used for dental materials characterization

Reem A. Hany<sup>1,\*</sup>

<sup>1</sup> Dental Biomaterials Department, Faculty of Dentistry, Cairo University, Egypt

\* Corresponding author e-mail: [Reem.Ahmed@dentistry.cu.edu.eg](mailto:Reem.Ahmed@dentistry.cu.edu.eg)

**Abstract:** Spectroscopy is a term that describes the interaction of matter with electromagnetic radiation. Several forms of interaction exist: absorption, emission, diffraction and scattering of radiation. Therefore, spectroscopy is used to characterize/detect matter (atoms, molecules, and nuclei) based on the produced spectra and following their interaction with radiation. The electromagnetic spectrum is a range of frequencies of the electromagnetic radiation and the corresponding wavelengths and photon energies. Also, X-ray photoelectron spectroscopy (XPS) belongs to the family of photoemission spectroscopies in which electron population spectra are obtained by irradiating a material with a beam of X-rays. Chemical states are inferred from the measurement of the kinetic energy and the number of the ejected electrons. In addition, X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for quantitative determination of crystal phase content and composition and can provide information on unit cell dimensions.

**Keywords:** Characterization, Infrared spectroscopy, X-ray photoelectron spectroscopy, X-ray powder diffraction.

The infrared (IR) radiations are invisible to the human eye. IR radiations appear at a longer wavelength compared to the visible region. The frequency of IR radiations is therefore lower compared to that of the visible light, this in turn means that energy associated with the IR radiations is inferior to that of the visible light and greater than that of microwaves<sup>1,2</sup>.

**Citation:** Reem A. Hany. Tools used for dental materials characterization. *Biomat. J.*, 1 (3),9 – 16 (2022)

<https://doi.org/10.5281/znodo.5829408>

Received: 10 February 2022

Accepted: 27 February 2022

Published: 20 March 2022



**Copyright:** © 2022 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

### Infrared spectroscopy (IR)

Vibrational spectroscopy is the common label given to describe measurements involving both infrared (IR) and Raman spectroscopy (RS). As an approach, vibrational spectroscopy is used to measure molecular vibrations resulting from absorption of light/photons. Upon irradiation with infrared light, certain bonds respond by vibrating faster. This response can be detected and translated into a visual representation called a spectrum. Therefore, IR spectroscopy “is the measurement of the interaction of infrared radiation with matter by absorption, emission, or reflection”. It is used to study and identify chemical substances or functional groups in solid, liquid, or gaseous forms. It can be used to characterize new materials or identify and verify known and unknown samples<sup>3,4</sup>.

The method or technique of infrared spectroscopy is conducted with an instrument called an infrared spectrometer (or spectrophotometer) which produces an infrared spectrum. Two main modes of vibrations are commonly known; stretching (where the distance between the two atoms and hence the bond length are affected) and bending (where the slant between the two bonds is altered)<sup>5,6</sup>. Further classification of the types of motions would include two stretching modes: symmetric (where the two atoms simultaneously move toward and away from the central atom) and anti-symmetric (where one of the atoms move toward the central atom, while the second moves away). There are also four bending modes: scissoring ( $\delta$ ), rocking ( $\rho$ ), wagging ( $\omega$ ) and twisting ( $\tau$ )<sup>6</sup>.

Another concern is the bond strength, where a single bond is weaker compared to a double bond, which in turn is weaker than a triple bond. Therefore, a single bond needs less energy and appears at a lower wavenumber ( $\bar{\nu}$ ). Mass of the atoms is another consideration <sup>7</sup>. IR spectroscopy is often used to identify structures because functional groups give rise to where heavier atoms would vibrate more slowly compared to the light atoms characteristic bands both in terms of intensity and position (frequency). The positions of these bands are summarized in correlation tables as shown below, fig. (1) <sup>7</sup>.

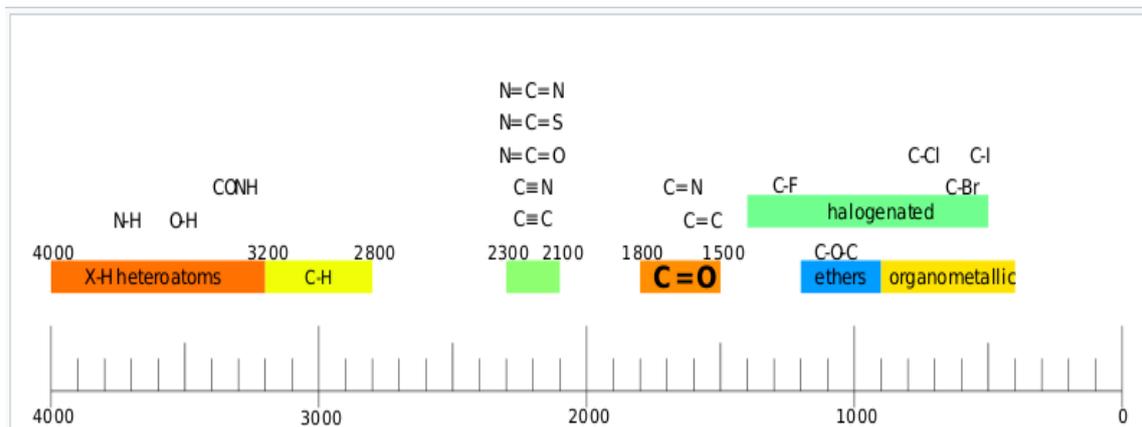
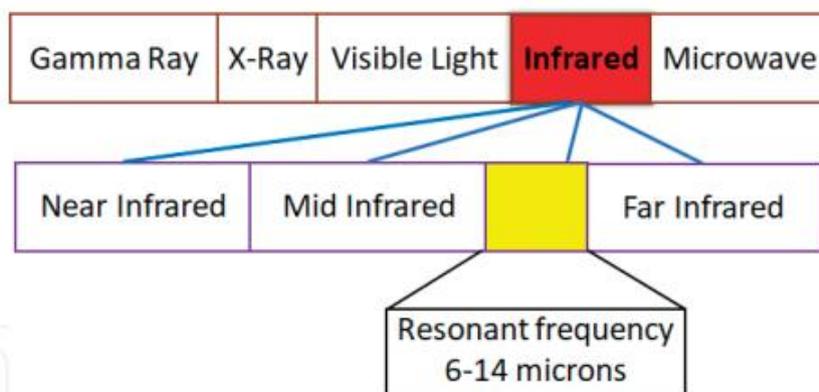


Fig.(1): List of main IR spectroscopy bands.

### Zones of the IR region <sup>8</sup>

Three main zones can be identified in the IR region, fig(2):

- i. Near IR (high energy): 0.8 to 2.5 $\mu$ m (12000 $\text{cm}^{-1}$  – 4000 $\text{cm}^{-1}$ )
  - Analyzing mixtures of aromatic amines.
  - Determination of protein, fat, moisture, oil content.
- ii. Middle IR: 2.5 to 15 $\mu$ m (4000 $\text{cm}^{-1}$  – 667 $\text{cm}^{-1}$ ) (also known as vibration- rotation region)
  - This region is divided into:
    1. Group frequency region: 4000 $\text{cm}^{-1}$  – 1500 $\text{cm}^{-1}$ .
    2. Fingerprint region: 1500 $\text{cm}^{-1}$  – 667 $\text{cm}^{-1}$ .
- iii. Far IR (low energy): 15 to 1000 $\mu$ m (667 $\text{cm}^{-1}$  – 10 $\text{cm}^{-1}$ )
  - Study of inorganic or organometallic compounds.
  - Sensitive to changes in overall structure of the molecule.



Fig(2): Section from the electromagnetic spectrum showing regions of IR.

### IR regions<sup>9</sup>

A spectrograph is often interpreted as having two regions

- functional group region:

In the functional region there is one to a few troughs per functional group.

- fingerprint region:

In the fingerprint region there are many troughs which form an intricate pattern which can be used like a fingerprint to determine the compound.

### IR theory

Infrared spectroscopy exploits the fact that molecules absorb frequencies that are characteristic of their structure. These absorptions occur at resonant frequencies, i.e. the frequency of the absorbed radiation matches the vibrational frequency. The energies are affected by the shape of the molecular surface energies, the masses of the atoms, and the associate vibrations.

### IR sample preparation

The infrared spectrum of a sample is recorded by passing a beam of infrared light through the sample. When the frequency of the IR is the same as the vibrational frequency of a bond or collection of bonds, absorption occurs. Examination of the transmitted light reveals how much energy was absorbed at each frequency (or wavelength). This measurement can be achieved by scanning the wavelength range using a monochromator.

This technique is commonly used for analyzing samples with covalent bonds. Simple spectra are obtained from samples with few IR active bonds and high levels of purity. More complex molecular structures lead to more absorption bands and more complex spectra.

#### a. Gas samples

A simple glass tube with length of 5 to 10 cm equipped with infrared-transparent windows at both ends of the tube can be used for concentrations down to several hundred ppm. Sample gas concentrations well below ppm can be measured with a White's cell in which the infrared light is guided with mirrors to travel through the gas.

#### b. Liquid samples

Liquid samples can be sandwiched between two plates of a salt (commonly sodium chloride, or common salt, while potassium bromide or calcium fluoride are also used). The plates are transparent to the infrared light and do not introduce any lines onto the spectra.

#### c. Solid samples

Solid samples can be prepared in a variety of ways. One common method is to crush the sample with an oily mulling agent (usually mineral oil). A thin film of the mull is applied onto salt plates and measured. The second method is to grind a quantity of the sample with a specially purified salt (usually potassium bromide). This powder mixture is then pressed in a mechanical press to form a translucent pellet through which the beam of the spectrometer can pass. A third technique is the "cast film" technique, which is used mainly for polymeric materials. The sample is first dissolved in a suitable, non-hygroscopic solvent. A drop of this solution is deposited on surface of NaCl cell. The solution is then evaporated to dryness and the film formed on the cell is analysed directly. Care is important to ensure that the film is not too thick otherwise light cannot pass through.

It is typical to record spectrum of both the sample and a "reference". This step controls for a number of variables (to eliminate the instrument influence). The simplest reference measurement is to simply remove the sample (replacing it by air).

### IR Advantages<sup>10</sup>

1. All kinds of material can be analyzed.
2. IR can provide a molecular fingerprint that can be used when comparing samples. If two pure samples display the same IR spectrum it can be argued that they are the same compound.
3. IR is most useful in providing information about the presence or absence of specific functional groups.
4. Fast, easy and less expensive.
5. Very small amount of sample is required.

**IR Disadvantages**<sup>10</sup>

1. IR spectra cannot be obtained for Mono atomic substances e.g.: helium, argon.
2. IR spectra cannot be obtained for homonuclear diatomic molecules like O<sub>2</sub>, N<sub>2</sub>.
3. Cannot determine the molecular weight of the compound.
4. Does not give information about the relative position of different functional groups in the molecule.
5. Works best for pure substances but not for complex mixtures.

**Fourier Transfer IR (FTIR) [alternative to Normal IR]**<sup>11</sup>**Principal**

- 1) Light from source is split by central mirror into 2 beams of equal intensity.
- 2) Beams go to two other mirrors, reflected by central mirror, recombine and pass through sample to detector.
- 3) Two side mirrors, one fixed and other movable:
  - By moving the second mirror, light in the two paths travel different distances before recombined.
  - Constructive & destructive interference occurs.

**Advantages of FT IR Spectrophotometer**

FT-IR spectrometers have numerous performance advantages over traditional dispersive infrared instrumentation. Virtually all infrared spectrometer manufacturers are now using FT designs instead of dispersive. The benefits of upgrading to an FT-IR from an existing dispersive infrared instrument are spectral quality, data collection speed, reproducibility of data, and ease of maintenance and use.

**X-ray photoelectron spectroscopy (XPS)**

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique based on the photoelectric effect that can identify the elements that exist within a material (elemental composition) or are covering its surface, as well as their chemical state, and the overall electronic structure and density of the electronic states in the material. XPS spectra can also be used to obtain information on the chemical composition of the surface of the sample and the depth distribution of chemical species<sup>12</sup>.

XPS is a powerful measurement technique because it not only shows what elements are present, but also what other elements they are bonded to. It is often applied to study chemical processes in the materials in their as-received state or after cleavage, scraping, exposure to heat, reactive gasses or solutions, ultraviolet light, or during ion implantation<sup>13</sup>.

XPS is routinely used to analyze inorganic compounds, metal alloys, semiconductors, polymers, elements, catalysts, glasses, ceramics, teeth, bones, medical implants, bio-materials, coatings, viscous oils, glues, ion-modified materials and many others. Somewhat less routinely XPS is used to analyze the hydrated forms of materials such as hydrogels and biological samples<sup>13</sup>.

**Measurement and basic principle**<sup>14</sup>

A typical XPS spectrum is a plot of the number of electrons detected at a specific binding energy. Each element produces a set of characteristic XPS peaks. These peaks correspond to the electron configuration of the electrons within the atoms, e.g., 1s, 2s, 2p, 3s, etc. The number of detected electrons in each peak is directly related to the amount of element within the XPS sampling volume.

**The basic principle of XPS is the photoelectric effect, the phenomenon for which Einstein received his Nobel prize. Three possibilities are evident**

1. The photon may traverse through the atom without significantly interacting with either the orbital electrons or the nucleus.

2. The photon may be scattered by the atomic orbital electron resulting in a partial loss of photon energy. This process is called Compton scattering.
3. The photon may interact with the atomic orbital electron such that there is total and complete transfer of the photon's energy to the electron.

This is the basic process in XPS. Given that the photon energy is greater than the binding energy of the electron in the atom, the electron is then ejected from the atom with a kinetic energy approximately equal to the difference between the photon energy and the binding energy. Therefore, the basic equation for XPS is:

$$E_b = h\nu - E_k$$

Where ( $E_b$ ) is the electron binding energy, ( $E_k$ ) is the electron kinetic energy, measured by the instrument, and ( $h\nu$ ) is the photon energy ( $h$  is Planck's constant and  $\nu$  is the X-ray frequency). Measuring the kinetic energy allows one to calculate the binding energy, and by knowing the binding energy, we can identify the atom.

### **Instrumentation** <sup>12</sup>

The main components of an XPS system are the source of X-rays, an ultra-high vacuum (UHV) chamber with metal magnetic shielding, an electron collection lens, an electron energy analyzer, an electron detector system, a sample introduction chamber, sample mounts and a sample stage with the ability to heat or cool the sample.

### **Peak identification** <sup>12</sup>

The number of peaks produced by a single element varies from 1 to more than 20. Tables of binding energies that identify the shell and spin-orbit of each peak produced by a given element are included with modern XPS instruments, and can be found in various handbooks and websites. Because these experimentally determined energies are characteristic of specific elements, they can be directly used to identify experimentally measured peaks of a material with unknown elemental composition.

### **Practical guides for using XPS** <sup>12,13</sup>

#### **Variability**

There are many sources of variability, all of which should be assessed. Usually, the most notable changes in intensity are due to variations in x-ray power, particularly, during warm-up after the instrument has just been switched on. Find out how long this takes and let the instrument equilibrate before taking measurements.

#### **Advantages of XPS**

1. Non-destructive.
2. Surface and elemental sensitivity.
3. Characterize all elements (except H & He).

#### **Disadvantages of XPS**

1. Expensive.
2. Samples must be compatible with high vacuum environment. So, if your sample will outgas when placed under vacuum, XPS is not the right test for your needs.
3. Challenges with reproducibility. Similar to other surface analysis techniques, XPS is associated with a 10% relative error in repeated analyses.

## X-ray Power Diffraction

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for quantitative determination of crystal phase content and composition and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing <sup>16</sup>.

### Fundamental Principles of (XRD) <sup>16,17</sup>

XRD methods are based on the ability of crystals to diffract X-rays in a characteristic manner allowing a precise study of the structure of crystalline phases. Max von Laue, in 1912, discovered that crystalline substances act as three-dimensional diffraction lattices for X-ray wavelengths. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample.

The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray). According to Bragg's Law:

$$n\lambda = 2d \sin \theta$$

Where,  $n$  is the order of diffraction,  
 $\lambda$  the wavelength of the incident beam in nm,  
 $d$  is the lattice spacing in nm,  
 $\theta$  the angle of the diffracted beam in degree.

This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to  $d$ -spacings allows identification of the mineral because each mineral has a set of unique  $d$ -spacings. Typically, this is achieved by comparison of  $d$ -spacings with standard reference patterns.

### Instrumentation (How Does It Work?) <sup>16</sup>

X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. In general, XRD methods only use the characteristic radiation with the highest intensity, the  $K\alpha$  radiation, and remove most of the remaining radiation by using appropriate filters or monochromator.

### Special methods (Energy-dispersive XRD) <sup>17,18</sup>

The method presented previously is for the commonly used angle-dispersive measurements, meaning that a monochromatic beam is used while the angular position of the diffraction peaks is measured. An alternative method called energy-dispersive consists of the use of a white beam (polychromatic beam over the complete available wavelength range) and the detection of diffraction peaks at a fixed ( $2\theta$ ) angle by using energy detectors.

## Applications<sup>17,18</sup>

X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds). Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology (qualitative and quantitative phase analysis). It is used to study the crystalline content, identify the crystalline phases, spacing between lattice planes, and epitaxial growth of crystallites. Since every material has its unique diffraction patterns so materials and compounds can be identified by using a database of diffraction patterns.

## Applications include

- Characterization of crystalline materials.
- Identification of fine-grained minerals that is difficult to determine optically.
- Determination of unit cell dimensions.
- Measurement of sample purity.

## Advantages<sup>19</sup>

1. Powerful and rapid (< 20 min) technique for identification of an unknown mineral.
2. It provides a definite mineral determination.
3. Minimal sample preparation is required.
4. Non-destructive.
5. XRD units are widely available.
6. Data interpretation is relatively straight forward, highly sensitive and reliable.

## Disadvantages<sup>19</sup>

1. Must have access to a standard reference file of inorganic compounds (d-spacings).
2. Requires tenths of a gram of material which must be ground into a powder.
3. For unit cell determinations, indexing of patterns for non-isometric crystal systems is complicated.
4. Peak overlap may occur in high angle 'reflections'.
5. The use of harmful radiations.

## References

1. Hollas JM. *Modern Spectroscopy*. 4th ed. Chichester: John Wiley & Sons, Ltd.; 2004.
2. Harris DC. *Quantitative Chemical Analysis*. New York, NY: W.H. Freeman and Co; 2007.
3. Theophanides T, editor. *Introduction to Infrared Spectroscopy – Materials Science, Engineering and Technology*. Rijeka, Croatia: InTech; 2012
4. Hesse M, Meier HBZ. *Spectroscopic Methods in Organic Chemistry*. 2nd ed. Stuttgart: Georg Thieme Verlag; 2008.
5. Monnier GF. A review of infrared spectroscopy in microarchaeology: Methods, applications, and recent trends. *Journal of Archaeological Science: Reports*. 2018;18:806-823.
6. Krivanek OL, Lovejoy TC, Dellby N, Aoki T, Carpenter RW, Rez P, et al. (October 2014). "Vibrational spectroscopy in the electron microscope". *Nature*. 514 (7521): 209–12.

7. Lagos MJ, Batson PE (July 2018). "Thermometry with Subnanometer Resolution in the Electron Microscope Using the Principle of Detailed Balancing". *Nano Letters*. 18 (7): 4556–4563.
8. Shadman S, Rose C, Yalin AP (2016). "Open-path cavity ring-down spectroscopy sensor for atmospheric ammonia"
9. Jaleh B, Fakhri P. Infrared and Fourier transform infrared spectroscopy for nanofillers and their nanocomposites. In: *Spectroscopy of Polymer Nanocomposites*. Netherlands: Elsevier; 2016. pp. 112-129 [13].
10. ISO 20473:2007. Optics and Photonics—Spectral Bands.
11. Smith BC. *Fundamentals of Fourier Transform Infrared Spectroscopy*. 2nd ed. Boca Raton, FL: CRC Press; 2011.
12. D. Briggs and M. P. Seah, *Practical Surface Analysis: Auger and X-Ray Photoelectron Spectroscopy* (Wiley, Chichester, 1996).
13. J. F. Watts and J. Wolstenholme, *An Introduction to Surface Analysis by XPS and AES* (Wiley, Chichester, 2003).
14. K. Siegbahn, *Electron spectroscopy for atoms, molecules, and condensed matter*, *Science* 217, III (1982).
15. C.J. Powell, D.M. Hercules, A.W. Czanderna, in: A.W. Czanderna, D.M. Hercules (Eds.), *Ion Spectroscopy for Surface Analysis*, Plenum Press, New York, 1991, p. 417.
16. Bish, DL and Post, JE, editors. 1989. *Modern Powder Diffraction*. *Reviews in Mineralogy*, v. 20. Mineralogical Society of America.
17. Moore, D. M. and R. C. Reynolds, Jr. 1997. *X-Ray diffraction and the identification and analysis of clay minerals*. 2nd Ed. Oxford University Press, New York.
18. Babu, S.S., Specht, E.D., David, S.A., Karapetrova, E., Zschack, P., Peet, M., et al., 2007. Time-resolved X-ray diffraction investigation of austenite and transformation to bainite. In: *Proceedings of the First International Symposium on Steel Science*.
19. Dinnebier, R.E., Billinge, S.J.L., 2008. *Powder Diffraction, Theory and Practice*. The Royal Society of Chemistry.