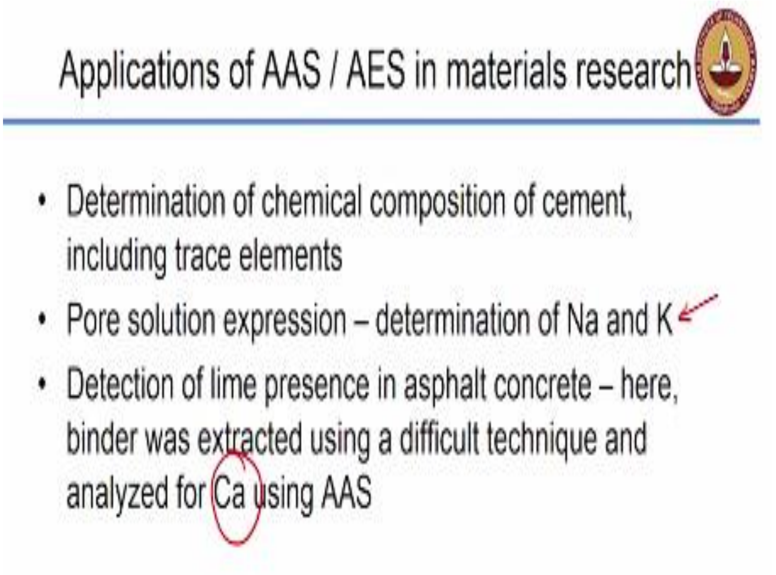
Characterization of Construction Materials
Prof. Manu Santhanam
Department of Civil Engineering
Indian Institute of Technology – Madras

Lecture – 54
Spectroscopy Techniques – UV and IR spectroscopy – Part 1

(Refer Slide Time: 00:12)



Applications of AAS / AES in materials research

- Determination of chemical composition of cement, including trace elements
- Pore solution expression – determination of Na and K
- Detection of lime presence in asphalt concrete – here, binder was extracted using a difficult technique and analyzed for Ca using AAS

Previously we were talking about how atomic absorption and emission spectroscopy can be conducted to analyze the composition as well as the content of different species that are present inside your cementitious samples. So, I was at the stage where I was going to explain the pore solution expression from cementitious pastes to try and understand the alkali composition inside cementitious pastes.

(Refer Slide Time: 00:41)

Extraction of pore solution from concrete

Paste cast in containers and cured in sealed condition

Pore solution extractor

Paste specimens are placed inside the mechanical press

200 - 400 MPa

Filter extracted solution in a syringe filter

Dilution

Pore solution (5- 10 ml possible)

Cold storage for ICP testing

Check pH of the solution

Characterization of Construction Materials

So, pore solution expression is something that only a handful of labs across the world do. The idea is simply to squeeze pore solution out of your cementitious paste or concrete at very high pressures to analyze the extent of sodium or potassium and other anionic species like hydroxyl or sulfate that are present inside your pore solution.

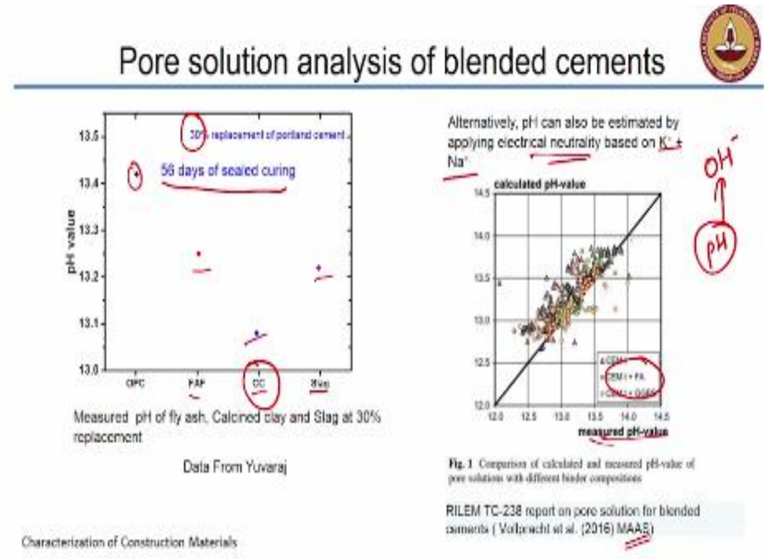
Now, the understanding of the pore solution composition helps us to understand how much free ionic species are actually available in the system; that has several connotations towards the durability aspects of the concrete itself. If you have a lot of conductive ions in the pore solution, that means the overall conductivity of the concrete is also going to be high. When conductivity is high, phenomena such as corrosion propagation will also happen in a much faster manner. One of the common things that we observe is when we replace cement with supplementary materials like slag or fly ash or silica fume, the performance in terms of corrosion propagation improves because the system becomes a lot more resistive. That means its conductivity is going to be lower than pure ordinary Portland cement systems. Now, that conductivity lowering is primarily because of the removal of alkalies from pore solution and the uptake of the alkalies in the hydrated supplementary cementitious material system.

So this experiment that I am showing you here is just a proof of that happening. So for this, the paste samples were cast in cylindrical containers and cured in a sealed condition. So these are the pastes here and water is actually on top to ensure that there is perfect curing happening of these cementitious paste samples. So at the required age, in this case of course 28 days, you remove the paste by breaking open the cylinder, remove the paste, and then you are putting your cylindrical specimen, inside this pore solution extractor.

So all these extractors are some sort of a die. It is a very compact die, you put your specimen inside this die and simply compress the specimen to such an extent that at very high pressures, the pore solution which is present inside the specimen or sample will be extracted out. So that is what is being done in this pore solution extraction. We apply pressures to the tune of 200 - 400 MPa to extract these pore solutions. Primarily, we are almost crushing your cementitious paste, but please remember this is not a uniaxial test, that means the specimen does not get compressed along only one direction, because the die being around the sample, when the sample gets compressed, it is not able to expand in the lateral direction. So, it is essentially undergoing more or less a triaxial sort of load. So, you are crushing it completely to extract the solution out, and if you are lucky, you will be extracting a few milliliters out of this specimen. And I am saying if you are lucky because for many of the specimens, you really have to go to very high pressures before you can actually get any pore solution out.

So, this pore solution is extracted in a syringe filter and you may want to actually dilute this pore solution to ensure that you have sufficient amount available for analysis. So 5 to 10 milliliters is possible, but sometimes we will be lucky to get 1 or 2 milliliters. So, sometimes we have to do dilution to get a larger fraction of the sample for analysis and what analysis can you do? One is obviously you can directly check the pH of the pore solution, pH gives an indication of the extent of alkalinity of your material. The other aspect is obviously you can store it for testing using inductively coupled plasma (ICP) to make out the extent of ionic species like sodium or potassium that is present inside this pore solution.

(Refer Slide Time: 04:44)



Pore solution analysis of blended cements

Measured pH of fly ash, Calcined clay and Slag at 30% replacement

Data From Yuvaraj

Alternatively, pH can also be estimated by applying electrical neutrality based on K⁺ + Na⁺

Fig. 1 Comparison of calculated and measured pH-value of pore solutions with different binder compositions

RILEM TC-238 report on pore solution for blended cements (Vollpracht et al. (2016) MAAS)

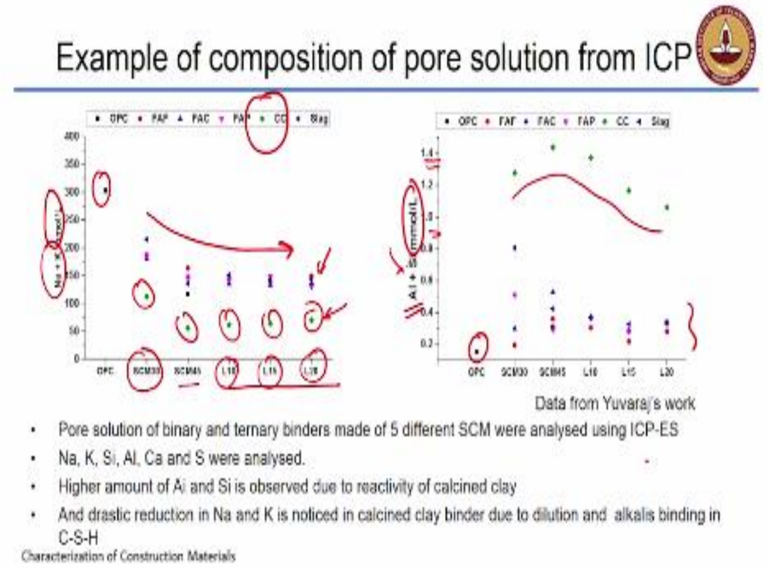
Characterization of Construction Materials

So, let us see the results for a set of cement pastes that were actually analyzed by Yuvaraj, one of my PhD students. So here what is shown is after 56 days of sealed curing, blended cementitious systems where 30% of the cement was replaced by the blending materials, in this case fly ash, calcined clay, and slag. So you can see the pH variation after 56 days. For plain OPC, the pH is around 13.4. For fly ash, it is about 13.25. For calcined clay, it is close to 13.1 and for slag it is about same 13.2, more than 13.2. So, you can see that the variation in pH is not significant, but nevertheless given that a difference of one in pH essentially means the difference of 10 times as far as hydroxyl ion concentration is concerned, because it is on a log scale. So, even a difference between 13.4 and 13.1 is fairly significant. However, lowered pH of the cementitious systems that employ very high reactive blending systems like calcined clay, even this lowered pH is not sufficiently low enough to cause corrosion of the reinforcing steel. Very often a common issue that you have to contend with is that people do not want to use blending materials especially like silica fume or calcined clay because they feel that they tend to completely consume the calcium hydroxide or portlandite in the system leading to a lowering of the pH, but experimental results have clearly shown not just here, but several other published experimental data clearly shows that the pH drop, although it is significant from the viewpoint of direct comparison with OPC, is not significant enough to really lead to any level of corrosion of the reinforcing steel.

Now, instead of determining the pH, you can also estimate the pH by applying electrical neutrality based on the composition of sodium and potassium that is present in your system. So, in your pore solution, at any given stage after a sufficient degree of hydration has taken place, the only species that will be available in appreciable amounts are sodium, potassium, which are the positively charged species and for balancing you need to have a negatively charged species, in this case will be OH^-. So when you apply an electrical balance to sodium and potassium using OH^-, you are obviously using that to determine the pH of your system. When you apply an electrical balance by OH^-, you know that $pH = \log [OH^-]$ or $-\log [H^+]$. So, the higher the OH^-, the higher will be the pH of your system.

So here, this is experimental data published in materials and structures for several different cementitious blends incorporating fly ash and slag. What is plotted on the Y-axis is the calculated pH value applying electrical neutrality and on the X-axis is the measured pH value, and you can see that the line of equality, most points are situated along the line of equality that indicates that applying this estimation based on electrical neutrality is significantly good as far as determination of pH is concerned.

(Refer Slide Time: 08:12)



Example of composition of pore solution from ICP

Data from Yuvaraj's work

- Pore solution of binary and ternary binders made of 5 different SCM were analysed using ICP-ES
- Na, K, Si, Al, Ca and S were analysed.
- Higher amount of Al and Si is observed due to reactivity of calcined clay
- And drastic reduction in Na and K is noticed in calcined clay binder due to dilution and alkalis binding in C-S-H

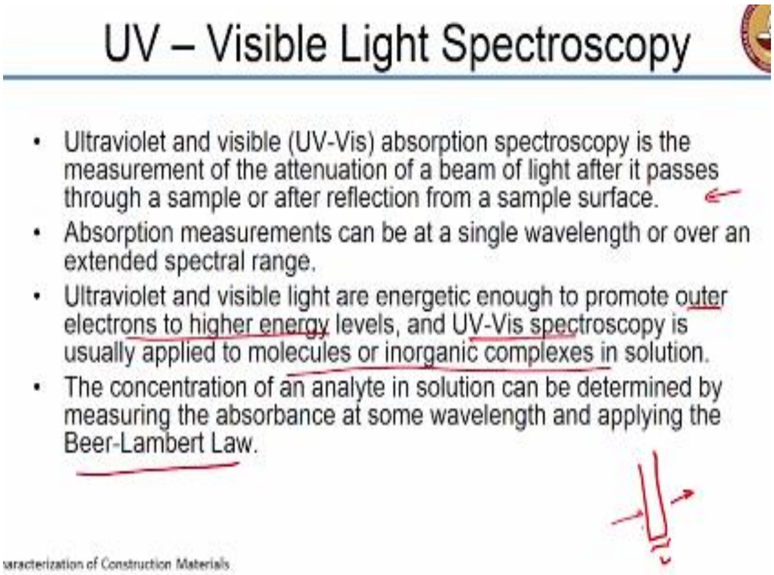
Characterization of Construction Materials

Now, again, this is pore solution extracted from different cementitious blends in Yuvaraj's study and again these were studied using ICP spectroscopy. So here, you can see the composition plotted on the Y-axis in terms of the total amount of sodium and potassium ions in solution. For OPC, it is about 300, but what you see is for all the blended cement systems, this concentration of the ionic species in solution is significantly lowered, especially for the case of highly reactive species; in this case it is calcined clay. Calcined clay is a very highly reactive aluminosilicate, which almost consumes all of your alkalis in the hydrated structure of the calcined clay product. Now, what you also have here are the supplementary cementitious materials like fly ash, slag or calcined clay at 30% replacement. Here, it is at 45% replacement. So, you can see the net lowering of the alkali concentration actually happening when you increase the extent of supplementary material. Now, these are cases where you have the supplementary material at 30%, but then you have extra amounts of limestone at 10, 15 and 20% added into the system to make it a ternary blended system. So, what you can clearly see is even for the ternary blended systems, there is a significant lowering of your alkali composition in the pore solution, especially for the cases that involve a very highly reactive aluminosilicate such as calcined clay. Now, because the aluminosilicate in calcined clay is highly reactive, there is also a greater tendency for the alumina and silica from the calcined clay to come into the pore solution.

So what is plotted here on the right side is the alumina plus silica concentration in pore solution and any system that involves calcined clay are the only ones which actually show significant quantities of alumina and silica in the pore solution, you do not really get that much from the other species, especially you do not get anything from the OPC because it is almost close to 0, in which case you do not really see much alumina and silica in the pore solution.

Now, please remember this is comparison in millimoles per liter (mmol/L). So, the relative concentration of alumina and silica is at the range of 1 to 1.4 even in the case of calcined clay, but here we are talking about Na + K, which is in 50s or 100s or 150s (mmol/L) range. So there is no comparison, that is why people do not typically measure the Al+Si in pore solution. People only measure typically the alkalis because alumina and silica is almost practically a trace element as far as the pore solution is concerned.

(Refer Slide Time: 11:01)



UV – Visible Light Spectroscopy

- Ultraviolet and visible (UV-Vis) absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface.
- Absorption measurements can be at a single wavelength or over an extended spectral range.
- Ultraviolet and visible light are energetic enough to promote outer electrons to higher energy levels, and UV-Vis spectroscopy is usually applied to molecules or inorganic complexes in solution.
- The concentration of an analyte in solution can be determined by measuring the absorbance at some wavelength and applying the Beer-Lambert Law.

aracterization of Construction Materials

So, an alternative technique to Atomic Absorption Spectroscopy or Atomic Emission Spectroscopy because it operates nearly at the same level is Ultraviolet-Visible Light Spectroscopy. Essentially, we do not apply this to solids directly, we actually apply it to soluble sort of materials where you can actually form a solution and measure directly the absorption or attenuation of ultraviolet visible radiation that passes through the sample.

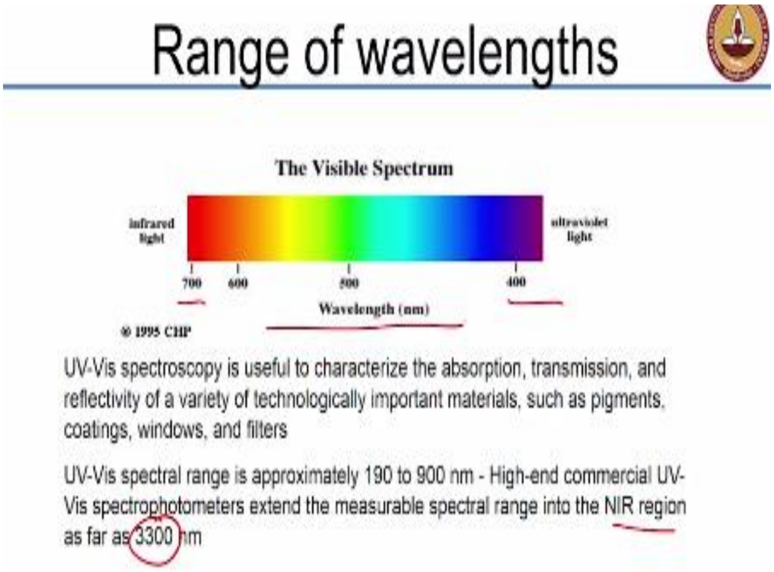
So, again here, the principle is the same. Measurement of attenuation of a beam of light after it passes through a sample or after reflection from the sample surface. Now, again, here you can set up your instrumentation in such a way that absorption can be measured either at a single wavelength, you can separate your radiation into different specific wavelengths and then measure absorptions of each or you can extend the range of wavelengths over which the entire study is being done by using appropriate polychromators.

So, just to repeat ultraviolet and visible light has an energy that is enough to promote outer electrons to higher energy levels. They do not really have the level of energy required to knock off inner shell electrons. So, outer shell electrons are loosely held and they can be transferred to higher energy levels by ultraviolet and visible light. Generally, we apply UV visible spectroscopy to molecules or inorganic complexes in solution. We are actually having these materials in solution rather than actually applying energy to desolvate and get these atoms into the gaseous phase, what we are simply doing is choosing materials that can form complexes in solution itself and analyzing the extent of the material with respect to the attenuation of ultraviolet-visible light.

In several cases, we come across measurements of turbidity. What happens in turbidity measurements, we take a clay or fine particulate matter and disperse it in water and measure how much light is actually reflected and prevented from crossing the sample. So, we can actually use that for particle size measurements. So, somewhat similar to that is ultraviolet-visible light spectroscopy, where we actually make solutions of the materials that we are trying to analyze and then look at what wavelengths of the ultraviolet-visible light are getting absorbed because of the presence of that element inside the solution. We can also get a reference analysis done by directly measuring the radiation passing through the solvent itself rather than having the solute also in place, we can just have the solvent in place and measure a blank sample. And that way we can actually understand how much is the concentration of this material inside the system.

Now, in this case, obviously, Beer-Lambert law can be applied because we know that our system is homogeneous with respect to a completely dissolved substance inside the solution. That means if you have a passage of light through this sample, you know exactly what length the passage occurs through and you also have an idea about the fact that the solution is uniform or homogenous. In the case of atomic absorption spectroscopy, we were not very sure of applying Beer-Lambert law because the path length was not certain. We also did not know how much atomization efficiency was there for the furnace that we used in the system. In this case, because you know that you are already forming a solution, you can actually use that for the measurement quite easily.

(Refer Slide Time: 14:41)



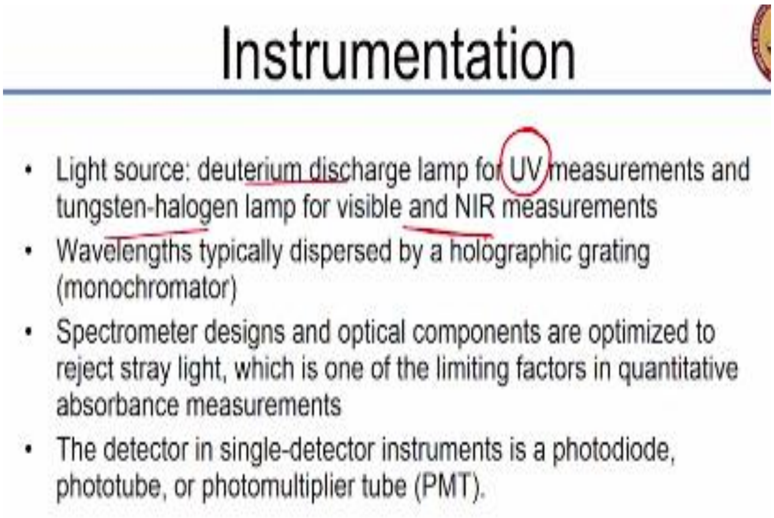
Range of wavelengths

UV-Vis spectroscopy is useful to characterize the absorption, transmission, and reflectivity of a variety of technologically important materials, such as pigments, coatings, windows, and filters

UV-Vis spectral range is approximately 190 to 900 nm - High-end commercial UV-Vis spectrophotometers extend the measurable spectral range into the NIR region as far as 3300 nm

So the range of wavelengths as I said, it is UV-visible range, so we are talking about 700 nm, which is the far end of visible range to less than 400 nm, which goes into the ultraviolet light range. So in some cases, high-end UV-visible spectrophotometers can actually go as far as the Near Infrared Region (NIR), nearly 3300 nm. They can actually go to as high as 3300 nm; but of course, we are more interested in the smaller wavelengths because that is where we get the better resolution with respect to elemental analysis.

(Refer Slide Time: 15:17)



Instrumentation

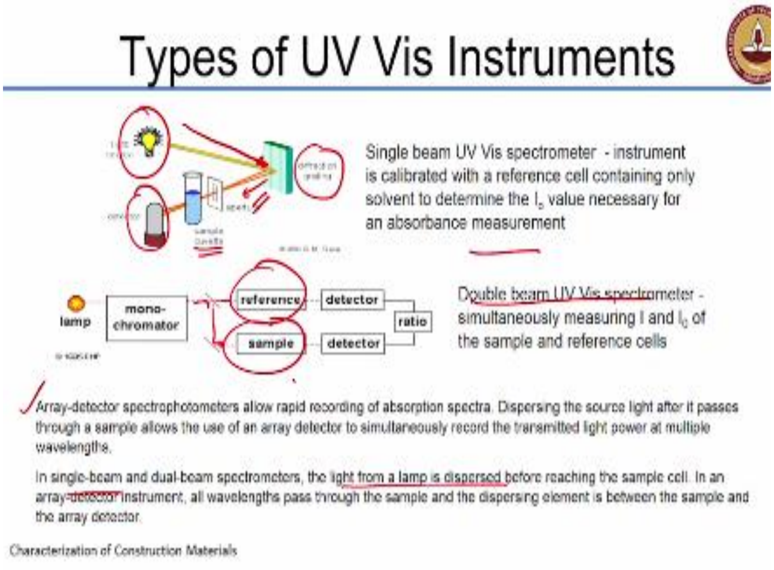
- Light source: deuterium discharge lamp for UV measurements and tungsten-halogen lamp for visible and NIR measurements
- Wavelengths typically dispersed by a holographic grating (monochromator)
- Spectrometer designs and optical components are optimized to reject stray light, which is one of the limiting factors in quantitative absorbance measurements
- The detector in single-detector instruments is a photodiode, phototube, or photomultiplier tube (PMT).

So, what instrumentation is there is it is quite similar to what you have with Atomic Absorption Spectroscopy. So, the light source in the case of atomic absorption was a hollow cathode lamp. In this case, we have a deuterium discharge lamp, basically that gives out ultraviolet radiation or you can also have a tungsten-halogen lamp, which is mainly more towards the infrared sort of wavelength. So, if you want to cover a range of wavelengths, then you need to actually employ the kind of discharge lamp which gives you the right level of radiation wavelength.

Wavelengths are typically dispersed by a holographic grating, which is nothing but a monochromator. So, obviously, the radiation is composed of several different wavelengths. What we need to do is send a specific wavelength through the sample, so that is basically your monochromator.

Spectrometer designs and optical components are optimized to reject the stray light. Now please remember in this entire system because we are operating in the visible range, there is always going to be interference from stray light, which is coming from elsewhere, not directly from this radiation source. So, you need to design your system carefully so that the stray light is not allowed to get through the sample. And detector, again is quite similar to what you had in the case of Absorbance Spectroscopy, it is a photodiode or photomultiplier tube (PMT).

(Refer Slide Time: 16:37)



Types of UV Vis Instruments

Single beam UV Vis spectrometer - instrument is calibrated with a reference cell containing only solvent to determine the I_0 value necessary for an absorbance measurement

Double beam UV Vis spectrometer - simultaneously measuring I and I_0 of the sample and reference cells

Array-detector spectrophotometers allow rapid recording of absorption spectra. Dispersing the source light after it passes through a sample allows the use of an array detector to simultaneously record the transmitted light power at multiple wavelengths.

In single-beam and dual-beam spectrometers, the light from a lamp is dispersed before reaching the sample cell. In an array-~~detector~~ instrument, all wavelengths pass through the sample and the dispersing element is between the sample and the array detector.

Characterization of Construction Materials

So, I will just show you again the instrumentation here (shown in figure), that is the light source. Your light passes through this holographic grating to ensure that you are able to separate out wavelengths. The aperture enables that you are perfectly pointing your beam to the sample directly. This is a sample cuvette, it is nothing but it is similar to a test tube essentially in which you have the sample, which is dispersed in a solution and then you have a detector on the other end.

Now, I said earlier that the sample cuvette can be made to have a blank sample also. That means only the solvent is used, so that becomes your reference and then you have the other system with your sample. So, what you need to do is take the UV spectroscopy through the reference material, then take it again through the sample which is dissolved in the reference material and then do a comparison to determine what should be the radiation absorbed by the specific species that are present inside your sample.

So, you can either have a single beam UV-visible spectrometer in which case you need to keep the sample cuvette just having the solvent first and then the sample cuvette where the sample is dispersed in the solvent or a double beam spectrometer, where what you are simply doing is splitting the beam into two, so one goes directly to the reference and one goes to the sample and measure both simultaneously. So, that is called a double beam UV-Visible spectrometer. So most high-end spectrometers would be double beam spectrometers, but today we also have the array-detector spectrometers. So, here you do not necessarily need to break the wavelength into specific ranges. So, you can actually have the entire beam passing through the sample and analyze all the wavelengths that are getting absorbed or transmitted through the sample. So, that is basically array-detector spectrometers. So, there are different ranges. The earliest ones were the single beam, then you had the double beam and today we have the array detector. So, again here, in single and dual beam spectrometers, the light from the lamp is dispersed. That means, it is broken into specific wavelengths before it reaches a sample. In the array-detector spectrometers, it directly comes to the sample, so that you analyze all the wavelengths at once.