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#### Lecture – 58 Analytical Techniques for Assessing Soil Pollution Continued

Welcome friends to this third lecture of module 12 of this NPTEL online certification course of environmental soil chemistry. In this week, we are talking about different analytical techniques for measurement of pollutants in the soil. So, in the previous 2 lectures, we have covered some instruments and some analytical techniques for measurement of inorganic and total nitrogen.

Also we have started with the determination of inorganic phosphorus. For determination of inorganic phosphorus, we have discussed the Mehlich extractant and we started with discussion of the ICP-AES or inductively coupled plasma atomic emission spectrometry and now we are going to discuss the principle and other important aspects of ICP-AES.

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# **Determination of inorganic pollutants**

#### Instruments for Inorganic P

#### 1. ICP-AES-principle

Excited electrons emit energy at a given wavelength as they return to ground state after excitation by high temperature Argon Plasma. The fundamental characteristic of this process is that each element emits energy at specific wavelengths peculiar to its atomic character. The energy transfer for electrons when they fall back to ground state is unique to each element as it depends upon the electronic configuration of the orbital. The energy transfer is inversely proportional to the wavelength of electromagnetic radiation



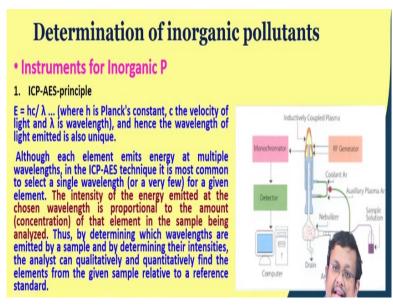
So, the principle of ICP-AES basically depends on some excited electrons. Now, the excited electrons, I mean when we excite the electrons of a compound or an any element by some external sources, in this case this is basically argon plasma. So, these excited electrons emit energy at a given wavelength as they return to the ground state after excitation by high temperature argon plasma.

So, what happens when we energize the electrons of a compound by the high temperature of argon plasma? The electrons basically go to the higher orbitals or excited states and when they come back to the ground state after excitation, they emit some energy at given wavelengths. Now, the fundamental characteristics of this process is that each element emits energy at specific wavelengths particular to its atomic character.

So, the wavelength at which these elements emit the light is very much wavelength specific and also depends on its atomic character. So, the energy transfer for electrons when they fall back to the ground state, you know when they fall back to the ground state is unique to each element as it depends upon the electronic configuration of the orbital and the energy transfer is inversely proportional to the wavelength of electromagnetic radiation.

So, the energy transfer is less if the wavelength is high and vice versa. So, this is basically the principle of the ICP-AES on which it works. Now, we all know that the excited electrons when they move back to their ground state, they emit some energy at specific and this energy emission goes at a particular wavelength of light.

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Now, you all know this equation that is E = hc by lambda where h is Planck's constant and c is the velocity of light and lambda is the wavelength. So, the wavelength of light emitted is also unique and this is the principle of working for ICP-AES okay. Now, although it is very important to remember that each element emits energy at multiple wavelengths, in the ICP-AES technique, it is most common to select a single wavelength or a very few of wavelengths for a given element.

Now, the intensity of the energy emitted at the chosen wavelength, for example we have selected a specific wavelength or a group of wavelengths, so we measure the intensity of the energy that is emitted when the excited electrons come back to their ground state. So, when the excited electron comes back to their ground state, they emit the energy and the intensity of the energy emitted at the chosen wavelength is proportional to the amount of or the concentration of that element in the sample being analyzed.

So, depending on the concentration, the intensity of the energy emitted will also vary. So, if there is a high concentration of that particular element in that sample, then the intensity of the energy emitted will be higher. So, thus by determining which wavelengths are emitted by a sample and by determining their intensities, the analyst can quantitatively and qualitatively find the elements from the given sample relative to a reference standard.

So, when we measure a reference standard and when we see the particular wavelengths at which we are getting the emitted energies and also their intensities, we can measure which element is present and what is their concentration. So, this is basically the principle of ICP-AES. This is a very sophisticated technique and this is also very precise, dynamic and very accurate technique.

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# **Determination of inorganic pollutants**

#### Instruments for Inorganic P

1. ICP-AES-principle

The wavelengths used in AES ranges from the upper part of the vacuum ultraviolet (160 nm) to the limit of visible light (800 nm). As borosilicate glass absorbs light below 310 nm and oxygen in air absorbs light below 200 nm, optical lenses and prisms are generally fabricated from quartz glass and optical paths are evacuated or filled by a non absorbing gas such as Argon.



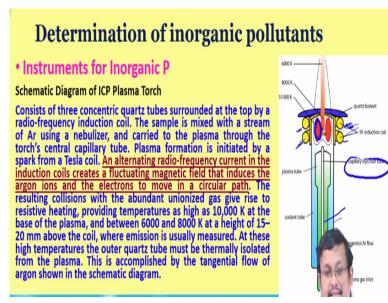
Now, the wavelengths used in atomic emission spectrometry or this ICP-AES ranges from the upper part of the vacuum ultraviolet that is 160 nanometer to the limit of visible light which is around 800 nanometer in the total electromagnetic spectrum. Now, as borosilicate glass

absorbs light below 310 nanometer and oxygen in air absorbs light below 200 nanometer, optical lenses and prisms are generally fabricated from quartz glass.

And optical paths are evacuated or filled by non-absorbing gas such as argon because if there is a presence of oxygen, there will be absorption of light. So, that is why they are either evacuated or filled by non-absorbing gas like argon. So, this is a picture of this ICP-AES instrument as you can see and this ICP-AES instrument is also very, very costly instrument and it is a standard gold method for measurement of different elements.

And these instruments you can see in all the standard environmental soil chemistry or soil chemistry laboratory or soil fertility laboratories. There is another variant of ICP that is called ICP-MS and we will discuss this ICP-MS in the later course of this module. So, this is the picture of ICP-AES.

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Now, why it is called ICP? Why it is called inductively coupled plasma? So, to understand the reason behind this name, we have to see the schematic diagram of ICP plasma torch and how it operates. So, this picture basically shows this diagram of this ICP plasma torch and as you can see here this consists of 3 concentric quartz tubes surrounded at the top by a radiofrequency induction coil.

So, here you can see there are 3 concentric quartz tubes okay. At the middle there is a sample, you know this is basically a capillary injection tube and after that there is a plasma tube and at the outermost there is a coolant tube okay. So, there are 3 concentric quartz tubes

surrounded at the top by a radiofrequency induction coil. So, this is the radiofrequency induction coils. The sample is mixed with a stream of argon.

So, the sample is being basically injected mixed with the stream of argon using a nebulizer. You remember we have talked about the nebulizer in the construction of this ICP. So, basically this sample is mixed with a stream of argon because it is inert in nature using a nebulizer and then carried to the plasma. So, this is the plasma as you can see here, carried to the plasma through the torch's central capillary tube.

So, this white is the central capillary tube as you can see. So, this sample aerosol is basically injected towards this plasma by this capillary injection tube and plasma formation is basically initiated by a spark from a Tesla coil. Now, an alternative radiofrequency current in the induction coils creates a fluctuating magnetic field. So, you can see they are the radiofrequency induction coils, this is the radio frequency induction coil.

So, an alternative radiofrequency current in this induction coil is generated which creates a fluctuating magnetic field that induces the argon ions and the electrons to move in a circular path. So, there will be a circular path of motion of this argon gases and also the electrons, and when there is a movement of these argon gas, so as a result there will be collision with the abundant unionized gas give rise to resistive heating.

So, what happens? There is a Tesla coil, so plasma formation is initiated, you can see that argon is injected in this plasma tube and this plasma formation is initiated by a Tesla coil and an alternative radiofrequency current is generated in this radiofrequency induction coil which induces these argon ions which are present in this plasma tube basically to rotate with the electrons.

And as a result of these rotation, there is the resulting collision with the abundant unionized gas which gives rise to the resistive heating providing temperature as high as 10,000 Kelvin at the base of the plasma. As you can see here at the base of the plasma the 10,000 Kelvin temperature is there and between 6000 to 8000 also you can see at height of 15 to 20 millimeters above the coil where emission is usually measured.

So, basically this high temperature is helping the sample or the element which are present in this aerosol to completely energized and completely ionized. This is the reason that this high temperature plasma is being generated. Again, there are three concentric rings and in this concentric ring, the middle, the innermost ring basically is the capillary injection tube which basically generates the sample aerosol mixed with argon gas.

And also there is another concentric ring where the plasma where the argon flow tangentially and also there is a coolant tube. So, basically the argon is introduced to create the plasma. The plasma is being created by igniting it with the Tesla coil and creating a circular flow of this argon by inducing a current radiofrequency current in the radiofrequency coil and there is a resistive collision with the unionized gas creating high temperatures.

This plasma and this high temperature help in the complete evaporation or complete dissociation of the elements which are present in aerosol. So, at this high temperature the outer quartz tube must be thermally isolated from the plasma and this is accomplished by a tangential flow of argon as you can see in this schematic diagram. So, this is how this the ICP plasma torch basically works.

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Now, passing the argon gas through this magnetic coil and then applying a spark basically creates the plasma by atomizing the population of the argon molecules. Now, these charged molecules then have an inelastic collision. I told you there is a resistive collision So, basically there is an inelastic collision with the neutral argon that propagates to the plasma torch, which

depends on the generation of the high frequency electric current produced by the electromagnetic induction known as the inductive coupling.

So, that is why it is known as inductively coupled plasma. This plasma is generated by inductive coupling. Now, the torch will remain light as long as the magnetic field is present to encourage the movement of atomized particles of the argon. As soon as it is switched off, the torch will not be working anymore. The sample is then introduced in an aerosol via nebulizer, the much higher temperature of the torch in the ICP leads to the atomization of essentially all sample molecules.

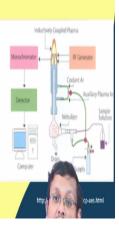
So, a complete atomization of the all sample molecules it is required that you create a very high temperature that can be only created by the production of the plasma and for creating that plasma you require inductive coupling and for that inductive coupling you require this radiofrequency coils. So, this is how this plasma torch basically works and this is the central working principle of this ICP-AES.

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## **Determination of inorganic pollutants**

#### Instruments for Inorganic P

Once the plasma torch has atomized the sample, the molecules are in an excited state. A detector then measures the light emitted by the sample as it returns to a ground state to determine which elements are present. Compared to AAS, ICP-OES is able to quickly detect many elements (~60 per minute), and the instrument's detector determines this rate. ICP-OES also features a much larger dynamic range than AAS, meaning that less sample manipulation is necessary. The biggest discrepancy comparing ICP-OES and AAS is the higher price associated with the purchase of an ICP-OES instrument.



Now, once this plasma torch has atomized the samples, the molecules are in excited states and a detector then measure the light emitted by the sample as it returns to ground state to determine which elements are present. Now compared to atomic absorption spectrometry, we will discuss this technique later on. Now, compared to this AAS technique, these ICP-OES or ICP-AES, we generally use these two names very interchangeably, ICP atomic emission spectrometry or ICP optical emission spectrometry. So, ICP-OES is able to quickly detect many elements, around 60 elements per minute and the instrument's detector determines this rate. ICP-OES or ICP-AES also features a much larger dynamic range than AAS, meaning that less sample manipulation is necessary. The biggest discrepancy comparing the ICP-OES and other like AAS is the higher price associated with the procurement of ICP-AES. ICP-AES is very costly instrument as compared to all other instruments.

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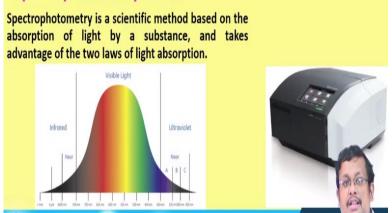
So, we have discussed the ICP-AES. The second important thing for measurement of inorganic phosphorus is known as spectrophotometer and sometimes you see people are using a term called colorimeter also. So, what is the difference we will see. Now, before measuring the concentration of orthophosphates or inorganic phosphate in spectrophotometer, we need to extract the phosphorus.

So, for extracting the phosphorus we need to have some kind of extracting solutions. So, there are 2 types of extracting solution we generally use, one is called Bray and Kurtz's number 1 method, which is required for acidic to near neutral soils and this extractant basically composed of 0.03 normal ammonium fluoride in 0.025 normal HCl at pH 3.5. And the other method is known as Olsen's methods.

This method is required for neutral, alkaline and calcareous soil and Olsen extractant is basically 0.5 molar sodium bicarbonate.

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#### Spectrophotometry basics



Now, spectrophotometry is a scientific method. You can see here is a picture of spectrophotometer. So, the spectrophotometry is a scientific method based on the absorption of light by a substance and takes advantage of two laws of light absorption and these laws are known as Beer's and Lambert's law, we will discuss them. Now, remember that this is the total electromagnetic spectrum and based on that which portion.

This is an electromagnetic spectrum which starts with the ultraviolet rays and then visible light, near infrared rays. So, basically which portion of the light is being utilized by the spectrophotometer gives the name of the spectrophotometer. If the spectrophotometer is using only visible light, then it is called visible spectrophotometer. If it is using UV plus visible portion of the electromagnetic spectrum, it is known as UVV spectrophotometer and so on and so forth.

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#### Colorimeter vs. Spectrophotometer

A colorimeter is generally any tool that characterizes color samples to provide an objective measure of color characteristics. In chemistry, the colorimeter is an apparatus that allows the absorbance of a solution at a particular frequency (color) of visual light to be determined. Colorimeters hence make it possible to ascertain the concentration of a known solute, since it is proportional to the absorbance.

A spectrophotometer is a photometer (a device for measuring light intensity) that can measure intensity as a function of the color, or more specifically, the wavelength of light. There are many kinds of spectrophotometers. Among the most important distinctions used to classify them are the wavelengths they work with, the measurement techniques they use, how they acquire a spectrum, and the sources of intensity variation they are designed to measure. Other important features of spectrophotometers include the spectral bandwidth and linear range. The most common application of spectrophotometers is the measurement of light absorption.



So, let us first discuss these 2 techniques called Beer's and Lambert's law, but before going to Beer's and Lambert's law, I want to discuss what is the difference between a colorimeter and spectrophotometer. You will see that these two terms are very much used alternatively by the soil scientists while they discuss about the inorganic phosphorus measurement. However, there are some differences. What are the differences?

So, a colorimeter is generally any tool that characterize color samples, now colorimetric comes from color. So basically, they characterize color samples to provide an objective measure of color characteristics. So in chemistry, the colorimeter is an apparatus that allows the absorbance of a solution at a particular frequency or color of visual light. So, this is very important.

So at a particular frequency of visible light, it measure the absorbance by solution, this is basically the utility of colorimeter. So, colorimetry makes it possible to ascertain the concentration of known solute since it is proportional to the absorbance. So, colorimeter deals with the color of the solution, it basically deals with the specific frequency of the visible light and it measures the absorbance by a solution.

And by measuring the absorbance it measures the concentration of a particular solution. Now a spectrophotometer on the other hand, it is a photometer which is a device for measuring light intensity. So, a spectrophotometer basically measures the light intensity and also it measures the intensity as a function of the color or more specifically the wavelength of light. There are many kinds of spectrophotometers as I have already told you in the previous slide. Among the most important distinction used to classify them are the wavelengths they work with just like UV spectrophotometer, visible spectrophotometer and so on and so forth, and the sources of intensity variation they are designed to measure, these are some important considerations. So, other important features of spectrophotometer include the spectral bandwidth and linear range.

So, the most common application of spectrophotometer is the measurement of light absorption. Basically, we generally measure the light absorption by spectrophotometer.

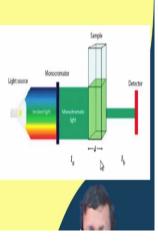
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# **Determination of inorganic pollutants**

### Spectrophotometry basics

The instrument allows light to pass through a cuvette containing a sample of the solution which absorbs some of the incoming beam.

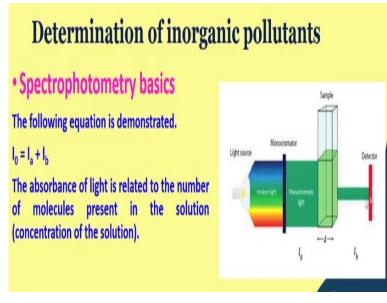
When the ray of light of a given wavelength and intensity  $(I_0)$  comes into contact perpendicularly with the solution of a tinted chemical compound, the compound will absorb part of the light radiation  $(I_a)$ . The remaining light  $(I_b)$  will pass through the solution and strike the detector.



Now, the basics of spectrophotometry say that instruments allow light to pass through a cuvette. So, cuvette is a specialized container which contains the samples. So, the instrument basically allows light to pass through this cuvette containing the sample which absorbs some of the incoming beam. So, if there is an incoming light, incident light, and then we are using monochromatic to convert them to a monochromatic light.

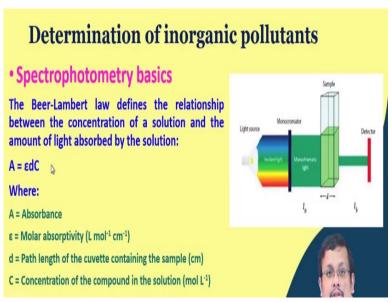
When the monochromatic light passes through a sample in the cuvette some amount is absorbed and some amount will be transmitted. So, when a ray of light of a given wavelength of an intensity, suppose the wavelength of the intensity I0 it is the incident ray comes into contact perpendicularly with the solution of a tinted chemical compound, the compound will absorb part of the light radiation which is denoted by Ia. And the remaining light that is Ib will pass through the solution and strike the detector at the other end. So, if we combine Ia plus Ib that will sum up to the incident wavelength intensity and d is basically the path length.

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So, this is the basics of the following equation. Considering all these things, the following equation can be demonstrated where I0 = Ia + Ib, I0 is the total where Ia is the absorbed intensity and Ib is the transmitted intensity. So, absorbance of light is related to the number of molecules present in the solution that is in other words concentration of the solution.

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So, the Beer-Lambert's law defines the relationship. So, I told you that this Beer-Lambert's law are the very basic laws which governs the spectrophotometry. Now, this Beer-Lambert's law defines the relationship between the concentration of a solution and the amount of light

absorbed by the solution. So, the basic form of this Beer-Lambert's law equal to A equal to this eta dC where A is the absorbance, we know that.

This eta is basically the molar absorptivity and d is the path length of the cuvette containing the sample in centimeters and C is the concentration of the compound in the solution. So, you can see that this absorbance is basically the multiplication of molar absorptivity, path length and also the concentration of the compound in the solution. So, this is the basic forms of this Beer-Lambert's law.

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# **Determination of inorganic pollutants**

#### Spectrophotometry basics

Lambert's Law : absorbance and path length are directly proportional Beer's Law: concentration and absorbance are directly proportional to each other

| Beer-Lambert law equation is as follows: |  |
|--|--|
| $I=I_0e^{-\mu(x)}$                       |  |
| Where,                                   |  |
| I: intensity                             |  |
| I <sub>0</sub> : initial intensity       |  |
| μ: coefficient of absorption             |  |
| x: depth in metre                        |  |

So, what is Beer-Lambert's law? In simplified form Lambert's law says absorbance and pathlength are directly proportional to each other and Beer's law says concentration and absorbance are directly proportional to each other. If you just consider this, obviously this absorbance and path length are proportional to each other and absorbance and concentration are also proportional to each other.

So, these are basically 2 laws and we are combining them together to combine Beer-Lambert's law. So, in terms of intensity, this Beer-Lambert's law equation can be followed where I is the intensity and I0 is the initial intensity and e you know exponential, mu is the basically coefficient of absorption and x is the depth in meter okay. So, Beer-Lambert's lumber law equation can be expressed in terms of this form also okay.

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## Spectrophotometry basics

The Beer-Lambert law states that the quantity of light absorbed by a substance dissolved in a fully transmitting solvent is directly proportional to the concentration of the substance and the path length of the light through the solution.

Because Beer's law states this, it means we can both calculate the concentration of a solution by using the absorbancies, or plot a graph of various concentrations, align them to their correct absorbencies, and use a colorimeter to find the concentration of an unknown solution

So, the Beer-Lambert's law states that the quantity of the light absorbed by a substance dissolved in a fully transmitting solvent is directly proportional to the concentration of the substance and the path length of the light through the solution, which we have discussed just right now because Beer's law states this, it means we can both calculate the concentration of the solution by using this absorbance or plot a graph of various concentration.

Align them to their correct absorbancies and use the colorimeter to find the concentration of an unknown solution. So, by using this relationship, if we meet the, so this is very important, we can see here the pathlength d is where we are using the specific unit, the path length is basically fixed, so this d is constant, so basically the absorbance varies with the concentration of the solution.

So, by measuring the intensity of the light, we can measure the concentration of the solution. So, this is how we utilize the Beer-Lambert's law for measurement of a concentration of the solution.

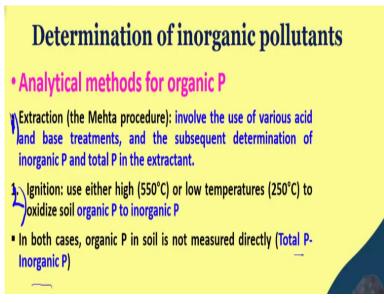
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# Analytical methods for total P The two most widely recommended procedures for determining PT are Sodium carbonate fusion method and the Perchloric acid digestion method. Other alkaline and acid digestion methods that use NaBrO/NaOH and H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>0/HF, respectively, can also be employed for this purpose

Now, we have talked about the analytical methods for inorganic phosphorus. So, analytical methods for total phosphorus, there are 2 most widely recommended procedures for determining the total phosphorus or we call it PT are sodium carbonate fusion method and the perchloric digestion method.

Now, other alkaline and acid digestion methods which use these different components can be also used for this purpose also, but the major 2 methods which are generally used are sodium carbonate fusion method and perchloric acid digestion method for measurement of total phosphorus.

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So, what about the organic phosphorus. Organic phosphorus is also very important. So, there are 2 methods for measurement of organic phosphorus. So, the first method, this is actually

the first method and this is actually the second method. So, the first method is known as extraction or Mehta procedure. Our second method is known as the ignition procedure. Now, one thing is clear that both of these methods are not measuring directly the organic phosphorus.

They are indirectly measuring organic phosphorus, how? They are either measuring total phosphorus, inorganic phosphorus and thereby subtracting them to get the organic forms of phosphorus or they are measuring the organic phosphorus which are converted to the inorganic phosphorus. So, this extraction or Mehta procedure basically involves the use of various acids and base treatments and the subsequent determination of inorganic phosphorus and total phosphorus in the extractant.

Whereas this ignition method use either high that is 550 degrees centigrade or low temperature that is 250 degrees centigrade to oxidize soil organic phosphorus to inorganic phosphorus. However, in both cases, they are not directly measuring organic phosphorus, they are indirectly measuring the organic phosphorus by subtracting this inorganic phosphorus from the total phosphorus okay.

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# **Determination of inorganic pollutants**

#### Analytical methods for Salts

- The accumulation of soluble salts in the soil profile obstructs crop growth by increasing the osmotic potential of the soil solution and inducing specific ion toxicities or nutrient imbalances
- The principal cations: sodium, calcium and magnesium
- The principal anions: sulphate and chloride
- Minor amounts of potassium, bicarbonate, carbonate and nitrate ions may also be present.
- High concentrations of sodium at cation-exchange sites disperse solids and impede water and air movement

Alright. So, let us wrap up here. We have covered the inorganic nitrogen and organic. We have covered the inorganic nitrogen. We have also covered the total nitrogen and now we have covered the phosphorus, both inorganic phosphorus and total phosphorus and organic phosphorus. In the third lecture, we will start with determination of different salts, what are the methods of determination of different salts and other trace elements.

We will discuss them in details and then we will be discussing different organic pollutants, how to measure different organic pollutants also in the subsequent lectures. So, friends, let us wrap up here. Please stay tuned and let us meet our in our next lecture that is in the fourth lecture of week 12 to discuss in details about determining the analytical techniques for determination of salts and also with other trace elements and organic pollutants. Thank you very much.