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Nanocytotoxicity

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Abstract: Nanotechnology is widely used in our daily life including its use in medicine and dentistry. While choosing the nanoparticle for the use in the field of nano dentistry its chemical, physical, along with the biological aspect of nanostructures should be taken into consideration. A nanoparticle is a small particle that ranges between 0.1 to 100 nanometres in size.
Nanoparticles can exhibit significantly different physical and chemical properties to their larger material counterparts. Some nanoparticles are used for oral disease preventive drugs, prostheses and for teeth implantation. Nanomaterials further deliver drugs, preventing and curing some oral disease (oral cancer), tooth anti-sensitivity and enamel surface polishing.

Keywords: *Nancytotoxicity,nanoparticle,greennanotechnology,physicochemical factors,surface charge,how to reduce nanocytotoxicity.*

I. Introduction

Nanoparticle cytotoxicity is defined as the extent to which the interaction of nanoparticles with cells disrupts cellular structures and/or processes essential for cell survival and proliferation.(1)

Nanotoxicology focuses on determining the adverse effects of nanomaterials on human health and the environment.(2)

I. Routes of nanoparticles entry

Nanoparticles may be high risk both for patient and staff. In addition to patients, the workers who most likely come into contact with dental nanomaterials in the production, research, and development are in the risk of nanomaterial's toxicity.

Nanomaterials may introduce to the staff body through inhalation. The nanomaterials may enter the body then into the bloodstream (or lymph fluid) via absorption through oral mucosa. They may also enter through the digestive tract after swallowing. They can be distributed to different organs (liver, spleen, kidneys, heart, lungs, and brain) by systematic pathway. They may also directly translocate to the brain via nerves.(3)

I.1. Injection Route

In drug delivery purposes, by injection NPs can enter the systemic circulations where they affect the circulatory system, central nervous system. (4)

I.2. Dermal Route

Formulations that contain the NPs such as cosmetic preparations and wound dressings which contains NPs of silver, titanium serve as a dermal route entry of NPs. Skin toxicity

of nanoparticles is yet controversial. It was found that the adverse health effects for the topical application of sunscreens containing TiO_2 nanoparticles are not found, while other studies confirm adverse effects of nanosized particles and human dermal cells. (4)

I.3. Inhalation Route

As most of the dental nanomaterials are directly applied in the oral cavity or maxillofacial region during polishing or mechanical grinding. Due to their smaller size, NPs could penetrate the respiratory system and enter systemic circulation. They cause various lung diseases such as asthma, emphysema or even lung cancer, based on the concentration and physicochemical properties of NPs. From lung they travel to other organs such as bone marrow, brain or heart and lead to more severe diseases including Alzheimer, Parkinson or cardiac malignancies. (4)

I.4. Oral Route

Oral ingestion of NPs from dental fillings contain nanoparticles can cause brain damage. Titanium dioxide NPs could cause various pathological effects in a dose-dependent manner, such as blood-brain barrier destruction, cellular oedema and brain tissue necrosis.(4)

II.The physicochemical factors governing nano-cytotoxity:

1. Size

Cytotoxicity induced by nanomaterials results from the interaction between the nanomaterial surface and cellular components. As the diameter decreases, the surface area of the particle increases exponentially. Thus, even when particles have the same composition, they can have significantly different levels of cytotoxicity depending on both particle size and surface reactivity. Additionally, particle size induces significant differences in the cellular delivery mechanism and distribution in vivo. Size affects absorption, distribution and cellular uptake of nanoparticles. (5)

1.1. Absorption

To generate cytotoxicity and inflammatory response in animal models, it is essential that the nanoparticles should migrate across the epithelial barrier. In this respect, the size of the nanoparticles plays a key role in cytotoxicity. Different sized nanoparticles show specific distribution patterns in the respiratory tract. Cytotoxicity induced by inhaled silver nanoparticles of different sizes were assessed; 18, 34, 60, and 160 nm. It was found that silver nanoparticles in sizes of 18 and 34 nm induced lactate dehydrogenase (LDH) expression, which is a marker of cell damage, in a dose dependant manner. Meanwhile, there was no dose-dependent cell damage when 60 and 160 nm nanoparticles were used. It was justified that the increased surface area of the NPs was the most likely factor contributing to the toxicity of the silver nanoparticles(5).

1.2. In Vivo distribution and Clearance:

The distribution of nanoparticles in vivo, or pharmacokinetics, is also an important consideration in assessing cytotoxicity. Nanoparticles with a diameter greater than 6 nm cannot be excreted by the kidneys and accumulate in specific organs, such as the liver and spleen, until clearance by the mononuclear phagocyte system causing serious side effects. This pharmacokinetic characteristic of nanoparticles is dependent on particle size and surface chemistry.

The in vivo distribution of gold nanoparticles according to size was evaluated. The sizes used were from 10 to 250 nm. The in vivo distribution after intravenous injection in a rat model was assessed. It was found that 10 nm nanoparticles were distributed differently than their larger counterparts. 10 nm NPs were found in almost all organs, including the blood, liver, spleen, kidneys, testes, thymus, heart, lungs and brain. Meanwhile, most nanoparticles larger than 50 nm were detected only in the blood, liver and spleen.

1.3. Cellular Uptake:

One of the major factors determining cellular uptake efficiency and mechanism is nanoparticle size. With respect to particle size, nanoparticles are internalized into the cell through various pathways, such as phagocytosis and pinocytosis. Sizes suitable for uptake range from 10 to 500 nm. Large particles are most likely to be engulfed via macropinocytosis.

Gold nanoparticles typically form a surface coated layer with serum proteins when incubated with cells. Serum-layered gold nanoparticles usually induce receptor-mediated endocytosis, which is dependent on particle size. The uptake efficiency of gold nanoparticles as a function of size was evaluated. Gold nanoparticles ranging from 1 to 100 nm were incubated with Hela cells, and the 50 nm nanoparticle showed maximal uptake efficiency by receptor-mediated endocytosis. (5)

A similar experiment using ligand-coated gold nanoparticles showed that a diameter of 40–50 nm was the critical cutoff point for receptor-mediated nanoparticle internalization. This phenomenon is tightly related to the nanoparticle's binding and its cellular surface receptors.(5)

2. Surface

2.1. Surface Area

A larger surface area may cause higher reactivity, resulting in possibly harmful effects when used in fillers, cosmetics, and as drug carriers. Smaller particles occupy less volume, such that a larger number of particles can occupy a unit area, resulting in increased pathophysiological toxicity mechanisms, for instance oxidative stress, ROS generation and mitochondrial perturbation. It has yet to be determined what features of nanoparticles cause such biological toxicity. It was found that the size of the nanoparticle alone may not be responsible for toxicity, but that the total number per unit volume may be important.

The relationship between a nanoparticle's surface area and its biological toxicity was assessed with different nanoparticle surface areas and it was found that the total surface area played a critical role in lung inflammation rather than the size.(5)

2.2. Effect of Surface Charge:

Surface charge also plays an important role in toxicity of nanoparticles as it largely defines their interactions with the biological systems. Various aspects of nanomaterials such as selective adsorption of nanoparticles, plasma protein binding, blood-brain barrier integrity, and transmembrane permeability are primarily regulated by surface charge of nanoparticles.

Positively charged nanoparticles show significant cellular uptake compared to negatively charged and neutral nanoparticles, owing to their enhanced opsonization by the plasma proteins. Moreover, they have also been shown to induce hemolysis and platelet aggregation owing to which causes severe toxicity to the system.

For example, positively charged Si nanoparticles have been shown to be more cytotoxic compared to neutral and negatively charged Si nanoparticles which display minimal to no cytotoxicity issues. Neutral nanoparticles show limited cellular uptake and are useful in applications where nonspecific interactions with cells and the cellular uptake is not desired and could be done by modifying the nanoparticle surface with hydroxyl group to produce neutral charge. (6-8)

2.3. Effect of Surface Coating and Surface Roughness:

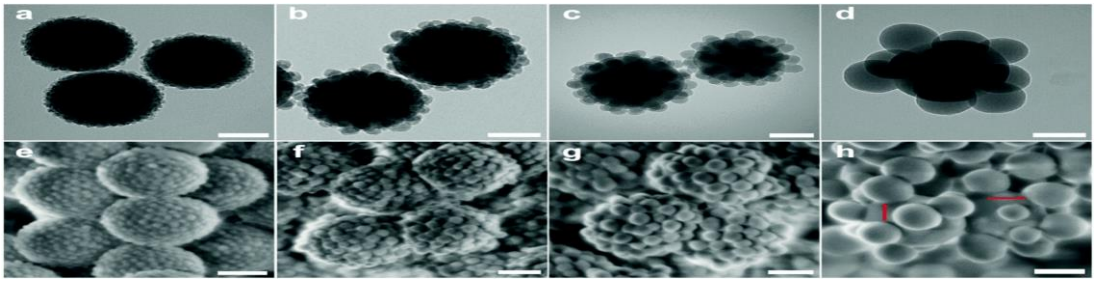
Surface coating can affect the cytotoxic properties of nanoparticles by changing their physicochemical properties such as magnetic, electric, and optical properties and chemical reactivity and can alter the pharmacokinetics, distribution and accumulation of nanoparticles.

It has been known that the presence of oxygen, ozone, oxygen radicals and transition metals on nanoparticle surfaces leads to the generation of ROS and the induction of inflammation.

However, on the other hand, surface coating could also be employed to reduce the toxicity of the nanoparticles. In general, surface coating can eliminate the adverse effects of nanoparticles. In particular, proper surface coating can lead to stabilization of nanoparticles as well as preventing release of toxic ions from nanomaterials.

Surface coarseness dictates the strength of nanoparticle-cell interactions and promotes cell adhesion. Pore structure is critical in cell-nanoparticle interactions. It has been demonstrated that size dependent hemolysis effect of mesoporous silica nanoparticles is only observed when the nanoparticles have porous structure. (6)

- The rough silica nanoparticles demonstrate a high efficiency of intracellular delivery of therapeutic proteins in cancer cells, causing significant cell inhibition, so controlled surface roughness could be used for the delivery of therapeutic proteins. Using “neck-enhancing” approach to synthesize stable rough silica nanoparticles with controllable surface roughness. By increasing the shell particle size from 13 to 98 nm while fixing the core size at 211 nm. Shell nanoparticles with the mean sizes of 28, 54, 98, 135 and 175 nm were fabricated using the Stöber method by reacting at 70, 60, 50, 40 and 30 °C, respectively. The reactions were first carried out for 20 minutes for the formation of shell particles (28, 54, 98 and 135 nm). For the shell particle of 175 nm. Absolute ethanol (50 ml) was mixed with deionized (DI) water (3.8 ml) and ammonium hydroxide solution (2 ml) at 25 °C. Then, TEOS (3 ml) was added to the solution. After 6 h, the as-synthesized nanoparticles were separated by centrifugation and washed with ethanol. The final product was obtained by drying at 100 °C overnight. After that, aminosilane was grafted to create positively charged surfaces. (9)



3. Morphology

Nanomaterials come in varied shapes including fibres, rings, tubes, spheres, and planes. Basically, shape dependent nanotoxicity influences the membrane wrapping processes *in vivo* during endocytosis or phagocytosis. It has been observed that endocytosis of spherical nanoparticles is easier and faster as compared to rod shaped or fibre nanoparticles and more importantly spherical nanoparticles are relatively less toxic irrespective of whether they are homogenous or heterogeneous. Non-spherical nanomaterials are more disposed to flow through capillaries causing other biological consequences. (6)

Study conducted on spherical and rod-shaped gold NPs demonstrated that rod-shaped NPs undergo lower cellular uptake than spherical NPs. There were two possible explanations: first, membrane wrapping for rod-shaped NPs takes longer than for spherical NPs; second, surfactant molecules adsorbed onto the longitudinal axis of nanorods impinge upon the ligand binding on the NP surface that facilitates cellular uptake.(8)

4. Aggregation Status

Aggregation could be a potent inducer of inflammatory lung injury in humans. For certain types of chemicals, exposure at higher levels has been shown to lead to serious chronic diseases such as fibrosis and cancer. It is still under consideration to figure out what features are inducing such toxicological effect in a living organism. Aggregated carbon nanotubes have more toxic effects than well-dispersed carbon nanotubes and enhance pulmonary fibrosis(5)

Basically, the aggregation states of NPs depend on size, surface charge, and composition. It has been observed that carbon nanotubes are mainly accumulated in liver, spleen, and lungs without manifesting any acute toxicity but induce cytotoxic effects mostly because of accumulation of aggregates for longer periods. (10)

5. Effect of Aspect Ratio:

Moreover, it has also been observed that the higher the aspect ratio, the more the toxicity of particle. In case of asbestos induced toxicity, it was observed that asbestos fibres longer than 10 microns caused lung carcinoma while fibres >5microns caused mesothelioma and fibres >2microns caused asbestosis as longer fibre will not be effectively cleared from the respiratory tract due to the inability of macrophages to phagocytise them.The toxicity of fibres with long aspect is closely related to their plasma shelf life. The fibres that are sufficiently soluble in lung fluid can disappear in a matter of months, while the insoluble fibers are likely to remain in the lungs indefinitely.

It was also observed that long-aspect ratio particles (SWCNTs) produce significant pulmonary toxicity compared to spherical particles.(6)

6. Effect of Composition and Crystalline Structure.

Although it has been emphasized that particle size plays significant role in deciding toxicity of nanoparticles, we cannot simply ignore studies comparing toxicities for diverse nanoparticles chemistries having the same dimensions. These studies highlight that the composition and crystalline structure

of nanoparticles also influence their toxicity issues. In a study it was observed that nanosilver and nanocopper with their soluble forms caused toxicity in all tested organisms,

whereas TiO_2 of the same dimensions did not cause any toxicity issues, thus emphasizing role of compositions in determining the toxicities of NPs.(6)

Crystal structure also influences the toxicity of nanoparticles and it has been observed that rutile TiO_2 nanoparticles induce oxidative DNA damage, whereas anatase nanoparticles of the same size and chemical composition did not.

7. Effect of Concentration:

Moreover, generally, it has been observed that with increase in the concentration of nanoparticles, the toxicity increases. At a concentration of 100 μg/ml NPs decreasing the cell survival by 20% only. The NPs do not cause apoptosis, ROS generation, or serious morphological changes in cells at concentrations lower than 100 μg/ml. (8)

8. Effect of Solvents/Media:

Medium/solvent conditions have been known to affect particle dispersion and agglomeration state of nanoparticles, which in turn have effect on their particle size, thereby influencing the toxicity associated with nanoparticles.

It has been observed that particles of TiO_2, ZnO, or carbon black have significantly greater size in PBS than in water; Accordingly, the same nanoparticles exhibit different toxic manifestations when dissolved in different mediums. Although, the dispersing agent may improve the physicochemical and solution properties of nanomaterials formulations, they may also adversely affect the toxicity of nanomaterials.(6)

III. Methods for Reducing the Toxicity of Drug Carriers Based on Nanoparticles

There are many methods to prevent or limit the toxic effects of metallic nanoparticles and metal oxides. Studies have shown that changing the shape and size of particles, and methods to modify their surface, can lead to the formation of nanoparticles with the desired properties, but without a toxic effect. (11)

Nanoparticles used as drug carriers are exposed to a physiological medium consisting of high levels of salt and various proteins. Both of these factors affect the stability of nanoparticles. High salt concentration reduces electrostatic repulsion between nanoparticles, leading to their aggregation, while proteins are adsorbed on the surface of nanoparticles and change the size of particles and surface charge. (11)

III.1. Methods for the Synthesis of Metal and Metal Oxide Nanoparticles

At the stage nanoparticles are obtained it is possible to limit their potential toxic properties. The methods of producing nanoparticles allow products of various shapes and sizes to be obtained. Factors that affect these properties include process temperature, pH of the reaction, form of energy supply, reagents, and reaction environment. (11)

Nanoparticles can be obtained by chemical, physical, and biological methods. In chemical processes, nanoparticles are most often obtained in simple precipitation reactions. Initially, it leads to the formation of metallic particles, which stick together to form agglomerates. To inhibit the agglomeration process, stabilizing substances are introduced into the system or the temperature and pH of the system are controlled. (11)

In the case of metal nanoparticles intended for drug carriers, stabilizers perform two functions. First, they stabilize and protect nanoparticles against further agglomeration.

Secondly, they change the nature of the surface of nanoparticles, so the joining of nanoparticles with a drug become easier. (11)

Compounds containing sulfur, nitrogen, or oxygen easily react with metal ions initiating their reduction causing simultaneous stabilization of freshly formed nanoparticles. An example of obtaining metallic nanoparticles by the biological method is the synthesis of nano gold modified with para-aminobenzoic acid-quat-pullulan (PABA-QP) as a carrier of doxorubicin. Due to surface modification, higher drug loading was possible.(11)

III.2. Morphology of Metal and Metal Oxide Nanoparticles

By changing the method of synthesis, process parameters used, it is possible to obtain nanoparticles with spherical, elongated, cubic, triangular, and many other shapes. This results in compounds with different surface to volume ratios.

The relationship between the influence of the shape of AgNPs on cell toxicity was demonstrated and it was found that platelet-shaped AgNPs showed greater toxicity epithelial cell lines compared to spherical and wire-shaped nanoparticles. The concentrations of the analyzed nanoparticles were tested in the range of 1–300 μM. The results showed a low cytotoxicity profile of spherical nanoparticles, especially at lower concentrations.

Another study compared the shape effect of ZnO NPs on their toxicity and showed that nanowire-shaped particles had higher toxicity compared to spherical and cubic particles. (11)

III.3. Protective Coatings:

A different approach to modify the properties of metallic nanoparticles limiting their toxic effects, is to use appropriate surface modifications.

The main task of using coating compounds is to improve the stability of nanoparticles by preventing the release of ions from inside, preventing oxidation of the surface of nanoparticles and inhibiting agglomeration of nanoparticles. (11)

It was found that coating of AgNPs with a thin layer of SiO_2 minimized their toxicity by blocking the release of ions and contact of bacteria and/or cells. Natural compounds such as saccharides, hydrocolloids, and polyphenols can be effectively used as factors improving the biocompatibility of metal nanoparticles.

AuNPs were stabilized with karaya gum, which were used as the carrier of the anti-cancer drug. Also, rubber stabilized nanoparticles have been found to be biocompatible during cytotoxic studies and hemolysis because it acts as a reducing agent and gives nanoparticles colloidal stability. (11)

III.4. Surface Functionalization

An important method is to functionalize the surface of nanoparticles by introducing appropriate functional groups. Depending on the properties of the nanoparticles, their future use or the drug to be combined with the nanocarrier, a variety of ligands are used. In the case of drug delivery systems, such surface modifications allow the creation of appropriate mechanisms for loading and releasing the drug into target cells, changing their character to hydrophilic/hydrophobic, which improves drug solubility in the system and improves penetration through well-defined membranes. The most important groups that can be used as surface modifiers of metal nanoparticles are disulfide, amine, thiolate and

dithioline, carboxylate, and phosphine groups. It was found that by modifying the surface of ZnO NPs with polyethylene glycol, the cytotoxicity was reduced and increasing their cell compatibility. The use of polyethylene glycol reduced the formation of protein crowns, which led to lower cytotoxicity compared to pure ZnO NPs .

Due to the need to supply drugs to both hydrophilic and hydrophobic environments, it may be necessary to change the nature of the carrier surface. The increase of hydrophilic properties most often occurs by attaching carboxyl groups (-COOH). Using the addition of N-vinylpyrrolidone in the preparation of Ag NPs, it was possible to obtain a carrier for hydrophobic drugs in the aqueous medium(11).

Green nanotechnology:

Green nanotechnology is a branch of green technology that utilizes the concepts of green chemistry and green engineering, where the word "green" refers to the use of plant products. It reduces the use of energy and fuel by using less material and renewable inputs wherever possible. Green nanotechnology significantly contributes to environmental sustainability through the production of nanomaterials and nanoproducts, without causing harm or cytotoxicity to human health or the environment. The rationale behind the utilization of plants in nanoparticle formulations is that they are easily available and possess a broad variability of metabolites, such as vitamins, antioxidants, and nucleotides. For instance, gold (Au) nanoparticles, titanium dioxide and zinc oxide nanoparticles are also important metal oxide nanomaterials that have been synthesized from a number of plant extracts.(12)

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Fourier transform infrared spectroscopy (FTIR)

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Abstract: Fourier transform infrared spectroscopy (FTIR) is a largely used technique to identify the functional groups in the materials (gas, liquid, and solid) by using the beam of infrared radiations. Functional groups can be associated with characteristic infrared absorption bands, which correspond to the fundamental vibrations of the functional groups. A normal mode of vibration is infrared active (i.e., it absorbs the incident infrared light) if there is a change in the dipole moment of the molecule during the course of the vibration. Thus, symmetric vibrations are usually not detected in infrared.

Keywords: Fourier transform infrared spectroscopy.

I. Introduction

Fourier transform infrared spectroscopy (FTIR) is a largely used technique to identify the functional groups in the materials (gas, liquid, and solid) by using the beam of infrared radiations. An infrared spectroscopy measures the absorption of IR radiation made by each bond in the molecule and as a result gives spectrum which is commonly designated as % transmittance versus wavenumber (cm -1) (2). Infrared (IR) or Fourier transform infrared (FTIR) spectroscopy has a wide application range, from the analysis of small molecules or molecular complexes to the analysis of cells or tissues. taking advantage of infrared microscopy and of the use of IR radiation, it is used for the mapping of cellular components (carbohydrates, lipids, proteins) to identify abnormal cells.

FTIR spectroscopy has also been increasingly applied to the study of proteins.(1)

Infrared spectroscopy reviews the molecular vibrations. Functional groups can be associated with characteristic infrared absorption bands, which correspond to the fundamental vibrations of the functional groups. A normal mode of vibration is infrared active (i.e., it absorbs the incident infrared light) if there is a change in the dipole moment of the molecule during the course of the vibration. Thus, symmetric vibrations are usually not detected in infrared. In particular, when a molecule has a centre of symmetry, all vibrations which are symmetrical with respect to the centre are infrared inactive. In contrast, the asymmetric vibrations of all molecules are detected. This lack of selectivity allows us to review the properties of almost all chemical groups in one sample, and notably of amino acids and water molecules which can hardly be observed by other spectroscopic techniques. (1)

While this approach suffers from several limitations, it delivers unique information by addressing directly the properties of cofactors, amino acids, and water molecules, with very high sensitivity to structural parameters and electronic interactions. This justifies the experimental efforts that have been made to optimize its use and the interpretation of the data. (1)

Brief history:

The development of spectroscopy in non-visual wavelengths (IR region) was advanced simultaneously with the development of visual spectroscopy. Infrared light was first discovered by Sir Frederick William Herschel during his experiment, which was performed with mercury-in-glass thermometers illuminated by sunlight dispersed through a glass prism (Herschel 1800). He was really surprised when he found that not only the thermometers register heat beyond the red end of the visible spectrum, but the greatest amount of heat was found in this region. Later on, various scientists, including William Herschel's son, Sir John Frederick William Herschel, contribute to the infrared spectroscopy very effectively to measure the infrared spectrum practically. Jacquinot, Fellgett and Connes are the famous researchers along with other known scientists for their work in the early history of spectroscopy. The work of Rubens and Wood on FTIR interferogram and Rubens and von Baeyer in spectroscopy was known before the advent of Michelson interferometer. However, before 1980 some domestic high-resolution FTIR spectrometers were also reported. In the mid1960s, progress has been made in the infrared microscopy and developed techniques which enhanced the signal-to-noise ratio. In the late 1970s, the infrared microscope systems were introduced in the market and in the early stages of 1980s by Digilab and Spectra-Tech Company. (2)

The real advancement was made in FTIR spectroscopy with the availability of commercially accessible high-resolution instruments. Previous to 1980, the FTIR spectrometers resolution was 0.04 cm−1 which is inadequate and less efficient than the old-fashioned grating apparatuses. Revolution attained with the Bomem instruments having a maximum optical path difference (d MOPD) = 250 cm−1. In the traditional IR spectroscopy, specific IR radiations are selected for the analysis, which is a dull and time-consuming process. For example, a molecule containing O-H and C=O functional groups, different ranges of IR radiation were applied for the determination of O-H and C=O functional groups. This problem was solved with the advent of Fourier transform infrared spectroscopy (FTIR), where a pulse (eruption of energy) is bombarded on molecules; as a result, different parts of the same molecules received its characteristics IR radiation and displayed a time domain spectrum called Interferogram. The time domain spectrum (interferogram) is converted to frequency domain spectrum by the application of mathematical procedure known as Fourier transform. (2)

Principle of FTIR:

When infrared radiation is bombarded on a sample, it absorbs the light and creates various vibration modes. This absorption relates precisely to the nature of bonds in the molecule. The frequency ranges are measured as wavenumbers typically over the range of 4000–600 cm−1. The FTIR spectrum is measured as wavenumber because wavenumber is directly related to the energy and frequency, thus providing an easy way for interpreting the spectrum. Prior to the sample analysis, the background is recorded, to avoid air and water vapor contamination peaks. The proportion of the background and the sample spectrum are directly related to the absorption spectrum of the sample. The absorption spectrum indicating various vibrations of the bonds presents in the sample molecule.

Several modes arise due to the various bond vibrations. So, in this way one can easily identify the functional group in a molecule.

During an absorption process, the molecule absorbs only those frequencies of IR radiation which matched with the natural vibrational frequency of the bonds and hence increases the amplitude of vibrational modes of the molecules. However, all the bonds in a molecule cannot absorb the IR radiation irrespective to the matching frequency of IR radiations, until and unless it has a net dipole moment. Organic molecules mostly contain covalent bonds between the atoms, which are not stiff but rather behave like springs and always agitating at room temperature. This movement of the bonds in molecule gives various modes of vibration. There are two modes of vibrations: stretching and bending vibration. (2)

Sample forms and preparation for FTIR analysis:

Fourier transform infrared (FTIR) is one of the important analytical techniques that can be used for characterizing samples in the forms of liquids, solutions, pastes, powders, films, fibres, and gases. This characterization analysis is quite rapid, good in accuracy, and relatively sensitive. In the FTIR analysis procedure, samples are subjected to contact with infrared (IR) radiation. The IR radiations then have impacts on the atomic vibrations of a molecule in the sample, resulting the specific absorption and/or transmission of energy. This makes the FTIR useful for determining specific molecular vibrations contained in the sample (3). In short, the IR spectrum is divided into three wavenumber regions: far-IR spectrum (<400 cm-1), mid-IR spectrum (400-4000 cm -1), and near-IR spectrum (400013000 cm-1). The mid-IR spectrum is the most widely used in the sample analysis, but far- and near-IR spectrum also contribute in providing information about the samples investigated.

Sample preparation:

The sample preparation is very important for IR spectra analysis where the sample is placed in the cell or in the holder. It is very problematic because IR radiations are strongly absorbed by glass and plastic materials throughout the entire IR range. The cell is constructed of ionic materials, such as KBr or NaCl. The KBr plates are expensive, but they have advantages over NaCl, as they can record IR spectra from 400 to 4000 cm−1. However, NaCl plate is also largely used due to its low cost and recorded spectra from 650 to 4000 cm−1. NaCl is absorbed at 650 cm−1, and very few bands are supposed to absorb in this region; therefore, it is commonly used in the routine experiment. The CO2 and H2O from the atmosphere usually appeared in the compound spectrum which causes problem during the interpretation of the spectrum. Therefore, it is very important to run background spectrum so that it is automatically subtracted from the compound spectrum. Between the polished NaCl or KBr plates, a drop of liquid is placed, known as salt plate. After pressing the plates, a thin film is formed. The pair of plates is inserted in the holders. The spectrum obtained during this method is called as neat spectrum because it is free of solvent. Moreover, being ionic in nature, these salt plates are easily soluble in water; therefore, it is recommended that the compounds must be free of water. Three methods are available for solid sample. In the first method, the compounds are finely grounded with KBr salt and then pressed at high pressure to form pellets called KBr pellets. However, KBr absorb water which gives water peaks in the spectrum and hindered the peaks originated from the compounds. Nevertheless, if KBr plates are prepared carefully by avoiding the absorption of moisture, no peak will appear in the spectrum. The other advantage is that KBr is transparent below 400 cm−1. In another method called Nujol mull, the compound is finely grounded with the mineral oil called Nujol, as a result a thick suspension is formed which is placed between the plates. The main drawbacks of this method are the Nujol peaks which might interfere with compounds having peak in these regions. In the third method, the compound is dissolved in solvent Chloroform (CCl4) is mostly used, because it dissolves most of the organic compounds; however, like Nujol the CCl4 peaks appeared and interfere with the compounds peak at approximately 700 cm-1.

Attenuated total reflection (ATR)-FTIR:

Due to the drawbacks associated with KBr pellets and liquid cells method, FTIR measurements are largely achieved in attenuated total reflection (ATR) mode because of its simplicity as compared to the conventional transmission mode. Various samples such as liquids, solids, pastes, fiber pellets, powders, slurries, and many other are placed without any treatment on the ATR crystal. It is a fast technique and the data is obtained in a few seconds. This can be achieved practically without any major sample preparation. IR-ATR provided an advantage that the sample can be investigated without interruption. Thus, biofilm removal from its support, which modifies its structure significantly from its natural form, can be avoided. Additionally, very thin films and surface coverings can be examined, which are not available to normal chemical approaches. Particularly ATR is an

extremely good technique for polymer and membrane science. The key advantage of ATR is its capacity for the measurement of varieties of samples such as solid and liquid samples without the need of complex steps. In this approach, the IR ray enters the ATR crystal at 45◦ relative to the crystal surface and is entirely reflected at the crystal to sample interface. Because of its wavelike properties, the light is not reflected directly by the boundary surface but by a computer-generated layer within the optically less dense sample. Evanescent wave is a fraction of light which reached to the sample. The penetration depth depends on the wavelength, the refractive indices of the ATR crystal and the sample, as well as the angle of the incident light. Characteristically, it is of the order of a few microns (0.5–3 μm). The evanescent wave is attenuated in the spectral regions, where the sample absorbs energy. After one or numerous internal reflections, the IR beam exits the ATR crystal and is directed to the IR detector.

Instrumentation:

The typical FTIR spectrometer consists of an IR light source, interferometer, sample compartment, detector, amplifier, and computer. The light source generates radiation which strikes the sample passing through the interferometer and reaches the detector. Then the signal is amplified and converted to digital signal (interferogram) by the amplifier and analog-to-digital converter, respectively. Eventually, the interferogram is translated to spectrum through the Fast Fourier Transform (FFT) algorithm. Michelson interferometer is the main core of FTIR spectrometer.it consists of a beam splitter, fixed mirror, and a moveable mirror that translates back and forth, very precisely. The beam splitter is made of a special material that transmits half of the radiation striking it and reflects the rest half of the radiation. It works on the basis of principle that the light from the source is collected by collimating mirror and made its rays parallel, which strikes beam splitter and consequently splits into two beams. One beam is transmitted through the beam splitter to the fixed mirror, and the second is reflected off the beam splitter to the moving mirror. The fixed and moving mirrors reflect the radiation back to the beam splitter. Accordingly, both of these reflected radiations are recombined at the beam splitter, resulting in one beam that leaves the interferometer and interacts with the sample and strikes the detector. Principally, FTIR (Fourier transform infrared) is a method of obtaining infrared spectra, which includes initially the collection of an interferogram of a sample signal using an interferometer and then performance of a Fourier transform (FT) on the interferogram to obtain the spectrum. An FTIR spectrometer collects and digitizes the interferogram, performs the FT function, and displays the spectrum. (2)

Advantages:

Some of the major advantages of FTIR over the dispersive technique include:

Speed: Because all of the frequencies are measure simultaneously, most FTIR measurements are made in seconds rather than several minutes.

Sensitivity: Sensitivity is dramatically improved with FTIR for many reasons. The detectors employed are much more sensitive, the optical throughput is much higher (referred to as the Jacquinot Advantage) which results in much lower noise levels, and the fast scans enable the co-addition of several scans in order to reduce the random measurement noise to any desired level (referred to as signal averaging).

Mechanical simplicity: The moving mirror in the interferometer is the only continuously moving part in the instrument. Thus, there is very little possibility of mechanical breakdown.

Internally calibrated: These instruments employ a He-Ne reference laser as an internal wavelength calibration standard (referred to as the Connes Advantage). These instruments are self-calibrating and never need to be calibrated by the user. (1)

These advantages, along with several others, make measurements made by FTIR extremely accurate and reproducible. Thus, it is a very reliable technique for the positive identification of virtually any sample. The sensitivity benefits enable identification of even the smallest of contaminants. This makes FTIR an invaluable tool for quality control or quality assurance applications whether it be batch-to-batch comparisons to quality

standards or analysis of an unknown contaminant. In addition, the sensitivity and accuracy of FTIR detectors, along with a wide variety of software algorithms, have dramatically increased the practical use of infrared for quantitative analysis. Quantitative methods can be easily developed, calibrated, and can be incorporate into simple procedures for routine analysis. Thus, the Fourier transform infrared (FTIR) technique has brought significant practical advantages to infrared spectroscopy. It has made possible the development of many new sampling techniques which were designed to tackle challenging problems that were impossible by older technology.

Applications:

FTIR for Materials Characterization is an efficient spectroscopic technique to characterize the structure of the following materials.

1. Organic Compounds: FTIR is largely used for the study of organic molecules, which brought mainly two types of changes in the molecules: stretching vibration causes of change in the bond length and bending vibration causes of change in the bond angle. Change in the bond length usually occurred at higher frequency or energy because stretching required higher energy as compared to bending vibrations. (2)

2.Nanomaterials: Any solid materials with one of its dimensions fewer than about 100 nm are known as nanoscale materials or nanomaterials. This small size of the particle, abruptly, increases the surface/volume ratio, and, therefore, many vital physical and chemical characteristics are expressively improved, which are completely different from their bulk counterparts. Although, nanomaterials and their bulk counterparts organize the same materials, but smaller particles indicate absolutely diverse physicochemical or electromagnetic properties from their bulk counterparts.

3-FTIR in Biomedical Imaging: FTIR spectroscopic imaging is a chemical imaging technique which is very important to investigate the biological samples. For characterizing the biomedical sample, FTIR spectroscopy has advantages over other imaging techniques because it detects specific molecular vibrations in the chemical bonds of molecules. FTIR imaging technique does not required the dyes for labelling or visualization in various sample, and its application is largely reported in medical imaging samples. For instance, it is used in human colorectal adenocarcinoma studies. Similarly, the deposition of β-amyloid protein in human brain tissue slice, comprises the Alzheimer's diseases, have been investigated through FTIR spectroscopic imaging techniques. The ATR-FTIR imaging technique is important in the biomedical field. it is the key for the potential characterization of biomedical samples in tissue engineering. (2)

Miscellaneous Applications of FTIR Spectroscopy:

FTIR is an extremely important tool for the detection of large range samples in different fields. For instance, resins, adhesives, paints, coatings, polymers, metal oxides, and large number of drugs can be analyzed with the help of this technique. different natural samples such as gummy materials, solids, liquids, and solutions can also be investigated and identified with the help of FTIR. The identification of diverse range of organic and inorganic compounds can be studied through this technique. Polymers and polymer blends as well as indirect verification of trace organic contaminants on surfaces of various materials, routine qualitative and quantitative analyses can be performed. With the help of FTIR adhesives, coatings and adhesion promoters or coupling agents as well as thin film can be easily analyzed. The gaseous samples can be investigated using a gas cell for the headspace analysis or environmental monitoring process. (2)

Why Raman is Different from IR? (4)

IR requires change in dipole moment

Raman requires change in polarizability

Selection rules are therefore different and can be exclusive for centrosymmetric molecules which are IR inactive.

What is Raman spectroscopy?

Raman Spectroscopy is a popular technique for the analysis of molecular structure and is now considered complementary to infrared spectroscopy. Raman spectroscopy is based on the Raman effect, which was first found by the Indian physicist Chandrasekhara Venkata Raman in 1928. According to quantum mechanics, when photons interact with a molecule, the molecule may be advanced to a virtual state of higher energy. From this higher energy state, there can be a few possible outcomes. One such outcome can be that the molecule comes down to some vibrational energy level different than that of its beginning state, by producing a photon of some different energy. The difference between the energy of that scattered photon and the energy of the incident photon is the called the Raman Shift 1. Raman spectra are measured by exciting a sample using a high-intensity laser beam and passing the scattered light through a spectrometer. The energy difference between the incident light and the scattered light is called the Raman Shift. In the obtained spectrum, horizontal axis is the wavenumber of the Raman shift (cm−1) and the vertical axis is the intensity of the scattered light.

Comparison of Infrared vs. Raman:

Both spectroscopic techniques measure the same thing, vibrational energy, in different ways.

IR is an absorption measurement, while Raman measures scattered light from a laser source, which is superimposed with the vibrational structure of the molecule.

The selection rules are different: IR bands are active if the dipole moment of the vibrating molecule changes. While Raman band are active if the polarizability of the molecule changes.

Molecules of high symmetry frequently will not show IR activity

Example of FTIR analysis of dental Root canal sealer:ZnO/Siwak:(6)

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Thermal analysis of dental materials

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Abstract: The mostly used TA techniques for materials characterization are differential thermal analysis (DTA), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). TGA is mainly used to examine the decomposition of materials by monitoring mass change with temperature. DTA and DSC are widely used for examining the phase changes of materials, where DTA measures temperature difference and DSC measures heat difference.

Keywords: Thermal analysis; DTA; TGA; DSC.

I. Introduction

Thermal analysis (TA) is a group of analytical techniques that measure properties or property changes of materials as a function of temperature. These techniques are mainly applied for the characterization and investigation of structure decomposition, thermal stability, and phase transition. Many TA methods have been developed for a variety of examination purposes and are distinguished from one another by the property they measure. The mostly used TA techniques for materials characterization are differential thermal analysis (DTA), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). TGA is mainly used to examine the decomposition of materials by monitoring mass change with temperature. DTA and DSC are widely used for examining the phase changes of materials, where DTA measures temperature difference and DSC measures heat difference. The term differential is used since changes in a specimen are measured with respect to a standard reference material (1).

1. Differential Thermal Analysis (DTA)

Differential thermal analysis measures the temperature difference of the sample under investigation and a thermally inert material (generally alumina) known as the reference against time or temperature. This temperature difference is then recorded while the sample and the reference are subjected to a controlled identical temperature program (heated or cooled) in an environment at a controlled uniform rate (same heat flow) (1).

1.1 Principle of DTA:

As the sample is heated, it undergoes reactions and phase changes it can be detected relative to the inert reference, energy is emitted or absorbed, and a temperature difference is detected between the reference and the sample. The temperature difference between sample and reference (ΔT) should be zero when no thermal event or reaction occurs in the sample, because of similar thermal conductivity and heat capacity between the sample and reference. But when the sample undergoes thermal event such as physical or chemical changes, ΔT will be generated and becomes different. When there is a physical change in the sample then heat is absorbed or released. For endothermic reaction, such as melting, dehydration, vaporization, loss of water or solvent the heat

(energy) is absorbed and the temperature of the sample is decreased, so the sample would be at a lower temperature than that of the reference. While an Exothermic reaction, as crystallization, oxidation, polymerization the heat is released, and the sample temperature would be higher than the reference. These temperature differences between sample and reference produces a net signal, which is then recorded. A plot of the temperature difference reveals exothermic and endothermic reactions that may occur in the sample (2).

1.2 Sample presentation:

Almost any physical from of sample can be accommodated such as solid (amorphous or crystalline), liquid or gel, using various sample crucibles made from different materials (e.g.: platinum, aluminium). Sample size is usually small, a typical optimum sample weight of 50-100 mg (3).

1.3 Instrumentation:

DTA instrument is composed of fundamental components, figure 1. The sample is first loaded into a container and placed onto the sample pan or crucible (e.g., metallic or ceramic), figure 1. An equal quantity of inert material is placed in another container onto the reference pan. The dimensions of the pans should be nearly identical to be heated at a uniform rate. The sample and the reference weights must be equal, holders arranged symmetrically within a single heat source furnace and subjected to a common temperature program. The furnace and the holders are enclosed by an insulating material. As well, there is an electronic temperature regulator, programmer to ensure a constant rate of heating, and thermocouples for temperature regulation which are usually inserted into holders. The temperature difference between the sample and the reference are measured by the two thermocouples coupled in contact with the sample and with reference substance. The thermocouples are attached to an amplifier which converts the heat signal into an electrical signal and send the differential thermocouple outcome to the computer device to display in the form of a DTA curve or thermogram. The signal is only produced if a temperature deviation is observed; if the sample doesn't undergo any reaction, no signal is generated as no temperature difference is observed (4).

Characteristics of DTA Curve:

The temperature difference of a sample when heating or cooling are shown in a DTA curve or thermogram, figure 2. DTA curve is a plot between differential temperature (ΔT) and temperature of reference (T). DTA curve may be endothermic (downward plot) or exothermic (upward plot) (2).

A downward plot is endothermic, DTA curve demonstrate that the sample temperature is less than that of the reference material, whereas an exothermic reaction is represented as an upward plot where the specimen temperature is greater than that of the reference. This temperature difference between sample and reference produces a net signal, which is then recorded. if there is no reaction happening in the sample material, then the sample temperature remains the same as that of the reference material (2).

A DTA curve can be affected by various factors. These could be either physical factors such as adsorption, crystallization, melting, and vaporization or chemical factors such as oxidation and reduction. It can also be affected by the characteristics of the sample, such as amount, shrinkage, particle size, or instrumental factors such as the recording system sensitivity.

1.4 Interpretation of DTA thermograph (2):

-Line AB: no reaction in the sample material, value of ΔT is zero.

-Point B: initial temperature point, the curve rises from the baseline due to the exothermic reaction and it forms a peak BCD.

-Point C: the process of heat is completed. Maximum temperature peak or heat value. The peak temperature is the characteristic of the sample material.

¬-Point D: Heat is decreased up to D point, final temperature.

-BCD area under peak has a direct relation with the amount of reacting material, and this amount can be determined by comparing the area of a characteristic peak of the

sample with areas from a series of standard known samples analyzed under identical conditions.

1.5 Advantages (2,4):

1. Simple, Ease of use and adaptability.
2. Small sample size (tenth of a gram order), this allows the temperature to be homogeneous in the whole sample, avoiding a temperature difference along the sample that may affect results.
3. Both exothermic and endothermic reactions can be determined accurately.
4. DTA apparatus can operate over a wide temperature range, from −150 to 2400°C, using various heating and cooling programs. DTA feature is important for examining materials with high melting temperature such as ceramics and some metals.

1.6 Disadvantage (2,4):

1. Difficult to quantitatively obtain mass change during the test.
2. Complicated determination of phase transformation temperatures.
3. Low sensitivity and accuracy in quantity measurements of thermal analysis, when the absorbed or released heat during the measurements is not enough (too low) to be recognized; thus, the peaks associated with these thermal processes are not appreciated or are missed in the DTA curve.
4. Inherent limitation for its the development into a technique of high precision: The assumption of a constant value of the heat capacity of the sample and the assumption that the sample temperature is uniform at each time instant.

1.7 Applications (2,4):

1. Used to study the characteristics of materials, especially polymers it is based on measurement of properties like, melting point, decomposition temperature, crystallization and degree of polymerization can be assessed.
2. To distinguish exothermic and endothermic processes.
3. Qualitative identifications of material can be done by comparing the DTA of sample to DTA thermal curves of know materials.
4. DTA is widely used in the pharmaceutical and food industries.

2 Differential scanning calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is a thermal analysis method which measures the difference in the amount of heat or the heat flow rate (□H) between the sample and an inert reference as a function of time or temperature, while both are subjected to a controlled temperature program. DSC measures the energy required to keep both the reference and the sample at the same temperature (3).

DSC differs fundamentally from DTA in that the sample and the reference are both maintained at the temperature predetermined by the program. DSC is a calorimetric method, where heat flow (uptake or release) and energy differences are quantitatively measured. While in DTA, the temperature of the sample is monitored with respect to a reference sample, DTA is a qualitative technique which measures temperature differences and do not provide any quantitative data for energy (5).

2.1 Sample presentation:

Samples are typically solid, can be in powder form such as metals, ceramics, organic and inorganic materials and predominately polymers. Liquid samples can also be tested. Sample size is very small, the sample weight in DSC experiments is in the range of 5 to 20 milligrams (6). For sample and reference crucible, A variety of sample pans or crucibles are available in different materials to handle different kind of samples measurements according to the material used to study, figure 3 (7).

The standard aluminum sample pans can be used for solids and powders that do not decompose or boil in the range of -170° to 600 °C. They are used with most routine applications, can also be used for nonvolatile solid samples such as metals, and polymer

and inorganic materials provided that they do not react with aluminum. Platinum, copper, gold or alumina pans are used for samples which react with aluminum (e.g., biological samples). Also, they are used where high internal pressures are required or when sample of interest has a transition in high temperatures region (600-725°C), particularly useful in the specific heat capacity determination of liquids. In cases of undesirable metal-sample interactions occur, graphite pans are the method of choice(7).

2.2 Principle of DSC:

The basic principle of DSC, it studies what is the effect of heating on the samples. It measures the heat flow related to the thermal transitions in materials, as a function of time and temperature. Any event, such as loss of solvent, phase transitions, crystallization temperature, melting point, glass transition temperature of the sample, results in a change in its temperature. Thus, it provides qualitative and quantitative information about physical and chemical changes that involve endothermic (heat flow into sample), exothermic (heat flow out of the sample) processes or changes in heat capacity. The available DSC systems have a wide range of temperature capability, from -60 OC to >1500 OC (3).

2.3 Instrumentation:

DSC device may be one of two types: heat-flux DSC or power compensation DSC, the main difference is being mainly on their instrumentation design, depending on the principle of measurement used. The sample is placed in a crucible or a pan, then inserted in the cell of the machine, while the reference pan is empty. It's in this cell where the test is conducted, and the data is collected. Having extra material in sample pan means that it will take more heat to keep the temperature of the sample pan increasing at the same rate as the reference pan (8,9).

2.3.1 Heat-Flux DSC is also called ''quantitative DTA'' as it measures the temperature difference directly and then converts it to a heat-flow, energy difference. The sample and reference are interconnected by a metal disk and placed in a single furnace, figure 3a. As the furnace is heated at a linear heating rate, the heat is transmitted to the sample and reference pan through the metal disk. The difference of the temperature between sample and reference is due to the changes of heat capacity (Cp) of the sample (the empty reference side heats faster than the sample side during heating of the DSC cell, so the reference temperature increases a bit faster than the sample temperature). This temperature difference creates the heat flow signal and is measured as a function of heat. (1,3)

2.3.2 Power-compensated DSC belongs to class of heat-compensating calorimeters. The heat to be measured is compensated with electric energy by increasing or decreasing an adjustable Joule's heat. The sample and reference are placed in separate furnaces, where their temperatures are controlled and heated, by separate temperature controllers, and both have the same temperature figure 3b. As soon as changes in the sample occur, extra (for an endothermic effect) or less (for an exothermic effect), temperature differences between the sample and reference are compensated for by varying the heat required to keep both pans at the same temperature. The difference in power electrical input supplied to the sample and to the reference, to keep their temperatures as nearly the same as possible (the energy which is required to obtain zero temperature difference between sample and reference) is measured throughout the entire analysis. The energy difference is plotted as function of sample temperature (3,9).

2.4 Interpretation of DSC Curve:

The result of a DSC experiment is displayed in the form of a DSC thermograph, or a curve in which heat flow is plotted versus sample's temperature. Concerning interpretation of DSC thermographs, The following phenomena are the most common obtained

from a DSC experiment, no one sample would contain all the transitions shown in figure 4 (10).

(i) Glass transition temperature (Tg) which is the most common measured transition by means of thermal analysis techniques.

(ii) Crystallization (Tc), appearing as a well-defined exothermic process.

(iii) Melting of the specimen (Tm). Well-defined endothermic peak, since energy must be absorbed by the sample to get melted.

(iv) Heat of fusion ΔH which is determined by integrating the peak area.

(v) Cure reactions appearing as shallow and broad exotherms.

(vi) Moisture loss appearing as shallow and broad endotherms.

The area under the curve is directly proportional to heat absorbed or evolved by the reaction. The height of the curve is directly proportional to rate of the reaction.

On heating a polymer to a certain temperature, plot will shift a step downwards, there is more heat flow, where an increase in the heat capacity of the polymer occurs. This change in heat capacity that occurs at the glass transition, help to use DSC to measure a polymers glass transition temperature. After glass transition, the polymers have a lot of mobility, when they reach the right temperature, they will give off enough energy to move into ordered arrangements, the temperature at the highest point in the peak is usually considered to be polymer's crystallization temperature. If we heat polymer past its Tc, eventually another thermal transition will be reached, called melting Tm. When its reached, the polymers crystals begin to fall apart that is they melt. This means that the little heater under the sample pan must put a lot of heat into the polymer, to both melt crystals and keep the temperature rising at the same rate as that of reference pan. this extra heat flow during melting shows up as a big dip endothermic peak on DSC plot, figure 4 (11).

2.5 Advantages (2,4):

1. DSC is the most employed thermal analytical technique by the research community due to its low price, efficiency of handling and its relatively fast.
2. DSC is widely used to get information about glass transition temperature (Tg), melting point (Tm), crystallization temperature (Tc), the heat of crystallization (Hc), the heat of melting and heat absorbed or evolved during the cure reactions or decomposition reactions (9).
3. A very small amount of sample can be used and the sample present in any form can be tested in this technique.
4. A wide range of temperature control is possible.
5. 4. It can be used for studying many types of chemical reactions.

2.6 Disadvantages (2,4):

1. Inability to distinguish between samples having their thermal processes occur in the same temperature ranges (same melting points or glass transitions), the interpretation of the data becomes difficult due to overlapping of the peaks of phase transitions in the thermogram.
2. Interpretation of result is very difficult. It is highly dependent upon analyst experience. Subtle changes require detailed knowledge of chemistry and material information to understand.
3. The accuracy of the results decreases when trying to analyze nanomaterials or complex thermal processes.
4. DSC technique is sensitive to the heat-flow changes and the instrument calculates them as an average of multiple readouts. Using low heating rates or large quantities of samples could prevent this.

2.7 Applications (1,2,8):

1. Characterization of various kinds of samples for many applications can be done like polymers, pharmaceuticals, foods/biologicals, organic and inorganics chemicals and ceramics.
2. Material Identification: one of the primary uses of DSC, as to know if a polymer is semi crystalline or amorphous.
3. Phase transitions: determination of melting and crystallization points as well as phase transitions by measurement of the change of energy over temperature. DSC is widely used for examining polymeric materials to determine their thermal transitions. Important thermal transitions include the glass transition temperature (Tg), crystallization temperature (Tc), and melting temperature (Tm) as well as determining special properties of polymers such as crystallinity, curing status, polymer content, and stability.
4. Determination of Phase transformation and phase diagrams: the curve peaks of DSC reveal solid-state phase transformations over a temperature range.

3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is a technique in which the mass of a substance is monitored as a function of temperature or time as a sample is subjected to a controlled temperature program in a controlled atmosphere. It measures the change in weight of the sample during the process of heating or cooling. It is used to measure the phase changes, glass transition, and melting point. TGA is a powerful technique for the measurement of thermal stability of materials including polymers(4).

3.1 Sample presentation:

The sample pans (ceramic or platinum) can accommodate liquids, powders, films, solids, or crystal. The sample weight influences the accuracy of weight loss measurements, weight of the sample is up to 1g, typical sample is in mg, up to 50 mg of material is desirable in most applications and for volatile materials its around 20-100 mg of sample (12).

3.2 Principle of TGA:

TGA determines the amount and the rate of weight change of a substance with respect to temperature or time in controlled programmed conditions. The mass change profile (mass loss or mass gain) is continuously monitored and recorded as the sample is subjected to a controlled heating or cooling environment. TGA is used principally in the research and development of various materials to obtain knowledge and examine the strength of the material at a given temperature (thermal stability) as well as their compositional properties (e.g., fillers, polymer resin, solvents). Additionally, it is used to understand certain thermal events such as absorption, evaporation, decomposition, oxidation, and reduction, such events could bring drastic change in the mass of the sample.

3.3 Instrumentation:

TGA is conducted on an instrument referred to as a thermogravimetric analyzer, where mass, temperature, and time are considered its basic measurements. A thermogravimetric analyzer continuously measures mass while the temperature of a sample is changed over time. The fundamental instrument needed for TGA is a precision balance "Thermobalance" with a furnace designed to linearly increase temperature over time, which is regarded as the heart of a TGA unit (13).

Main components of TGA apparatus:

1. Highly sensitive scale, microbalance to measure weight change. The balance is located above the furnace and is thermally isolated from any thermal effects, to maximize the sensitivity, accuracy, and precision of weighing.
2. Sample holder or crucible could be made from platinum, aluminum or ceramic, it is necessary that the crucible should possess at least 100^{o}C higher thermal stability compared to experimental temperature conditions. The crucible holds the sample supported by the precision balance and located inside a programmable furnace.

3. Furnace with temperature programming facility, that is heated or cooled during the experiment, to control the temperature of the sample. The furnace can scan over a wide range of temperature 25 – 1200 ^{o}C and it is constructed of quartz. The balance and the furnace assembly are the two key components of thermobalance.

4. Facility to supply the gas, for providing inert atmosphere or oxidizing environment and an infrared spectrometer added to TGA allows identification of gases generated by the degradation of the sample.

5. Computer for observing the weight and temperature changes, where the balance is calibrated in a manner that a change in weight of the sample produces a proportional electrical signal. The computer collects, stores this electrical signal and converts it into weight or weight loss, which is then plotted on the thermal curve and calculate the weight-loss fraction or percentage.

3.4 Interpretation of TG curve

Data are obtained by plotting a graph between the mass change as a function of the temperature or time and are interpreted from TGA curve or thermogram, figure 6. This example of TG curve exhibits a single stage of decomposition.

In the curve, “Ti is the Initial Decomposition Temperature” represents the temperature at which the onset of decomposition is initiated and point at which the weight change attains a magnitude that can be detectable by a thermobalance.

“Tf is the final decomposition temperature” represents the temperature at which the decomposition reaction is completed and the point at which the weight change attains a maximum and cannot change further.

The values of Ti and Tf depend on the thermal stability of the sampling analyzed. The temperature at which no weight loss takes place indicates stability of the material (13).

The TGA curve is classified into the following seven different types based on their shapes, figure 7 (13).

Type i: No mass change over the entire temperature range used for analysis; the sample is considered stable. It may be because the thermal stability of the sample is higher than the temperature range of the sample.

Type ii: There is a mass loss region, which is then followed by a constant plateau line. This could be due to evaporation of volatile product(s) during drying, or polymerization. The sample decomposed due to dehydration.

Type iii: Single stage of weight loss or decomposition temperatures (Ti and Tf). the sample decomposes in one sharp step.

Type iv: Samples decompose in multi-stages, with relatively stable intermediate products.

Type v: Multi-stage decomposition with no stable intermediary. Heating rate may affect the plot, where at slow heating rate, type (5) resembles type (4) curve.

Type vi: Sample weight is increased, due to certain surface reactions (such as oxidation of metals) with atmosphere.

Type vii: Multiple reactions one after the other with respect to a rise in temperature. The increase in weight is due to the surface oxidation reaction, whereas the decrease in weight with further rise in temperature corresponds to the decomposition process, due to reduction. (Surface oxidation reaction followed by decomposition of reaction products).

3.5 Advantages (2.4):

1. It is a convenient and time-saving technique, can be easily implemented where any type of solid can be analysed with minimal sample preparation requirements.

2. It has high accuracy of balance, high precision of temperature controlling system and atmospheric conditions, allowing uniformity of the procedure.

3. Continuous recording of weight loss as a function of temperature ensures equal weightage to examination over the whole range of study.

3.6 Disadvantages (2,4):

1. TGA can study process which accompanies a mass change. Chemical or physical process which are not accompanied by the change in mass on heating or with no volatile product could not be studied. Limited to samples that undergo weight change.

2. It is very sensitive to any change, TGA is dependent on procedural details such as furnace heating rate, the atmosphere inside the furnace, sample size, or weight

3. Interpretation of the result is not always straightforward but rather complex.

4. Operation requires high control over temperature.

3.7 Applications (2,4,13):

TGA is particularly useful for the following material characterization determinations:

1. Thermal stability: is described as the ability of a material to maintain constant characteristics when exposed to heat. TGA is used to evaluate the thermal stability of a material and is mainly used for polymers. In a desired temperature range, if a material is thermally stable, there will be no observed mass change. Negligible mass loss corresponds to little or no slope in the TGA trace.

2. Compositional analysis for samples and multi- component materials: Upon increasing the temperature of a sample, it undergoes weight loss. The weight loss profile remains significant for chemists to determine the composition of a sample so that it is possible to understand the reaction steps involved in the decomposition process and to identify an unknown compound present in the sample or examine complex materials by removing or decomposing their constituents. And also evaluate thermal decomposition mechanisms of polymers which indicates evaporation or decomposition processes of a substance.

3. Corrosion studies: TGA can be used to analyze oxidation or other reactions with different reactive gases or vapours.

4. Evaluation of moisture and volatile contents in the sample materials lost during chemical reactions, for samples such as nanomaterials, polymers, polymer nanocomposites, fibers, paints, coatings, and films.

5. TGA can estimate lifetime, shelf life of a product.

6. TGA provides quantitative measurement of mass change in materials associated with transition and thermal degradation.

7. The TGA can determine the quantity of a filler in a polymer, to estimate the additive content.

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Chemical characterization techniques of dental biomaterials: a review

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Abstract: The aim of this review article is to investigate the various chemical analyses techniques commonly used to identify the identity of a material or the identity of its components to achieve a qualitative analysis. Also, a quantitative analysis is performed afterwards to figure out the quantity of the material's chemical constituents. The materials are probed, measured, and determined using a variety of analytical methods, techniques, and tools. This characterization is important in detecting materials' properties and thereby the appropriate choice of the dental material according to its use. Criteria for technique selection also include penetration depth and mean free path, resolution, detection limits, potential damage to the specimen, and specimen preparation requirements; our goal is to maximize information while minimizing damage.

Keywords: chemical analysis; characterization; spectroscopy; principle; scanning; microscopy.

I. Introduction

Chemical characterization techniques involve the identification of a material and the identification and quantification of its chemical constituents. as part of an assessment of the overall properties and the suitable application of the materials. It involves a measurement of the level of a leachable substance from the material, surface topographic analysis, microstructure and elemental analysis of unknown material according to its atomic configuration. Criteria for technique selection also include penetration depth and mean free path, resolution, detection limits, potential damage to the specimen, and specimen preparation requirements; our goal is to maximize information while minimizing damage. Within (microanalysis) it is necessary to identify trace components down to extremely low concentration (parts per trillion in some cases) and several techniques specialize in this aspect. In other cases, a high degree of accuracy in measuring the presence of major components might be the issue. Usually, the techniques that are good for trace identification are not the same ones used to accurately quantify major components. Therefore, the aim of this review to highlight the most commonly used techniques for both qualitative and quantitative analyses for dental materials (1).

1. Inductively coupled plasma spectroscopy (ICP):

ICP is an elemental analysis technique that uses an argon (Ar) plasma (ICP) to convert the sample into ions that are then measured using a mass spectrometer (MS), figure 1. It is a powerful characterization technique, capable of precisely identifying and measuring all elements in the periodic table and detecting up to 20 different trace elements simultaneously down to 1-10 ng of analyte element per liter in solution.

Plasma, referred to as the fourth state of matter, is a collection of positively charged particles, negatively charged particles (e.g., electrons) and excited species moving in random directions. When the temperature of a solid substance is increased at a fixed pressure, it is converted to liquid and then to gas. On further heating, the gas molecules start moving in random directions and when it is sufficiently heated, the atoms are ionized into freely moving charged particles and thus enter the plasma state (2).

ICP-MS is similar to inductively coupled plasma optical emission spectroscopy (ICP-OES), but ICP-OES uses an optical spectrometer to measure the light emitted from elements as they pass through the plasma, whereas ICP-MS measures the elements (ions) directly. Both techniques provide fast analysis of multiple elements in a sample, but ICP-MS provides much lower detection limits than ICP-OES, so it's a better choice for trace element analysis (3).

ICP-MS is typically used to analyze samples that are liquids (such as water) or that can be dissolved, or acid digested, to give a liquid. It is very versatile and can easily measure organic solvents, detect extremely small (nano)particles, or be connected to accessories that allow direct analysis of solid materials or gases.

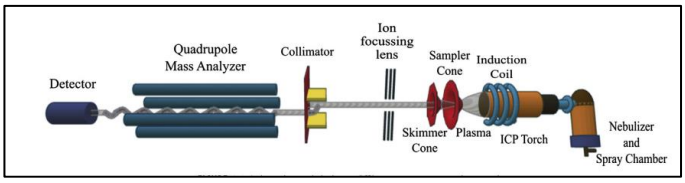


Figure 1. Inductively coupled plasma (ICP) mass spectrometer schematic diagram.

Principle of ICP:
There are six fundamental compartments of ICP-MS, figure 2:

1. The sample introduction system
2. Inductively coupled plasma
3. Interface
4. Ion lens
5. Mass analyzer
6. Detector.

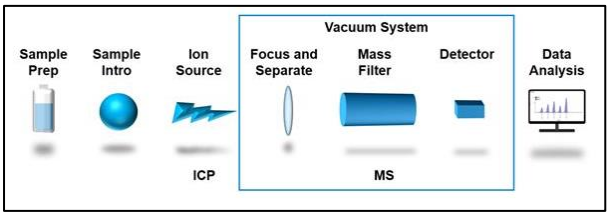


Figure 2. fundamental compartments of ICP-MS instrument.

1. Sample introduction system

ICP-MS is usually used to measure liquid samples. Liquid sample is pumped into a nebulizer, where the liquid is converted into a fine spray or aerosol mist using a jet of argon gas, figure 3. The aerosol mist passes through a spray chamber, where the larger droplets are removed. The fine droplets are carried by the argon gas flow to the ICP plasma torch. Because liquid sample analysis is more convenient, solid samples are often converted to liquids using acid digestion to dissolve the sample matrix, or acid extraction to extract the analytes into a solution for analysis (4).

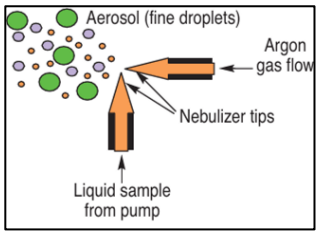


Figure 3. converting the liquid sample to aerosol mist.

Common diluents include dilute acids (e.g. hydrochloric acid) or alkali (e.g. ammonium hydroxide). Deionized water has been used as a diluent, however some elements are unstable in pure water, therefore acidic or alkaline diluents are preferred in most cases. Disadvantages of using dissolution media such as loss or contamination problems, dissolution medium causes loss of some elements and damage for the nebulizing system and plasma torch (4).

Solid sample analysis

A laser ablation (LA) device can be connected to an ICP-MS to perform direct solids analysis by LA-ICP-MS, figure 4. LA-ICP-MS involves placing the sample into a chamber on a special mount, then focusing a high energy beam from a pulsed laser onto the sample surface. Solid particles ablated and vaporized from the sample surface and swept up with a gas stream (usually helium) and carried to the ICP torch, where they are decomposed, dissociated, atomized, and ionized in the same way as for normal aerosol droplets. LA-ICP-MS is sometimes used for bulk (whole sample) analysis in applications such as quality control of metals, alloys, glasses, and ceramics where digesting the material might be difficult. In LA-ICP-MS the laser can be focused to a beam size of only a few microns, so analysis of small samples or a very tiny part of a larger sample is possible.

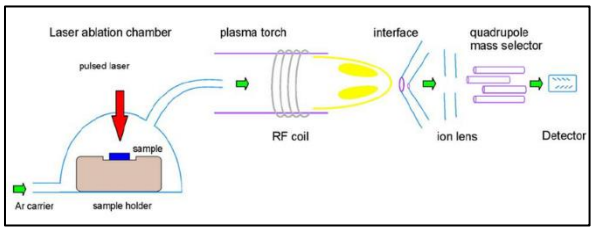


Figure 4. *Laser ablation ICP-MS*

1. Plasma (ICP) to convert the elements in the sample aerosol to ions

The plasma torch consists of concentric quartz tubes the inner tube containing the sample aerosol and Ar support gas and the outer tube containing an Ar gas flow to cool the tubes. The energy is provided by a radio frequency (RF) generator operating at about 1.5 KW produces an oscillating current in an induction coil that wraps around the tubes creating an oscillating magnetic field.

2. Interface region:

The generated ions are then extracted through the interfacial region which is a pair of coaxial nickel (or platinum) cones separate the plasma from the mass spectrometer vacuum chamber, figure 5. The movement of electrons and ions in the torch generate a tremendous amount of heat (10,000K) leads to a complete fragmentation of every sample molecule, leaving only their detectable, atomic constituents (5).

3. Ion lens

It focuses and guides the ion beam and prevent photons and other neutral species (such as non-ionized matrix components) from reaching the detector ◎ maximize transmission and therefore sensitivity◎ into the quadrupole mass analyzer. These uncharged particles would cause a high background signal, so they must be prevented from passing through the vacuum system and reaching the detector. This is usually achieved by positioning a 'photon-stop' in the ion path, or by deflecting the ion beam off-axis while the photons and neutrals, being uncharged, continue in a straight line and so are removed from the ion beam, figure 6.

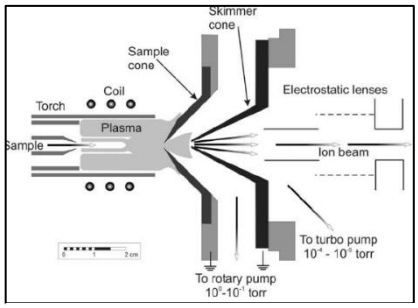


Figure 5. interfacial region cones.

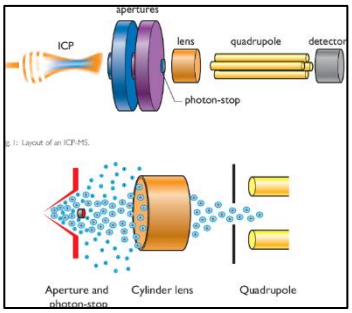


Figure 6. Ion focusing lenses

4. Mass spectrometer

Quadrupole is essentially a mass filter, separating ions based on their m/z ratio. A quadrupole consists of four parallel cylindrical metallic rods positioned in a square array. Radio frequency alternating current (AC) and direct current (DC) potentials are applied to the rods◎ electric field in the center through which ions pass.

6. Detector
7. Data processing

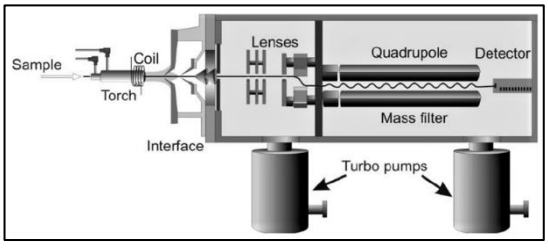


Figure 7. Quadrupole in ICP.

For conventional quantitative analysis, the software calculates the concentration of each element in the unknown samples by comparing the measured counts in the sample to the counts in a known-concentration reference solution.

Advantages of ICP:

1. It provides the broadest elemental coverage, extremely low detection limits (<0.1 part per trillion 'ppt') for nearly all the elements it can measure, and wide measurement range.
2. Multi-elemental technique.
3. Simple specimen preparation.
4. High throughput (about 40 specimens per hour).
5. Liquid and solid sample introduction systems.
6. Relatively small sample volumes required (typically 1-3 mL for solution mode).
7. Capable of isotope ratio measurement.

Disadvantages of ICP:

1. Equipment & Operating cost (argon).
2. Could not detect H and He; below the mass range of the mass spectrometer), Ar, N, and O (which are present at high level from the plasma and air), and F and Ne (which can't be ionized in an argon plasma).
3. Occurrence of interferences (e.g. polyatomic ions).

N.B. Polyatomic ions form in the high-temperature plasma, either due to incomplete atomization or from recombination reactions during the extraction of ions into the mass spectrometer. These ions may be derived from the sample matrix, reagents used for sample preparation, plasma gases (argon) or entrained atmospheric gases. For example, in samples containing chloride (or where hydrochloric acid is used during sample preparation), chlorine oxide (35Cl16O) and argon chloride (40Ar35Cl) are formed in the plasma. These ions share the same m/z ratio as vanadium (51V) and arsenic (75As) respectively. The presence of chloride may therefore lead to erroneous results for these analytes (4).

Dental example using ICP cumulative curve for ion release, figure 8 (6).

2. X-ray fluorescence spectroscopy (XRF):

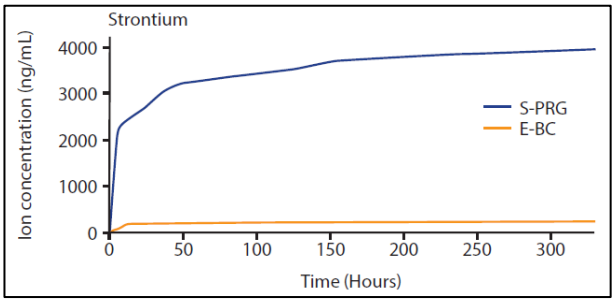


Figure 8. Comparison of average cumulative ion release of strontium over time in the prototype S-PRG sealer (S-PRG) and EndoSequence BC sealer (E-BC).

XRF is a non-destructive analytical technique used to determine the elemental composition of a wide variety of sample types including solids, liquids and loose powders. XRF analyzers determine the chemistry of a sample by measuring the fluorescent (or secondary) x-ray emitted from a sample when it is excited by a primary X-ray source. Each of the elements present in a sample produces a set of characteristic fluorescent X-rays "fingerprint" that is unique for that specific element, which is why XRF spectroscopy is an excellent technology for qualitative and quantitative analysis of material composition (7).

X-ray fluorescence process:

A solid or a liquid sample is irradiated with high energy X-rays from a controlled X-ray tube.

1. When an atom in the sample is struck with an X-ray of sufficient energy (greater than the atom's shell binding energy), an electron from one of the atom's inner orbital shells is dislodged.
2. The atom regains stability, filling the vacancy left in the inner orbital shell with an electron from one of the atom's higher energy orbital shells.
3. Electron drops to the lower energy state by releasing a fluorescent X-ray. The energy of this X-ray is equal to the specific difference in energy between two quantum states of the electron. The measurement of this energy is the basis of XRF analysis, figure 9 (7).

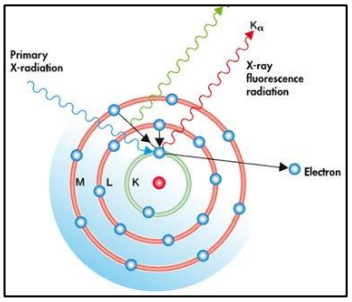


Figure 9. process of XRF radiation

Interpretation of XRF:

When X-ray energy causes electrons to transfer in and out of these shell levels, XRF peaks with varying intensities are created and will be present in the spectrum, a graphical representation of X-ray intensity peaks as a function of energy peaks.

The peak energy (x-axis) identifies the element; as the energy increases the atomic weight of the element increases, this is because the electrons of the heavier elements are bound tighter. While the peak height/intensity (y-axis) is generally indicative of counts which is the number of x-rays one can see that iron is present in a large quantity compared to the other elements because of the high number of counts, figure 10 (8).

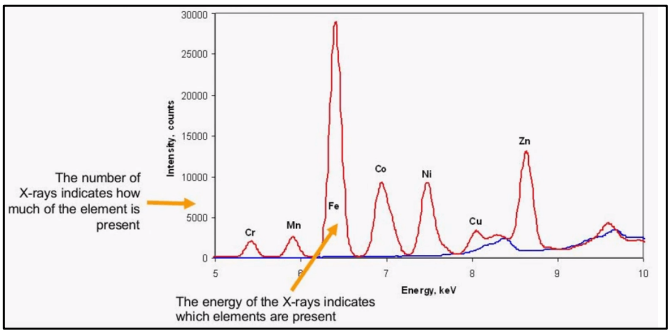


Figure 10. interpretation of XRF graph radiation

Types of XRF instrumentation:

Traditionally, XRF instrumentation is divided into two types according to how they discriminate the energies of the X-ray photons arising from the sample: Wavelength dispersive X-ray fluorescence (WDXRF) & energy dispersive X-ray fluorescence (EDXRF), figure 11.

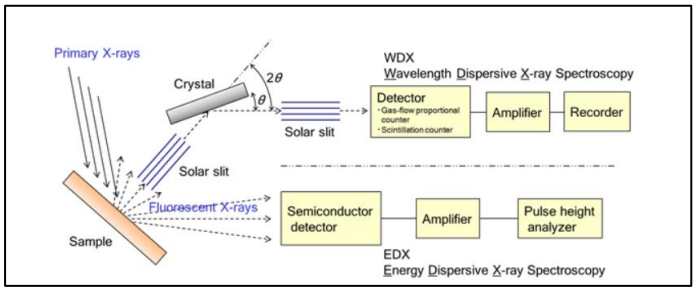


Figure 11. difference between WDXRF and EDXRF

EDXRF has a time advantage, as all elements are measured simultaneously, lower price, portable, relies on a semiconductor detector. WDXRF measures the elements one after another, has a high-resolution system and sensitivity (utilizing a crystal to disperse the fluorescence spectrum into individual wavelengths of each element, providing high resolution and low background spectra for accurate determination of elemental concentrations). Crystal material used is for example a synthetic thin film multilayer crystal giving higher sensitivity and resolution. Collimators further improve resolution by providing different angular divergences to restrict unwanted secondary x-rays from reaching the detector (9).

Advantages of XRF:

1. XRF is a rapid process.
2. Non-destructive.
3. XRF allows for simple sample preparation in the open-air nature of the instrument, and it has low running costs.
4. Wide elemental range for analysis.

Disadvantages of XRF:

1. Limited depth of penetration of X-rays does not exceed 1 mm (inhomogeneous samples are not analyzed accurately).

Poor sensitivity to light elements (Al, Mg); this problem is partially eliminated, for example, by purging the chamber with a sample with helium.

As an alternative, WDXRF can handle more complex samples, but it is more expensive, more time-consuming and requires more expertise to operate (10).

Example on XRF analysis representation, figure 12:

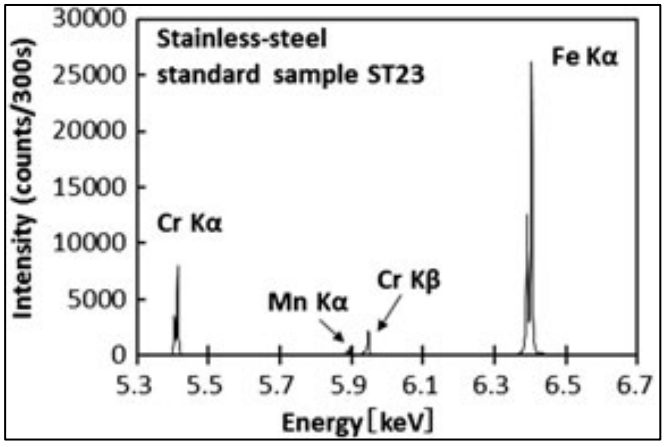


Figure 12. X-ray fluorescence spectrum of a stainless-steel standard sample (ST23: Fe 64%, Cr 22%, Ni 10%, Mn 1.6%, etc.; JFE Techno-Research Corp.) obtained with the polychromatic simultaneous wavelength dispersive Xray

3. Energy dispersive x-ray spectroscopy (EDX):

EDX spectroscopy is involved in the detection of elemental analysis or chemical characterization of a sample by using scanning electron microscope. EDX can detect elements from boron (atomic number 5) upwards.

Basic principle:

An electron beam strikes conducting solid sample's surface to eject 'core' electrons from an atom leaving a vacancy forming atom ionization, figure 13. Atom ionization occurs only when the amount of energy of the inbound electron is large enough to knock an inner orbital electron. In short, this energy from electron exceeds the binding energy of the shell, which is generally known as critical excitation energy. Consequently, a higher energy electron fills this vacancy & release energy (unique to each element) to reach a stable condition. This principle is known as Moseley's Law, which determined that there was a direct correlation between the frequency of energy released and the atomic number of the atom.

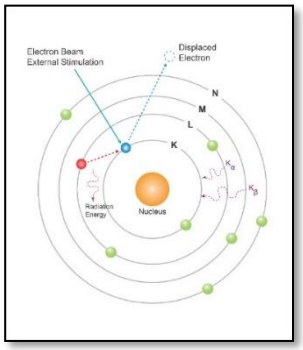


Figure 13. EDX principle

Sample preparation:

Size of the sample do not exceed 3-5 cm. Sample should be conductive for the electrons to react with. A highly polished surface is required for accurate quantitative analysis. Vacuum compatible materials (liquid could not be analyzed). Powder samples can be compacted into disks (11).

EDX apparatus consists of four basic components: the excitation source (electron beam or X-ray beam), the X-ray detector, the pulse processor, and the analyzer, figure 14. The X-ray detector converts X-ray energy into voltage electric signals. The pulse processor measures the detected signals and transfers them to the analyzer, where data is collected, processed and displayed as a spectra reporting the X-ray intensity versus energy

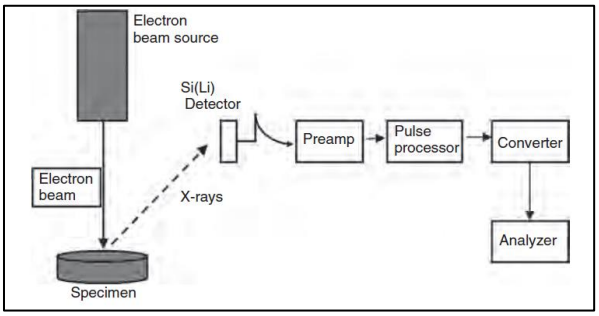
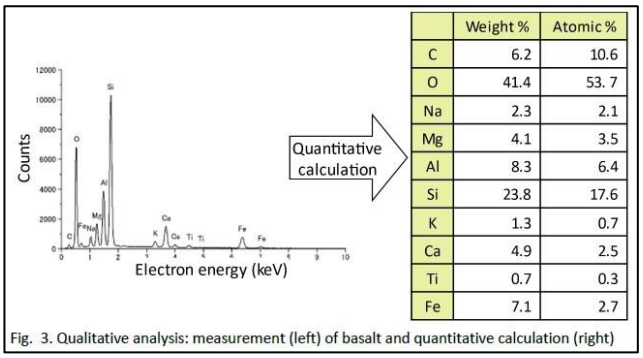


Figure 14. EDX apparatus.

Obtained data from EDX:



	Weight %	Atomic %
C	6.2	10.6
O	41.4	53. 7
Na	2.3	2.1
Mg	4.1	3.5
Al	8.3	6.4
Si	23.8	17.6
K	1.3	0.7
Ca	4.9	2.5
Ti	0.7	0.3
Fe	7.1	2.7

Fig. 3. Qualitative analysis: measurement (left) of basalt and quantitative calculation (right)

Figure 15. qualitative and quantitative analysis of EDX

Qualitative analysis is to identify elements contained in "unknown" materials using characteristic X-ray energies. Quantitative analysis is to identify the number of the emitted characteristic photons by the detector, figure 15. X-ray spectra are presented in a histogram with energy in keV on the x-axis and the number of counts on the y-axis

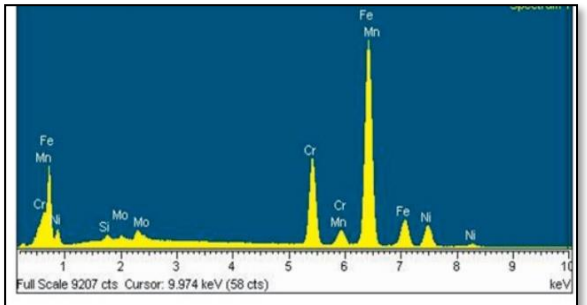
Advantages of EDX:

1. It has a very high mass sensitivity with a detection limit of 1000 ppm and excellent precision.
2. Surface sensitive: generate data from only the top couple of microns of SEM specimens.
3. It is a non-destructive technique.
4. The ability to scan areas and single spots; a large spatial range from about 1 mm2 to submicron2; elemental spectra are linked to image data generated by electron microscope; elemental maps, "dot maps," can be generated from the data.

Disadvantages of EDX:

1. Light elements below 11 atomic number is difficult to be analyzed (not a sensitive technique).
2. Surface roughness directly affects the results obtained. Therefore, samples must be carefully prepared to acquire surface smoothness.
3. Samples must be exposed to vacuum conditions, gases cannot be analyzed and liquids are limited to those that have very limited volatility and will not contaminate the system.
4. Non-conductive samples should be coated.
5. Insensitive method in bulk analysis.
6. Quantitative analysis of heterogonous materials often results in inaccurate data
7. Chamber dimensions often limit the size of samples.
8. The need for standards with a composition as similar as possible to the sample under investigation is a negative aspect when investigating new materials (13).

Dental example, EDX analysis of a stainless-steel alloy, figure 16:



Element	Weight %	Atomic %
Si	0.54	1.08
Cr	17.53	18.80
Mn	1.45	1.47
Fe	66.61	66.50
Ni	11.11	10.55
Mo	2.76	1.60
Totals	100	100

Figure 16. EDX spectrum suggests a stainless steel. The quantification results indicate that this is likely a 300 series and is a good match to alloy 316.

In both SEM/EDS and XRF, characteristic X-ray emissions are excited by an energetic source. The main difference between the techniques is the type of radiation used to excite the emissions. In SEM/EDS, it is an electron beam, whereas in XRF an X-ray beam excites the characteristic X-rays. Spectroscopy in both cases consists of measuring the energy of the emitted X-ray peaks, forming a spectrum that represents an elemental fingerprint of the sample. In XRF, because an X-ray source is used, the spectral background is lower, allowing small peaks to be recognized. This results in the ability to detect very low concentrations of an element. One technical limitation of a portable XRF is that light elements (P and below in the periodic table) are not detectable due to absorption of low-energy X-rays by air and the detector window. Thus, some elements making up the tooth and bone structure (P, O) are not detectable. This also applies to the principal components of the resin fillers in which the elements Si and O are not detectable, figure 17.

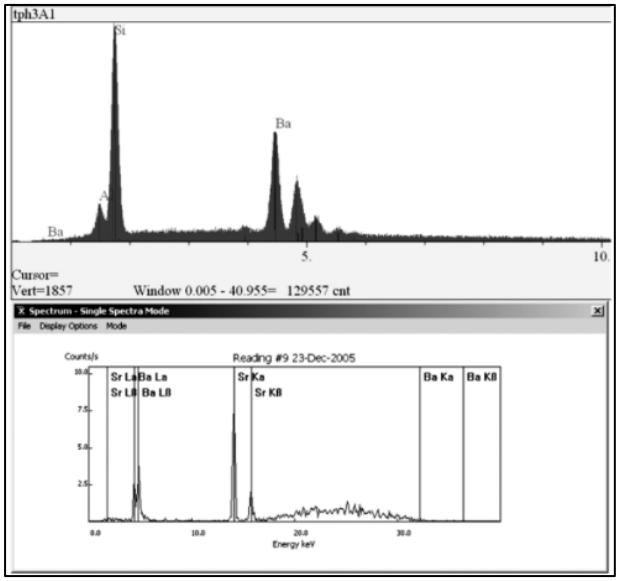


Figure 17. EDS spectrum (top) and XRF spectrum (lower) of TPH 3 resin. The silicon peak seen in the EDS spectrum does not appear in XRF spectrum, but Sr is seen in XRF spectrum due to the greater sensitivity of XRF.

The detection limit in EDS is around 1% concentration, whereas in XRF it is much lower: 10–100 p.p.m. for the elements of interest (0.00001–0.0001% concentration). Figure 17 shows an example of comparative analysis by the two techniques for the resin TPH 3. In the EDS spectrum, the Si peak is dominant, and Al and Ba are detected, while in the XRF spectrum, Ba and Sr are detected. Al will not be detected by XRF analysis as it is below P in the periodic table (14).

2. Conclusion

Chemical characterization techniques understanding is useful to identify the materials' properties and select the most appropriate analysis according to the type of the property needed to be tested.

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Introduction to Optical Analysis of Dental Materials: A Review

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Abstract: Optical properties such as color, translucency and surface gloss are critical factors in determining the esthetics of dental materials. Therefore, it is very important to understand the basics of optical measurement instruments. This review provides a simple introduction to the basic concepts for measurement of color, translucency, and gloss.

Keywords: *Optical properties, dental materials.*

I. Introduction

prosthetic materials of an important appearance characteristic of natural oral structures. Within the clinical setting when an indirect restoration is planned for an area of the face which is readily observed and the restoration would be easily assessed for harmony to adjacent existing natural structure, it would be ideal to quantify valid color information quickly and reliably using the patient's existing natural structure which has characteristics throughout the visible spectrum. Then this information could be used to facilitate the color formulation of the restoration such that the restoration could be made to have identical colors under various illumination conditions, within at least acceptable limits but more preferably within limits of perceived color difference (1).

Light illuminating an object can be (2):

Absorbed within it (a process largely responsible for color).

Transmitted through it (relating to the properties of transparency, opacity, and clarity).

Scattered within it (related to diffuse reflectance and transmittance, translucency, and some definitions of haze).

Re-radiated with lower energy (e.g., fluorescence).

Specularly (also called regularly) reflected (responsible for gloss).

The aim of this chapter is to illustrate the evaluation of three optical parameters, which are:

1- Color.
2- Translucency.
3- Gloss.

1- Color measurement:

The conversion of spectrophotometric measurements to three color parameters is described by the International Commission on Illumination (CIE) color space.
CIEXYZ and CIELAB are color-spaces designed to roughly fit with human luminance and color perception. CIEXYZ images are essentially images where the sensitivities are described by the CIE X, Y and Z receptors (which are hypothetical receptors designed to fit with human color discrimination behavior, corresponding to long-wave, medium-wave and short-wave respectively) (3).

CIELAB images can be created from CIEXYZ, where L describes the luminance channel, A describes a color opponent channel between red and green, and B describes a second color opponency channel between blue and yellow. This fits with various theories of how human color vision works (4).

A distinct advantage of the CIE L* a* b* color space is the simplicity of calculating a color difference between two colors using the following equation (1):

$$\Delta E = \sqrt{\Delta l^2 + \Delta a^2 + \Delta b^2}$$

where ΔL*, Δa*, and Δb* are the respective differences in the L*, a* and b* color parameters between two colors.

The key elements of color perception according to CIE system (5)***:***

1- Standard illuminant: D65 illuminant which corresponds to average northern sky daylight.
2- Standard illuminating and viewing geometries: CIE recommended four types of illumination and viewing geometries, shown in figure (1):

a) Normal/diffuse (0/d)
b) Diffuse/normal (d/0)
c) 45/normal (45/0)
d) Normal/45 (0/45)

The 45/0 illumination/observation geometry is the most widely used in spectrophotometers.

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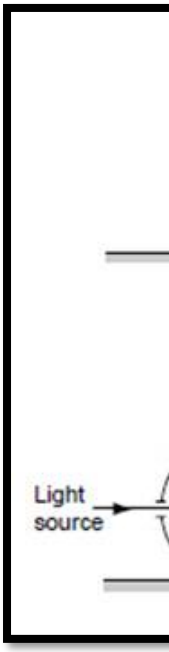

Figure (1) schematic diagram of the four CIE standard illuminating and viewing geometries

3- Standard observer:

Depending on the relative size of the area being viewed, the perception of color can change. In 1931, CIE defined color matching functions for a 2◦ view. Then in 1964 they published color matching functions for a 10◦ field of view (5).

Color measurement is mostly evaluated using spectrophotometers and colorimeters.

1.1. Colorimeters

The **colorimeters** are compact, hand-held, simple and cheaper instruments than spectrophotometers.

In colorimeters, objects are illuminated with a specific light source that simulates the standard illuminant. The reflected light passes through the primary filters: ***red, green, and blue***, which simulate the spectral sensitivity curve, and reaches the detector where it provides a response proportional to the tristimulus value. Therefore, colorimeters provide information on the **amount of red, green, and blue light reflected by the object**. This colorimetric information is useful for color evaluations that do not require complexity or precision (6).

1.2. Spectrophotometers:

A spectrophotometer is an analytical instrument used for the objective calculation of **reflected or transmitted radiation in the entire visible spectrum therefore, it is more accurate than colorimeters.** Spectrophotometers measure intensity as a function of the wavelength of the light source (7). Figure (2) is a schematic diagram showing the difference between colorimeter and spectrophotometer, where colorimeter quantifies color by measuring the three primary color components of light (red, green and blue), while spectrophotometer has a monochromator (prism) to enable it to scan the entire visible spectrum of light.

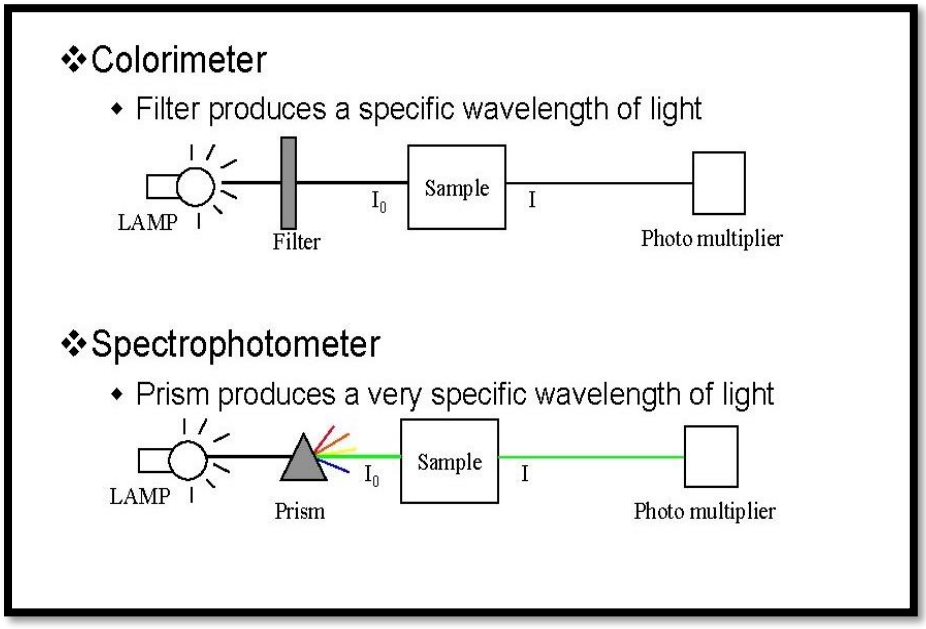

Figure (2) schematic diagram showing colorimeter versus spectrophotometer

Spectrophotometers are available in portable and bench-top instruments. The portable ones are used in color measurements of solid samples (teeth and dental restorations), while the bench-top type is mainly used for liquid samples.

A spectrophotometer is made up of two instruments: a spectrometer and a photometer. The spectrometer is to produce light of any wavelength, while the photometer is to measure the intensity of light. The spectrophotometer is designed in a way that the liquid or a sample is placed between spectrometer and photometer. The photometer (colorimeter and spectrophotometer) measures the amount of light that passes through the sample and delivers a voltage signal to the display. If the absorbing of light changes, the voltage signal also changes (7).

1.2.1. Basic principle of spectrophotometers:

Spectrophotometry is a procedure for determining how much light is reflected or transmitted by a sample by measuring the strength of light as a light beam travel through the sample. The fundamental theory is that light is absorbed or emitted over a certain wavelength spectrum by each compound (7).

1.2.2. Working parts of spectrophotometers (8):

All spectrophotometers contain four elements as shown in figure (3):

1. A source of radiation.

2. An optical system, or monochromator, to isolate a narrow band of wavelengths from the whole spectrum emitted by the source.

3. The sample (and its cell if it is liquid or gaseous).

4. A detector of radiation and its auxiliary equipment.

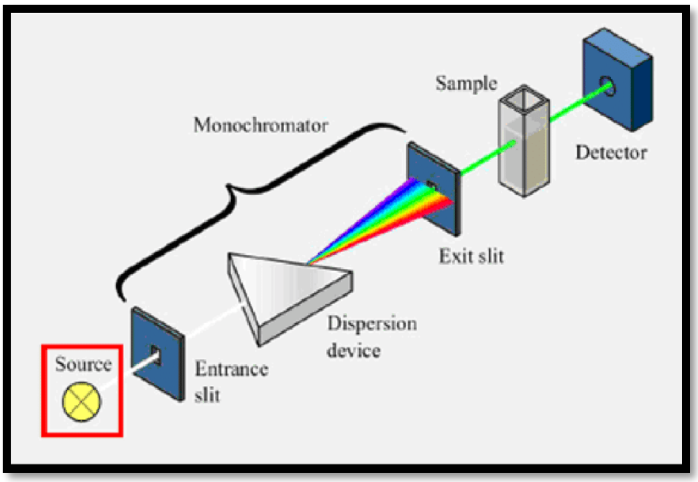

Figure (3) schematic diagram for spectrophotometer instrumentation

1.2.3. Working technique of spectrophotometer (8):

1. A sample solution is placed inside the spectrophotometer.

2. A light source shines light toward the sample.

3.A monochromator splits the light into each color, or rather, individual wavelengths. An adjustable slit allows only one specific wavelength of light through to the sample solution.

4. The wavelength of light hits the sample, which is held in a little container called a cuvette.

5. Whatever light passes through the sample is read and displayed on the output screen.

Both colorimeters and spectrophotometers must be calibrated each time before use.

1.2.4. Data obtained from spectrophotometers and its interpretation:

A spectrophotometer provides immediate spectral data.

ΔL (lightness) = $L_{reference} - L_{experiment}$, Δa (green - red) = $a_{reference} - a_{experiment}$, and Δb (yellow - blue) = $b_{reference} - b_{experiment}$.

$$\Delta E = \sqrt{\Delta l^2 + \Delta a^2 + \Delta b^2}$$

Figure (4) is an example for data obtained from a spectrophotometer of tooth color before and after bleaching. The instrument scans parts of the tooth (cervical, middle, and incisal) then provide quantitative data about each parameter.

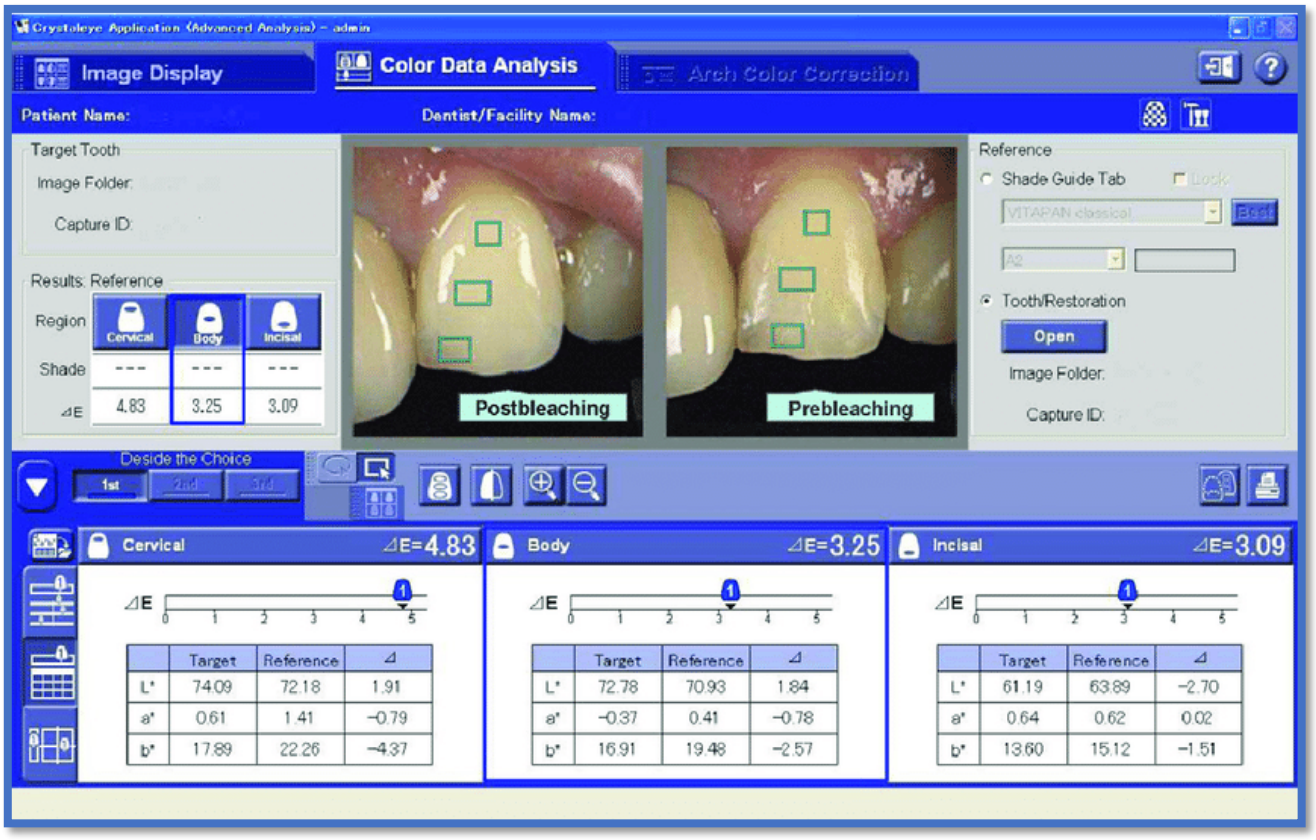

Figure (4) example from digital data obtained from a spectrophotometer

1.2.5. Data interpretation:

Interpretation of the data obtained from a spectrophotometer relies on the acceptability and perceptibility thresholds. **Perceptibility threshold (PT)** refers to the smallest color difference that can be detected by an observer. **Acceptability threshold (AT)** is the difference in color that is acceptable for 50% of observers corresponds to a 50:50%. The latest reported 50:50% PT/AT: ΔE_{00} = 0.8/1.8; ΔE_{ab} = 1.2/2.7 (9).

1.2.6. Measuring the color of liquid samples:

The color of liquid samples is evaluated using bench-top spectrophotometers.

a) <u>Opaque Liquids:</u>

To measure the color of opaque liquids, a reflectance spectrophotometer can be used. A glass test tube holder is mounted on the front of the device to hold the opaque liquid in the right location for color measurement. The measurement device shines light onto the sample and captures the illumination that reflects into the optics to quantify the color data (10).

b) <u>Translucent Liquids:</u>

A reflectance measurement will not work for clear liquids, which have color but are usually translucent. The wavelengths of light will go right through the sample instead of bouncing back. To measure translucent liquids, a spectrophotometer must be used in transmission mode (10).

Transmission spectrophotometers allow to put a liquid sample inside the instrument in glass test tubes or cuvettes. The device shines visible spectrum illumination through the sample and receivers on the other side capture the percentage of light that passes through at numerous wavelengths. A relatively transparent liquid will absorb some components of white light, while allowing other components to pass through. This data is used to quantify the color of the sample. Many benchtop spectrophotometers are capable of measuring in both reflectance and transmission modes (10).

1.2.7. Possible measurement errors:

a) Accuracy and repeatability of color measurements:

The two separate aspects of measurement error involve a lack of accuracy or validity and a lack of precision. Precision may be described with the repeatability of only the measuring device over time or the reproducibility of the entire measurement process, including specimen positioning. Accuracy of a color measuring device may be assessed by comparing a test instrument to a reference instrument which is considered to be correct (calibration), and precision assessed by comparing repeated measures of the same specimen or standard (7).

b) Edge loss:

Edge-loss has also been demonstrated for translucent pigmented maxillofacial materials, demonstrating that edge-loss may occur in either spectrophotometric or colorimetric measurement of translucent materials, depending on its inherent optical properties and the sizes of both the illumining light beam and the specimen port opening. In effect, edge-loss is caused by a shadow from the edge of the specimen opening within the translucent material, which allows the shadow to influence the intensity of the observation. Edge-loss can be avoided by avoiding a measurement system which uses an opening or aperture to position the specimen relative to the illumination and observation components. Such non-contact systems have been described which utilize a 45/0 illumination/observation geometry (7).

1.2.8. Advantages of spectrophotometers (1):

- **Comprehensive:** A spectrophotometer has more advanced hardware and can measure qualities that a colorimeter can’t, including metamerism and reflectance.
- **Adaptability:** You can typically adjust illuminance and observer settings to get just the right options on a spectrophotometer.
- **Powerful software:** By integrating with software, spectrophotometers offer a new, comprehensive way to review and analyze data outside of a built-in display.
- **They come in a variety of styles.** Spectrophotometers are available for a wide array of sample types, including powders, liquids, and transparent materials.

1.2.9. Disadvantages of spectrophotometers (1):

- **They are more complex:** With complexity comes sensitivity, and they may not be as suited for factory environments.
- **They can be more expensive than colorimeters:** Though price varies by model, spectrophotometers and their precise, broad range of information typically cost more than a colorimeter.

- **They may have more technology than necessary:** If you only need simple color measurements that a colorimeter can provide, a spectrophotometer may be more than you need.

2. Translucency

The translucency of a sample is determined by two parameters: the contrast ratio (CR) and the translucency parameter (TP) (11).

Contrast ratio *is defined as the ratio of the luminous reflectance of a translucent material on a black backing to the luminous reflectance of the same material on a white backing* (11).

In this definition, it is important to note that luminous reflectance is the Y

tristimulus value in reflectance as defined by the CIE. From this definition, it is obvious that when the two luminous reflectance values are identical, the material is completely masking the backings and CR is one, which is as high as possible for this measure. When the material is completely transparent, the luminous reflectance values are the values of the backings, respectively, and in this case, CR has the lower limit of the ratio of the luminous reflectance of the black backing to that of the white backing (11).

Translucency parameter *is defined as the color difference found for the material at a specified thickness, where the color difference was between the material when in optical contact with ideal black and white backings* (12).

TP and CR are also based on CIE colorimetry and therefore the illumination, the observer, and the color difference formula used for the color difference calculations must also be presented.

Both CR and TP are measured by ***a spectrophotometer*** like color, therefore all the key elements of CIE colorimetry are identified just as mentioned in color measurement.

CR = Y_B/Y_W, where (YB) is the luminance of black and (YW) is the luminance of white.

TP = $[(L^*B - L^*W)^2 + (a^*B - a^*W)^2 + (b^*B - b^*W)^2]^{1/2}$, where B and W refer to color coordinates over a black and a white background, respectively.

- ***The working principle of spectrophotometers, its advantages and disadvantages are the same for measuring translucency***

3. Gloss

Gloss is defined as '*The attribute of surfaces that causes them to have shiny or lustrous, metallic appearance.'* It is an important parameter affecting the appearance and quality of the products. We can find the gloss difference through our naked eye; however, this is subjective therefor it must be measured quantitatively for readily comparisons of different products (13).

The perception of gloss also relates to finish (the magnitude, frequency, randomness, and scale of curvatures), texture (changes in reflecting properties over the surface) and how a sample is illuminated and viewed (13).

A **glossmeter,** shown in figure (5) is an instrument which is used to measure specular reflection gloss of a surface (Figure 6). Gloss is determined by projecting a beam of light at a fixed intensity and angle onto a surface and measuring the amount of reflected light at an equal but opposite angle (14).

Figure (5) A gloss meter

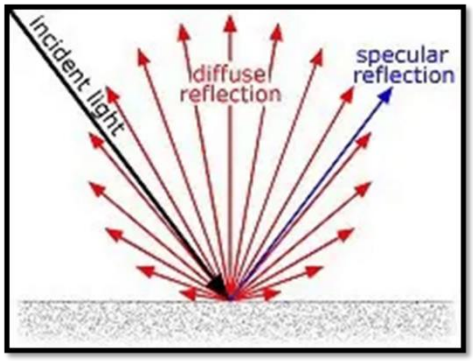

Figure (6) Diffuse Vs Specular reflection of light

3.1. Construction of gloss meter:

A typical glossmeter consists of a fixed mechanical assembly comprising a standardized light source that projects a parallel beam of light onto the test surface to be measured and a filtered detector located to receive the rays reflected from the surface (2), shown in figure (7).

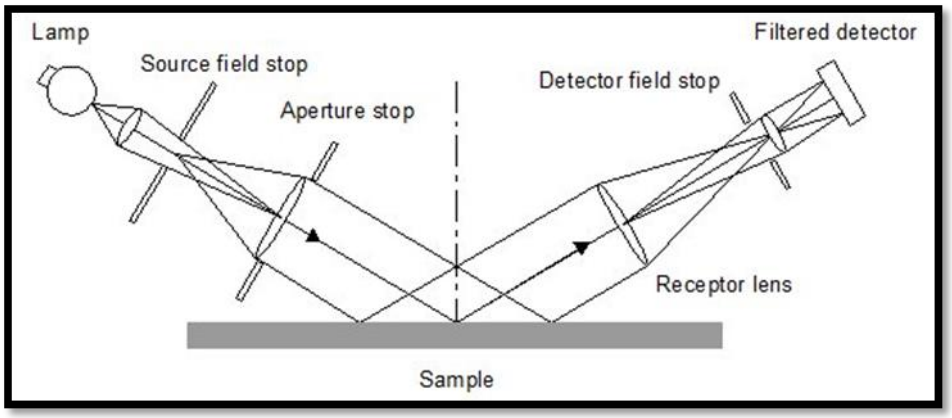

Figure (7) schematic diagram for a gloss meter

3.2. Instrument calibration:

The instruments are calibrated using reference standards that are usually made from highly polished, plane, black glass with a refractive index of 1.567 for the Sodium D line, and these are assigned a gloss value of 100 for each geometry (2).

3.3. Choosing the correct angle for gloss measurement

Measurement angle refers to the angle between the incident and reflected light. Three measurement angles (20°, 60°, and 85°) are specified to cover the majority of industrial coatings applications (15). The angle is selected based on the anticipated gloss range, as shown in the following table.

Gloss Range	**60° Value**	**Notes**
High Gloss	>70 GU	If measurement exceeds 70 GU, change test setup to 20°
Medium Gloss	10 – 70 GU	
Low Gloss	<10 GU	If measurement is less than 10 GU, change test setup to 85°

To determine the correct measurement, angle the surface should be assessed with the 60° geometry (15).

Matt surfaces which measure below 10 GU at 60°should be re-measured with the 85° angle (15).

High gloss surfaces which measure above 70 GU at 60° should be assessed using the 20° angle (15).

• The 60°degree angle is best employed on mid gloss samples 10-70 GU (15).

3.4. Understanding Gloss units

The measurement scale, Gloss Units (GU), of a glossmeter is a scaling based on a highly polished reference black glass standard with a defined refractive index having a specular reflectance of 100GU at the specified angle. This standard is used to establish an upper point calibration of 100 with the lower end point established at 0 on a perfectly matt surface. This scaling is suitable for most non-metallic coatings and materials (paints and plastics) as they generally fall within this range (16).

3.5. Advantages of Gloss meter (16):

Rapid measurement and instant reading.
Available in hand-held and bench-top types.
Wide varieties of materials can be tested.

3.6. Disadvantages of gloss meter (16):

It is not sensitive to common effects which reduce appearance quality such as haze and orange peel.
Haze is caused by microscopic surface structure which slightly changes the direction of a reflected light causing a bloom adjacent to the specular (gloss) angle. The surface has less reflective contrast and a shallow milky effect.
Orange peel is caused by an uneven surface formation of large surface structures distorting the reflected light.
Two high gloss surfaces can measure identically with a standard glossmeter but can be visually very different.

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