Mechanical Characterization of Bituminous Materials

Dr. M. R. Nivitha
Assistant Professor
Department of Civil Engineering
PSG College of Technology, Coimbatore

Lecture No 17
Chemical composition of bitumen Part-01

Today in this lecture, we are going to talk about the chemical composition of bitumen. So what do we understand by this term chemical composition. This is a very commonly used term right? So we go into the characterization of any material, we try to understand its chemical composition. So what does this term chemical composition mean? So this says what the material is composed of. What are the different elements that are present in this material and how are they arranged.

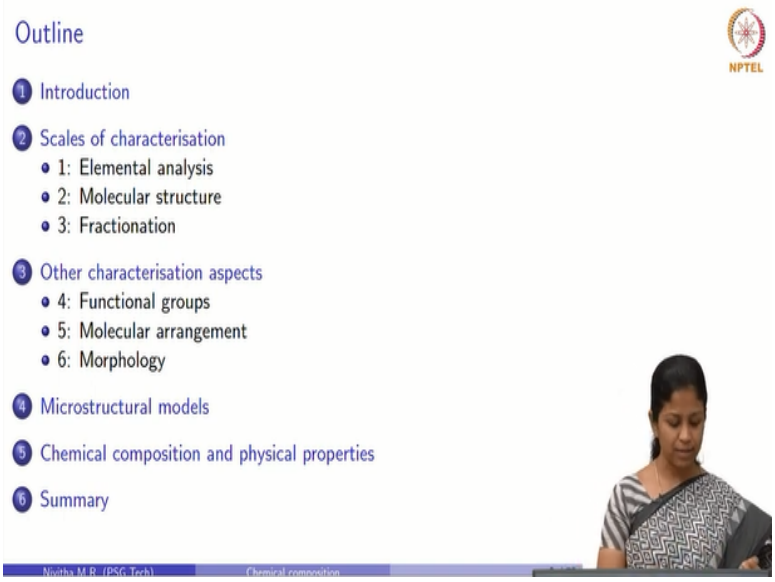
So why is that we are interested in studying the chemical composition of any material, including bitumen. So ultimately, we know that how a material behaves in a certain manner is because of what the material is composed of. So we need to understand the chemical composition of bitumen to relate it to how its performance is there in the field. This is very simple to say, but very difficult to perform as far as bitumen is concerned.

This is because of the highly complex chemical composition of bitumen, so I will tell you why it is highly complicated. Bitumen is not a designed material. If we want a material for a specific purpose, we design it for that particular purpose. Say for example, we want to design a polyethylene bag. So we know that it is used to carry weight till a particular range. So we say this is the property that I want. So I decide how many links should be there in that particular polyethylene chain, so that I will get a material of this particular property. I will also decide in what form it should be present. We know that polyethylene is CH_2, n number of CH2 arranged in a specific form. So I know that it has only CH_2, and I know what is that n there. I also know how it is arranged so that it will form a polyethylene bag with specific properties.

So this is possible for many designed materials, but bitumen is not a designed material. So in previous lectures, you know that how bitumen is produced. So it is a residue which we get from the refinery processing. So we do not have any control over the properties of this

residue. So this is the factor which makes the chemical characterization of bitumen, very complicated and very interesting.

(Refer Slide Time: 02:36)



So I will tell you what we are going to focus in this lecture. First I will introduce you to the chemical composition, some basics related to chemistry, which we will be using frequently in this particular lecture. Then we will also talk about the different scales of characterization, so we can represent the elemental composition at different scales. We can say what the material is composed of in terms of its elements, right? We can also say how these elements, join together to form molecules, and then a higher level of quantification how different molecules of identical nature, I will put identical within quotes at this point of time, because there is nothing identical we can define in bitumen, but based on a specific property, we can say these molecules will behave in an identical manner.

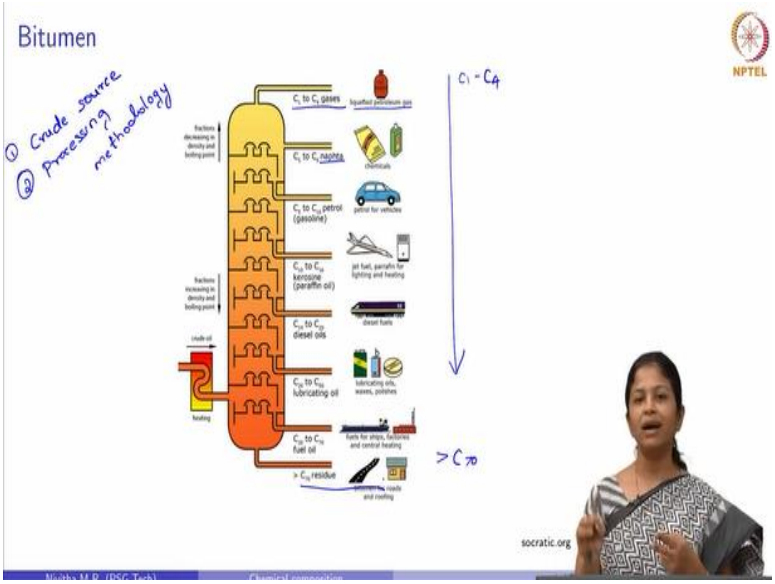
So that is the third technique we are using here. We also have other characterization techniques which focus on specific aspects of bitumen. If we want to extract a specific information then we have separate techniques for that. And then we will see some micro structural models. The information we are discussing in section two and section three are mostly experimental based.

Whereas what we are going to discuss in Section four are hypothetical models and some studies which are trying to verify those models. Finally, we will relate chemical composition to physical properties because ultimately, that is what we are interested in as pavement engineers. We want to see how the pavement behaves in a certain manner, and how the chemical composition of bitumen is going to influence it.

And finally, we will summarize. So in this lecture, we are going to divide this topic into three lectures in the first lecture will discuss about the introduction, and in the scales of characterization, I am going to focus on the elemental analysis, and the molecular structure. In the second lecture, I will focus on fractionation techniques and other characterization aspects for bitumen.

And in the third lecture, we will discuss about the microstructure models, chemical composition and its relation to physical properties, and then finally, we will summarize.

(Refer Slide Time: 04:49)



So to begin with in the introduction, so this figure you know right? This is the refinery processing of bitumen. So you should have discussed about this in detail in the lecture related to the refinery processing. So we know how bitumen is produced from crude oil. I will just do a small recap here to touch upon some important aspects which we will be using in this particular lecture.

So we know that bitumen is produced from the fractional distillation of crude oil. So we have crude oil, we take this crude oil put it in a distillation column. So we start getting lighter fractions. Again, we know that we have two types of distillation initially we start with an atmospheric distillation then we do a vacuum distillation, and finally the residue what we get is bitumen.

So if you do a distillation, there are different fractions coming up at different times. So first what we get is the lighter fractions with a carbon number from C_1 to C_4. So what is this carbon number here? When I say C_1, it is a molecule containing 1 carbon atom. When I say

C_4, it is a molecule containing 4 carbon atoms. So the first phase which is mostly liquefied petroleum gas, we have molecules, whose carbon number is from C_1 to C_4.

So very small molecules, only maximum of four carbon atoms attached together in a row. The next fraction is naphta, so here the carbon number is from C5 to C9. Then we get petrol which is used for vehicles. And then we also get kerosene, diesel oil, lubricating oil, fuel oil, and finally the residue. If we look at the carbon number we can see the carbon number keeps increasing as we come down.

So initially it starts from C_1 to C_4 and finally, when we come to bitumen, we have something which is C_{70}. So what do we mean by C70 here and they also mentioned it is greater than C_{70}. What do we mean by C_{70} here, which means that we have more than 70 carbon atoms attached in a single molecule. So you can imagine how big the molecule will be right? So we will focus more about this and how they influence the number of isomers in bitumen in the subsequent lectures.

So this is one factor related to the complexity of molecules which is present in the residue. There are two variables, which will highly influence the chemical composition of bitumen from the refinery perspective; the first one is the crude source. So we process crudes from different origin, right? Depending upon the origin, the properties of crude is going to vary. If we take a highly mature crude its chemical composition will be something different compared to a low crude of low maturity.

So depending upon the crude the properties are going to vary but we do not have any control over the properties of crude because in the refinery processing the lighter fractions are of predominant importance and crudes are selected to give maximum profit by extracting more amount of lighter fractions. So we do not have any control over the crude source that we get here.

So that is the first factor which is contributing to the variability in chemical composition. The second factor is processing methodology; we know that this vacuum residue what we get here right? This has to be post processed to get bitumen of specific grades. So we take this bitumen subject it to different post processing methods. So you know that in India, at least two different post processing methods are used.

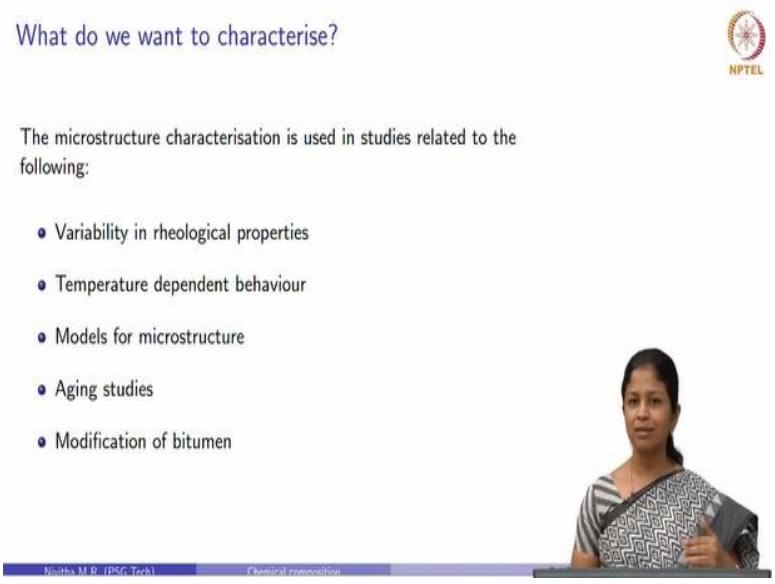
One is air rectification or partial air blowing, the other one is blending component blending. So these are two different processes which are used in India, there can be various other

processes also. So depending upon the processing methodology, the properties of the bitumen what we get are going to vary. So ultimately, I can have bitumen of a specific grade, but with entirely different chemical composition.

So in India we know that we are following viscosity grading system. We have four grades of bitumen VG 10, VG 20, VG 30 and VG 40. It is not necessary that two bitumen classified as VG 30 have to behave in identical manner, because these two bitumen can be produced from either two different crude sources, and it can be subjected to either of these two processing methodologies.

So depending upon where the bitumen comes its chemical composition is going to vary and this variation is further aggravated depending upon the processing methodology. So this is the first fact that we have to take into consideration when we are trying to characterize this material. So two bitumen classified under the same grade need not exhibit identical behaviour.

(Refer Slide Time: 10:01)



So when we want to characterize this material, we need to see what we want to characterize right? There are different perspectives, for which we need to characterize this material. There are different applications related to the characterization of bitumen, so I have listed some of the commonly used applications for micro structure characterization. The first one is variability in rheological properties.

Like I said earlier we have two bitumen of the same grade but when I put them in the field both of them are not going to give me the same design life, one might experience a say

example rutting in five years, the other might experience rutting in seven years. So we need to understand why this happens. So then we start coming down looking at the material at lower scales.

So then when you try to characterize the chemical composition, we might get some information, which can tell us why this material is behaving in a different manner, compared to the other right. So this is what is desired but this link is not fully established at this point in time. So we are trying, reworking and refining this link continuously as far as bitumen is concerned. So this is the first aspect for which we want to characterize the chemical composition, try to say why two bitumen behave in a different manner.

The second one is temperature dependent behaviour. Let us take two bitumen again classified under the same grade or if I measure some physical properties, they are going to show identical values. But when I look at the temperature dependent behaviour, the stiffness of one material can drop drastically compared to another material. So this is called as temperature susceptibility.

The manner in which, the stiffness of the bitumen varies with temperature. So we want to see how this temperature susceptibility varies for different bitumen and you know that we do not want this temperature susceptibility to drop as drastically as we see in some cases, we want that to be a gradual change. If it drops drastically we know that we are going to experience rutting at high temperatures and also fatigue cracking at low temperatures.

So we want to see why temperature susceptibility is high for some binders, whereas it is poor for some binders. So there are some studies which are available in this regard. People have measured the wax content in bitumen, and they have said that bitumen with higher wax content tend to have poor temperature susceptible properties. So that is another aspect, where this micro structure characterization and understanding its chemical composition is important.

Third one is models for micro structure. So if you want to model the micro structure of bitumen and try to predict its rheological response using this model, we want to say what this material is composed of, how it is present at the molecular level and higher up the ladder. So for this purpose we need to develop some models for micro structure and whatever model is hypothesized, we need to verify those models. So for that purpose we need to characterize its chemical composition at different scales.

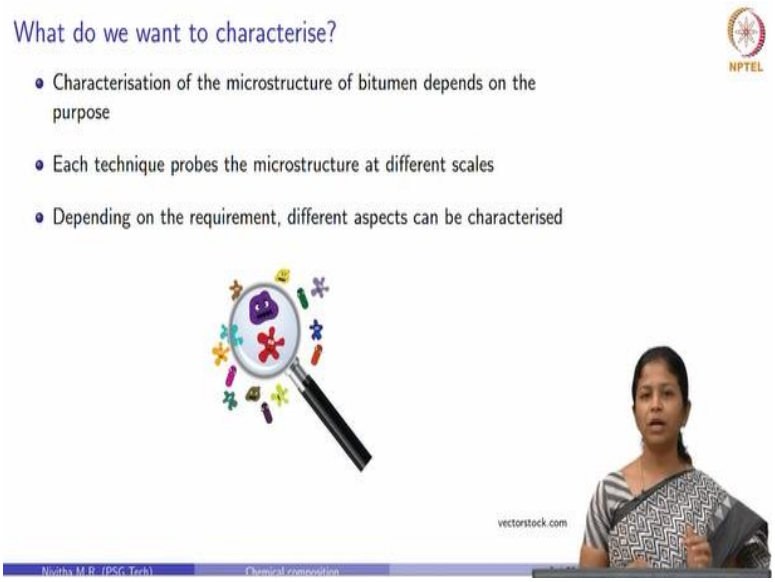
And the fourth application is aging related studies. So in subsequent lectures we will understand what aging is and how chemical composition is important in aging related studies. There are formation of oxides in bitumen when it is subjected to aging; aging is nothing but exposure of bitumen to environmental conditions. So this forms some irreversible compounds in this material which will increase its stiffness.

Again different bitumen can age in different manner and different functionalities present in each of them will influence how each bitumen ages. So again for those studies we need to quantify the components of aging at the chemical composition level. And finally we have modification of bitumen. So for today's traffic levels and increased load repetitions, we need materials with improved properties to withstand the wheel load and to serve for a longer design life.

So for that purpose we add some materials to bitumen to improve its properties. So those are called as modifiers. So when we want to add modifiers to bitumen, we need to say, what is the specific improvement in property we are desiring and for that we need to design these modifiers. So for that purpose we need to understand what these modifiers are, what is its chemical composition, how it interacts with some functionalities present in bitumen.

So again for that we need to look at this modified bitumen from the micro structure level. So these are some of the very commonly used applications. There are n number of other applications for which the micro structure characterization is important, but in this lecture I will just limit to these five topics.

(Refer Slide Time: 15:04)



When we want to characterize bitumen, so previously we had said we are seeing some five different cases, right? So can I use one particular technique to characterize the micro structure for each of these five applications? It does not work that way for bitumen. So depending upon the purpose for which I am trying to characterize, I need to use different techniques. So each technique focuses some aspect of this material.

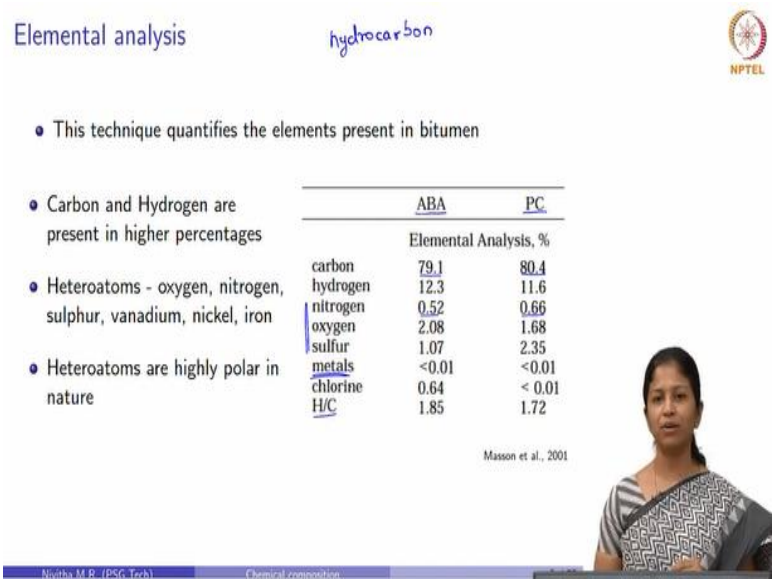
It is like seeing an elephant, if you touch the front trunk right? We will feel it like a snake. So this is a very commonly used example. So if you touch some other part we will feel it like something else. So similar is the case for bitumen. Depending upon what technique I am going to use, I am going to see different representations of the microstructure. So if I want to use aging studies, I am going to identify functionalities.

If I want to use modifiers for bitumen, the Corbett fraction is most commonly referred. I will tell you what these are in the subsequent slides. So depending upon what we want to see from this material, we have to choose appropriate techniques. So that is the foremost information as far as characterization of chemical composition is concerned.

(Refer Slide Time: 16:16)

Now we will move on to the scales of characterization. We are characterizing this material at three different scales, like I said earlier. First we will start with the elemental analysis.

(Refer Slide Time: 16:27)



Elemental analysis says what this material is composed of at the elemental level. So we have different elements which are present in bitumen. I have shown you an example here of bitumen from two different sources. The first one is ABA and the second one is PC. So these are bitumen from two different crude sources. Let us see how the elemental analysis varies for each of these two bitumen.

Let us start with carbon, so carbon is the primary component which is present in bitumen. So we have carbon content of around 80% which is present in bitumen. We can see that the carbon content is approximately similar for these two types of bitumen. The next higher component is hydrogen, so we have hydrogen present about 12, 11 to 12 %. Again you can see the hydrogen content of these two bitumen is close.

So these are the two primary elements which are present in bitumen. That is why we call bitumen as a hydro carbon, hydrogen and carbon. Bitumen is called as a complex hydrocarbon. I will mention it here, because if you look at some literature related to bitumen they'll call it as hydrocarbon. The next set of elements are nitrogen, oxygen, and sulphur. These are called as hetero atoms, right?

Different types of atoms. That is why they are called as hetero atoms. So the more commonly occurring hetero atoms in bitumen are nitrogen, oxygen, and sulphur. So we have nitrogen content of about 0.52 to 0.66 %, oxygen around 1.68 to 2.08 %, and sulphur from 1 to 2.5 %. These are present in different proportions. Now they are present in very small concentration compared to carbon and hydrogen.

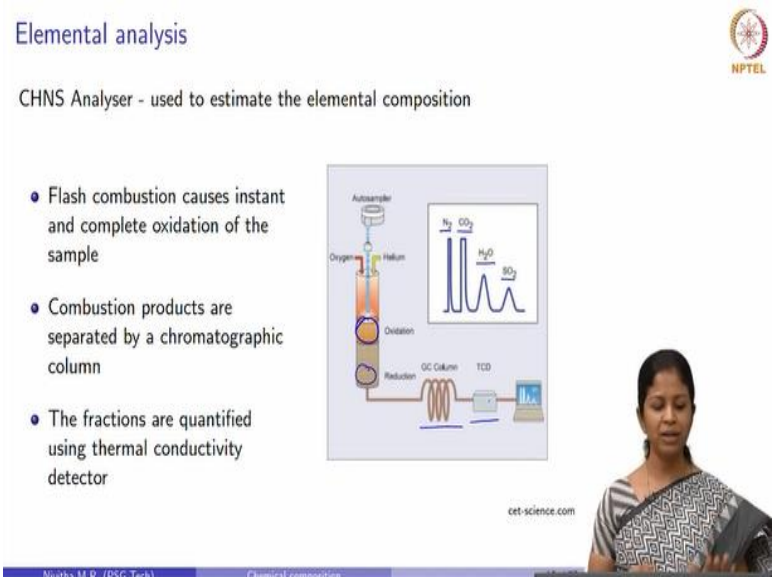
We civil engineers have this tendency to ignore materials which are present in very small percentage; we say very, very small - it can be neglected. But that is not the case as far as these hetero atoms are concerned. This is because these hetero atoms are highly polar in nature. So what do I mean by polar, polar materials are those which are highly reactive. So these hetero atoms form as points at which strong interactive forces are developed between different molecules.

So these hetero atoms though they are present in very small percentages, they have a higher influence on the properties of bitumen. So these two crude sources have different proportions of these hetero atoms and their physical properties are going to be completely different. Next we have metals of very small percentages and we also have chlorine with different concentrations in these two crude sources.

These metals again, they are present in very small concentrations in the order of ppm, few parts per million. But again, these metals are even more highly reactive than these hetero atoms. They form metal porphyrins. So what these porphyrins are? They are like big, complex molecules formed because of the high reactivity of these metals. So again, the concentrations of these metals are also very important.

And finally, they have quantified something as a hydrocarbon ratio. The ratio of hydrogen to carbon. This hydrocarbon ratio is very important because it says how many large molecules are present in my material. So I will tell you, I will give you an example about this hydrocarbon ratio, when we discuss the next slide.

(Refer Slide Time: 20:21)



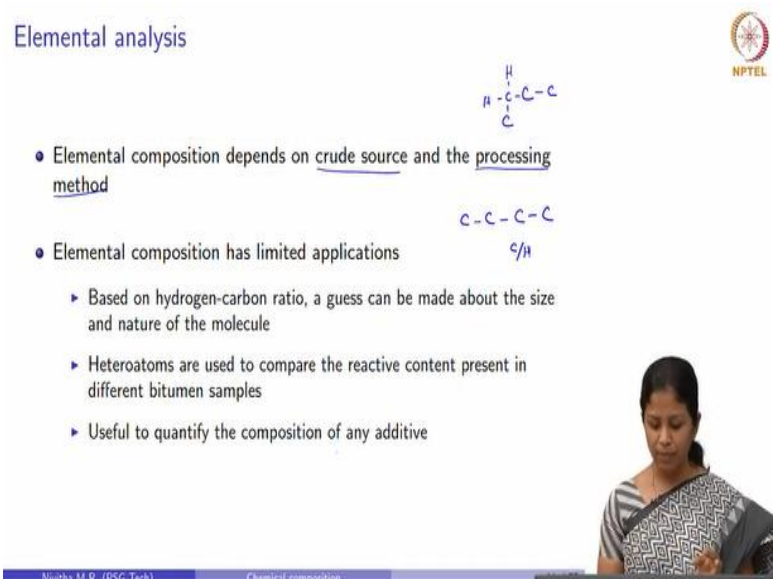
Next we will move on to how to measure this elemental analysis. So this elemental analysis is measured using a CHNS analyzer Carbon, Hydrogen, Nitrogen and Sulphur. These are the four elements which are measured using this particular analyzer. So how this technique works is we have bitumen which is placed in an oxidation column. So in this oxidation column, there is continuous supply of oxygen, so that all these four elements are completely converted to their oxides.

So if we have carbon, this carbon is completely converted to carbon dioxide. If we have hydrogen, the hydrogen is completely converted to H_2O. Similarly nitrogen and sulphur. Nitrogen is N2 and sulphur is sulphur dioxide. So all of them are completely converted to their respective oxides. So these oxides are now passed through a gas chromatographic column. So what does chromatographic column does is it separates all of them into different fractions.

Because at this point all of them are going to be present in a mixture form, so we need to first separate them. So this separation is performed using a GC column. So in the subsequent slides, I will tell you what a chromatographic column is and how we can separate different components of a mixture using this GC column. Then there is a thermal conductivity detector. So based on the conductivity, it measures, what is the type of oxide and what is the quantity of oxide that is passing through this TCD.

So using these two, we are able to quantify what is the proportion of each of these elements that are present in bitumen. Again for metals and oxygen, we have some other technique, but at this point of time I will not get into those details. So to quantify the major elements which are present in bitumen, the CHNS analysis will be sufficient.

(Refer Slide Time: 22:20)



So what is this application of this elemental analysis? This has very limited applications as far as bitumen is concerned, it is very useful when we try to understand the hetero atom content which is present in bitumen and metal content which is present in bitumen. To see whether bitumen with higher metal content is showing higher viscosity or higher reactivity to certain conditions.

So in these those applications we will use this information. Again we need to ensure that this elemental composition is going to depend upon crude source and the processing method, like we discussed earlier. And then the application wise - the first one is the hydrocarbon ratio. So if I take a molecule with a large number of hydrogen atoms, then it means that it is a smaller molecule.

Because when we draw the structure, we have number of carbon atoms, carbon which is present something like this. Now if this carbon or if this hydrogen is replaced with another carbon atom and again this hydrogen is replaced with another carbon atom and again here we have another carbon atom the molecule gets bigger. So the number of hydrogen atoms required to meet the 4 carbon number is very less.

So when we have a higher carbon to hydrogen ratio, which means that the hydrogen atoms are lesser the carbon number is high, the carbon atoms are higher. So this is going to tell us some information about the size of the molecule. The next information is hetero atoms: hetero atoms are used to compare the reactive content. Like I said earlier, we are going to use this information to compare reactivity of different bitumen samples.

The third one is, it is used to identify any additive which is present in bitumen. So we have bitumen of a specific chemical composition we are adding some other additive. So we need to quantify what are the elements which are present in that particular additive and how that element is going to interact with bitumen. Is there any new element that is formed or is there any change in the form of these elements?

So to identify all such information, we will be using the elemental composition information. So this is the applications as far as elemental analysis is concerned.