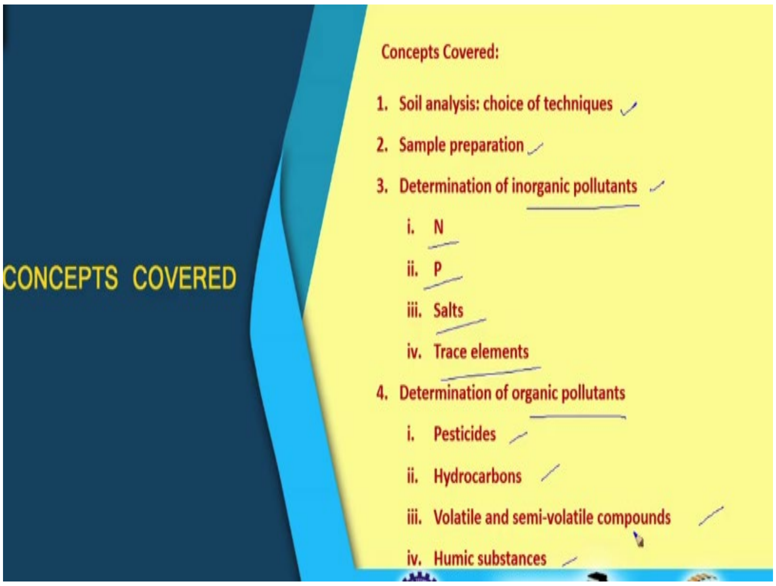
Environmental Soil Chemistry
Prof. Somsubhra Chakraborty
Department of Agricultural and Food Engineering
Indian Institute of Technology - Kharagpur

Lecture – 56
Analytical Techniques for Assessing Soil Pollution

Welcome friends to this last module of this online NPTEL certification course of environmental soil chemistry and in this last week or last module we are going to talk about the analytical techniques for assessing soil pollution.

(Refer Slide Time: 00:35)



CONCEPTS COVERED

Concepts Covered:

1. Soil analysis: choice of techniques
2. Sample preparation
3. Determination of inorganic pollutants
    - i. N
    - ii. P
    - iii. Salts
    - iv. Trace elements
4. Determination of organic pollutants
    - i. Pesticides
    - ii. Hydrocarbons
    - iii. Volatile and semi-volatile compounds
    - iv. Humic substances

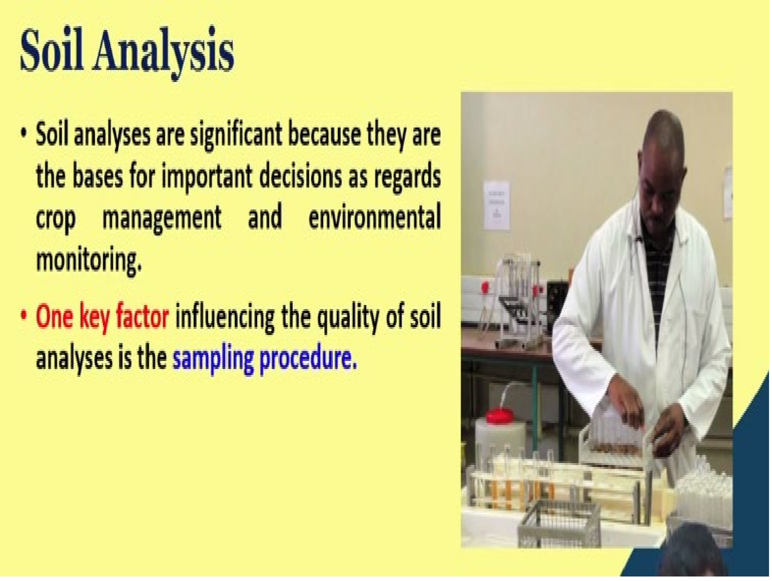
So these are the concepts which we are going to cover in this week. First of all, we are going to talk briefly about the soil analysis and how soil analysis is being done and what are the choices of the techniques, what are the considerations for selection of the techniques. Then how to prepare the samples, the sample preparation steps and then we will be talking about the determination of different types of inorganic pollutants.

Among the inorganic pollutants we are going to cover the nitrogen, then phosphorous, then different salts and trace elements. So we are going to cover all these and then once we cover the determination of inorganic pollutants, we are going to cover the determination of organic pollutants like pesticides, then hydrocarbons, then volatile and semi-volatile compounds and humic substances.

Remember soil is called contaminated when it is having higher concentration of either inorganic pollutants or organic pollutants or both of them which causes significant health damage for the human being and also creates hazard to the environment. So to determine whether a soil is really contaminated or not, you have to employ or you have to adapt certain methodology for error free or accurate measurement of different pollutants.

And in this chapter or in this module, we are going to discuss all these in details and then we are also going to discuss the different analytical techniques for example in case of nitrogen what are the different forms of nitrogen, inorganic nitrogen and how we generally measure those different forms by different instruments. We are going to have a brief overview of all the instruments which generally are being used by the scientist in advanced soil characterization laboratories. So let us start with the concept of soil analysis.

(Refer Slide Time: 02:59)



Soil Analysis

- Soil analyses are significant because they are the bases for important decisions as regards crop management and environmental monitoring.
- One key factor influencing the quality of soil analyses is the sampling procedure.

Now soil analysis are very significant because they are the basis for important decisions as regard to crop management and environmental monitoring. Remember the soil testing has to be done both from the point of view of crop management because you have to understand the soil fertility property and simultaneously you have to understand whether your soil is contaminated or not with certain inorganic or organic pollutants.

So to serve both this purpose, you have to do soil analysis with the sophisticated technologies. Remember one key factor which influences the quality of the soil analysis is the sampling procedure and subsequent soil preparation. We are going to discuss them in details in the next couple of slides. So soil analysis are very significant and we have to do the soil analysis both for maintaining or monitoring the soil fertility status as well as to monitor the soil environmental contamination or soil pollution level.

(Refer Slide Time: 04:08)

Choice of Soil Analysis Techniques

i. The sensitivity of the technique
ii. The specificity of the resulting signal
iii. The accuracy of calibration
iv. Cost-effectiveness
v. Specific purpose and the parameters to be determined in the analyses

Now there are several methods or several techniques for soil analysis numerous techniques. Now based on which points and which criteria we should select the most appropriate technique for certain soil analysis. Soil has different parameters for example we can measure the soil pH, soil electrical conductivity, different nutrient content, different heavy metals, different organic pollutants also.

So depending on different pollutants, we have to consider certain key points before selecting the most feasible technology. Now the first point is the sensitivity of the technique. The technique which you are going to follow for measuring certain soil parameter has to be highly sensitive. If it is not sensitive to that particular soil parameter, this is of no use. So the sensitivity of the technique is very important.

Whether there is a change in the concentration of a particular pollutant, if the method can identify that change, then it is called the sensitive technique. Now the specificity of the resulting signal. Now one common problem for most of the instruments which we use for environmental sample analysis is since the samples are complex in nature, their signals are also complex and it is difficult to identify the proper signal which you can particularly assign to a particular soil property.

So, it is a basically mix of signals from different fractions or different pollutants. So the specificity of the resulting signal is very important and you have to identify okay this is the signal which is responsible for this particular pollutant. So unless you do not get this particular resulting signal or specificity of the resulting signal, you cannot understand any particular pollutant. So, the specificity of the resulting signal is another important issue.

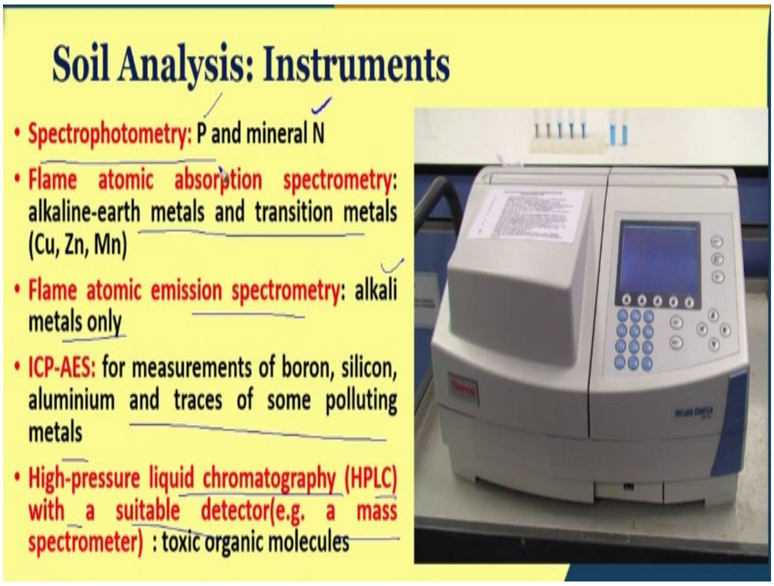
The accuracy of the calibration, whether you do any type of analysis, the calibration of the instrument is the most important thing. If the calibration is wrong, then the results are wrong. So the calibration is one of the most important process of measurement. For every analysis you have to calibrate the instruments using the prescribed steps and most of the instruments require their calibration before their run and most of the instruments require everyday calibration.

Some instruments require calibration after certain samples. So their frequency varies from once instruments and one technique to another technique. However, the calibration is universally required for all the instruments, which we are we are basically using for measuring different inorganic and organic pollutants. Now the specific cost-effectiveness is another important issue.

There may be numerous solutions for a particular problem. However, we have to select the one which gives the best possible solution with the reasonable cost. So depending on your budget, you can select the most cost-effective method for determining the different pollutants. Although the high valued instruments are laboratory standards and they are very accurate to measure the pollutant levels for different purposes.

However, due to the budget restrictions, sometime you have to go with some cost-effective instruments for measurement of different inorganic and organic pollutants. The fifth one is specific purpose and the parameters to be determined in the analysis. So this is another very important specific purpose in the parameters to be determined in the analysis. So, all these 5 factors are important to make a choice of soil analysis technique. So, you cannot neglect any of them while selecting them for soil analysis.

(Refer Slide Time: 08:52)



Soil Analysis: Instruments

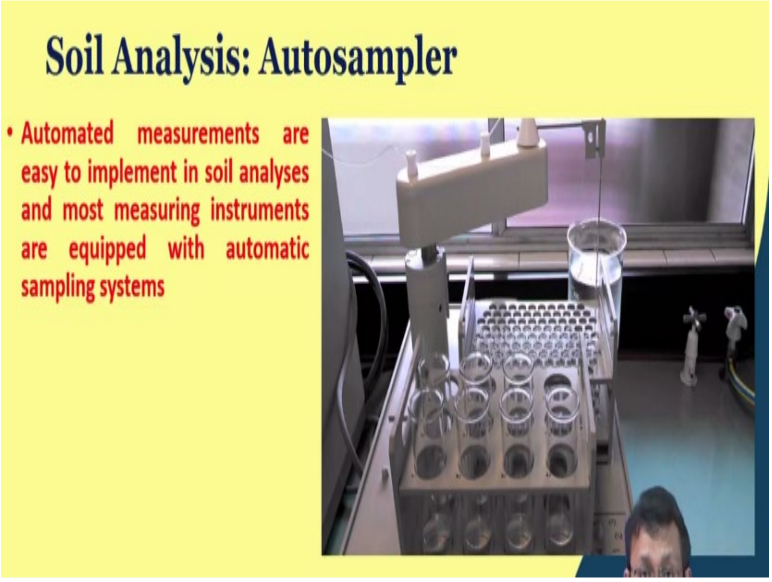
- Spectrophotometry: P and mineral N
- Flame atomic absorption spectrometry: alkaline-earth metals and transition metals (Cu, Zn, Mn)
- Flame atomic emission spectrometry: alkali metals only
- ICP-AES: for measurements of boron, silicon, aluminium and traces of some polluting metals
- High-pressure liquid chromatography (HPLC) with a suitable detector(e.g. a mass spectrometer) : toxic organic molecules

Now what are the general common instruments for measurement of different parameters on the soil. So spectrophotometry is a common method for determination of phosphorus and mineral nitrogen in the soils and I have produced here this is an UV spectrophotometer. So this UV spectrophotometer is used for measuring different soil parameters. Now apart from that, flame atomic absorption spectrometry is also used for determination of alkaline earth metals and transition metals like copper, zinc and manganese.

Flame atomic emissions spectrometry is basically used for alkali metals. ICP-AES, the full name of ICP-AES is inductively coupled argon plasma atomic emission spectroscopy and this is the technique which we use for measurement of boron, silicon, aluminum and traces of some pollutant mineral. And in case of toxic organic molecules, we generally go with this high-pressure liquid chromatography or HPLC with a suitable detector for example mass spectrometer.

So, these are some of the general instruments which you can see in most of the soil characterizing laboratory. So their specific purposes are also given. However, there are also certain instruments which are going to cover in this module which will show their usefulness for measurement of these different parameters.

(Refer Slide Time: 10:35)



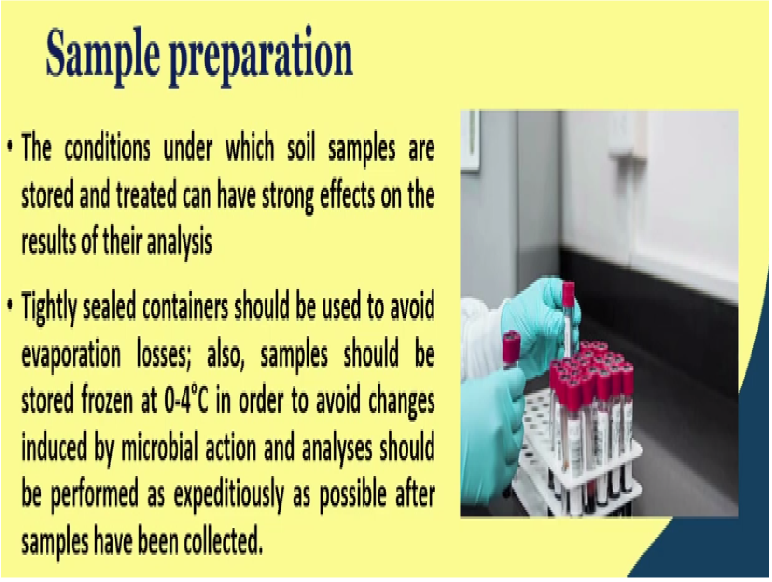
Soil Analysis: Autosampler

- Automated measurements are easy to implement in soil analyses and most measuring instruments are equipped with automatic sampling systems

Now apart from these instruments also, there is an attachment called autosampler. Now, this autosampler is basically an attachment for automated measurements. Now automated measurements are easy to implement in soil analysis nowadays and most measuring instruments are equipped with the automatic sampling system. As you can see here, it is an autosampler of atomic absorption spectrophotometer.

So these atomic absorption spectrophotometer can automate the sample analysis without any substantial human intervention. So, all these instruments which you use nowadays, all the sophisticated instruments like ICP-AES, like atomic absorption spectrophotometry, all these are having their autosampler attachment which can help for automated aspiration of the chemical from different wells or different solutions. So this is an autosampler, it is very important.

(Refer Slide Time: 11:47)



Sample preparation

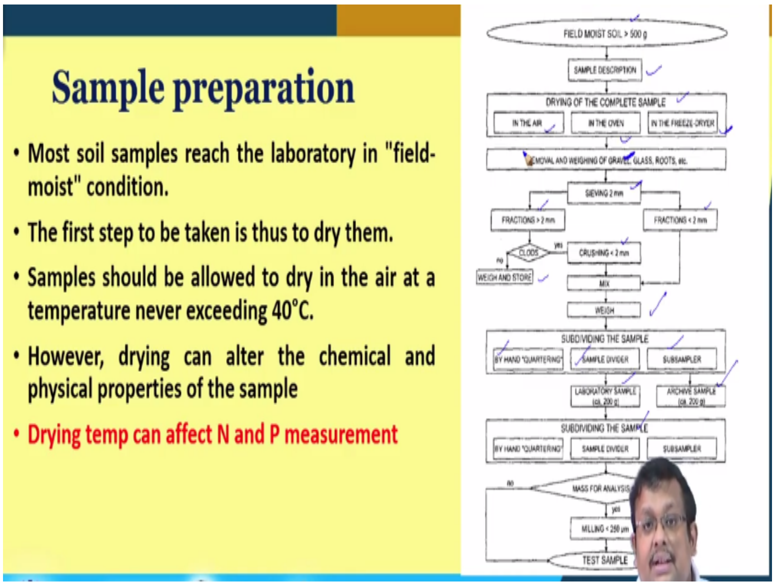
- The conditions under which soil samples are stored and treated can have strong effects on the results of their analysis
- Tightly sealed containers should be used to avoid evaporation losses; also, samples should be stored frozen at 0-4°C in order to avoid changes induced by microbial action and analyses should be performed as expeditiously as possible after samples have been collected.

Now let us consider very important part that is sample preparation. Now a good and reproducible and accurate measurement of pollutant always depends on good sample preparation. If your sample is not well prepared, then your results are also meaningless. So the conditions under which the soil samples are stored and treated can have a strong effect on the results of their analysis.

If the soils are not properly processed and stored and treated, the results will be erroneous. So, generally for environmental monitoring purpose, we use generally tightly sealed containers to avoid evaporation losses. Also samples should be stored frozen at 0 to 4 degree centigrade in order to avoid changes induced by microbial action and analysis should be performed as expeditiously as possible after samples have been collected.

So if we collect the samples and keep it in high temperature, obviously microbial activity will increase and as the microbial activity will increase obviously there will be changes in their physiochemical and biological properties of the sample. Now to stop that microbial activity, generally the scientists keep the soil samples tightly in the vials for 0 to 4 degree centigrade for and store them and analysis generally done as soon as possible after samples have been collected, so that no substantial changes are occurred.

(Refer Slide Time: 13:35)



Sample preparation

- Most soil samples reach the laboratory in "field-moist" condition.
- The first step to be taken is thus to dry them.
- Samples should be allowed to dry in the air at a temperature never exceeding 40°C.
- However, drying can alter the chemical and physical properties of the sample
- Drying temp can affect N and P measurement

Now remember that the most samples reach the laboratory in field-moist conditions. So this diagram basically shows in details about the different steps of sample preparation. So, let us consider that a field-moist samples with a weight of greater than 500 grams has been collected. So once we collect the soil sample, the next important step is to describe the sample.

Without description of the samples, it is meaningless because we cannot go back and see the same site and check whether there has been any change in the pollutant concentration or not. So the sample description is also needed for identifying the root cause for this pollutants. So once you do the sample description, now the second next step is the drying up the complete samples.

Now drying up the complete samples you can do this by air drying and also you can dry it in the freeze dryer, we will discuss freeze drying, and also you can dry it in the oven. Now in the oven when you dry, after you dry it in the oven you can remove and the gravels and grass roots and other debris from the soil for further analysis. Now once you sieve out all the gravel, glass, roots and other artifacts from the soil, then the next step is to sieve the material, specifically soil.

You know the soil is generally considered the material which has less than 2 millimeter particle size, so sieving is generally done to ensure that the particle size is less than 2 millimeter. Now after you sieve, you can keep it with more than 2 millimeter or fractions of less than 2 millimeter and then the fractions which are greater than 2 millimeter you can further crush them to less than 2 millimeter by milling process.

The clods can be further crushed and further mixed and those fractions which are less than 2 millimeter can be mixed well. So if there is no clods, then we can just generally weigh and store. So this is how we start with the field-moist samples. Then we do the sample description. Then we generally dry the complete samples. After drying the complete samples, we generally remove the artifacts and gravels, glass and roots and then we sieve them to keep less than 2 millimeter.

When the fractions are greater than 2 millimeter, we crush them and then further mix them. We weigh them. After we weigh them, then we can do the subdividing of the samples or sub sampling the sample by the hand quartering method, we will be discussing the hand quartering method, or by using different types of sample divider or subsampler. This sampling divider are used for laboratory samples of around 200 grams.

And subsamplers are generally used for archiving the samples and then the laboratory samples can be subdivided by hand quartering or by sample divider or by subsampler and mass for analysis is generally less than 2 gram and then we can do for further milling of less than 250 microns which further gives you the test samples. So if the mass for analysis is less than 2 gram, then further milling is done to get the test samples.

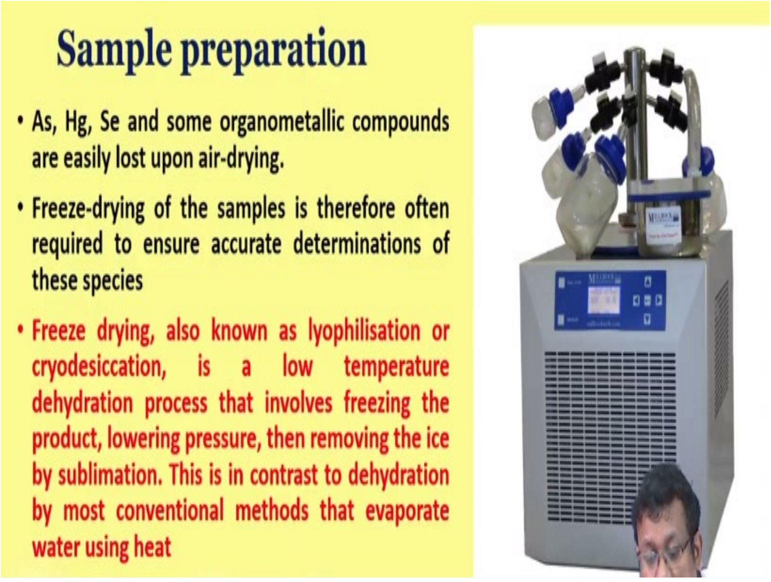
If the mass for analysis is not less than 2 gram, then we further go for the test samples, consider this as a test sample. So we will discuss all these steps in the subsequent slides. So, the most soil samples are reaching the laboratory in the laboratory in field-moist condition. So the first step to be taken is thus to dry them. We have already covered the drying of the complete sample. However, remember that complete drying.

So sample should be allowed to dry in the air at a temperature never exceeding the 40 degree centigrade. We generally want to maintain these 40 degrees centigrade so that there is no substantial changes in the organic matter because soil contain organic matter, if you increase the temperature the soil organic matter will be oxidized, we do not want that. Organic chemicals or organic molecules which are present in the soil can be oxidized if we increase the temperature.

So that is why we generally maintain the temperature at 40 degree centigrade. However, remember that drying can alter the chemical and physical properties of the sample. So, the drying temperature also can affect the nitrogen and phosphorous measurement. So drying has a profound influence in the soil testing, we can either dry it in the air which can more or less maintain the original composition.

However, when we dry them in the oven, there is a chance of degradation of soil organic matter or organic pollutants. Now so once we dry the soil samples, the next step is to gruel of the gravels.

(Refer Slide Time: 19:52)



Sample preparation

- As, Hg, Se and some organometallic compounds are easily lost upon air-drying.
- Freeze-drying of the samples is therefore often required to ensure accurate determinations of these species
- Freeze drying, also known as lyophilisation or cryodesiccation, is a low temperature dehydration process that involves freezing the product, lowering pressure, then removing the ice by sublimation. This is in contrast to dehydration by most conventional methods that evaporate water using heat

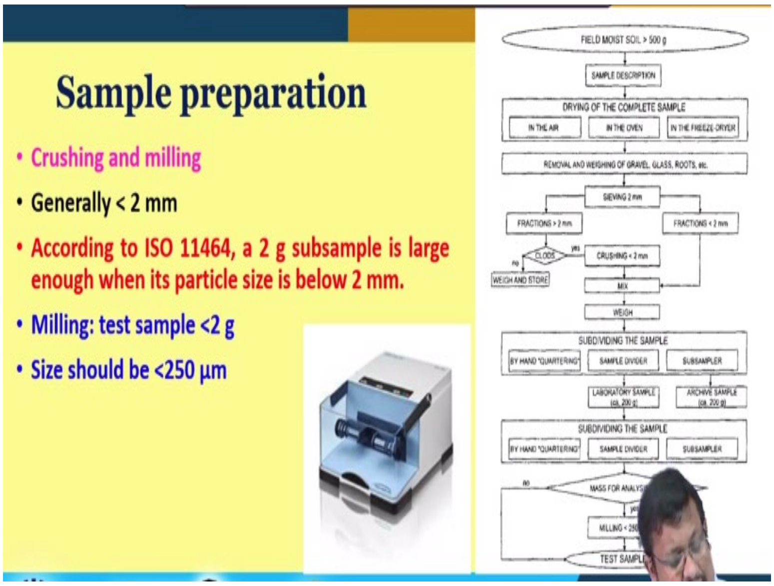
However, for drying you also remember one important thing that there are certain metalloids or organometallic compounds for example arsenic, then mercury, then selenium they can easily lost by air drying also. So air drying while it is known for keeping the original chemical and biological composition intact, certain these metalloids organometallic compounds like arsenic, then mercury, selenium they are easily lost by air drying also.

So for this, generally we go for the freeze drying or lyophilisation process. So freeze drying of the sample is therefore often required to ensure the accurate determination of these species. Now freeze drying also known as the lyophilisation or cryodesiccation it is a low temperature dehydration process. So what happens in this freeze drying. So it is a low temperature dehydration process that involves freezing the product.

So basically, we freeze the product lowering the pressure and removing the ice by sublimation. So this is in contrast to the dehydration by most conventional method that evaporates water using heat. So here we convert the moisture by removing the ice by sublimation process and this is an example of a freeze dryer which is used to freeze dry different materials.

So, samples which we generally use for measurement of organometallic compounds of arsenic, mercury and selenium can be freeze dried for their long-term storage without their loss in air drying. So this is a lyophilizer.

(Refer Slide Time: 21:54)



Sample preparation

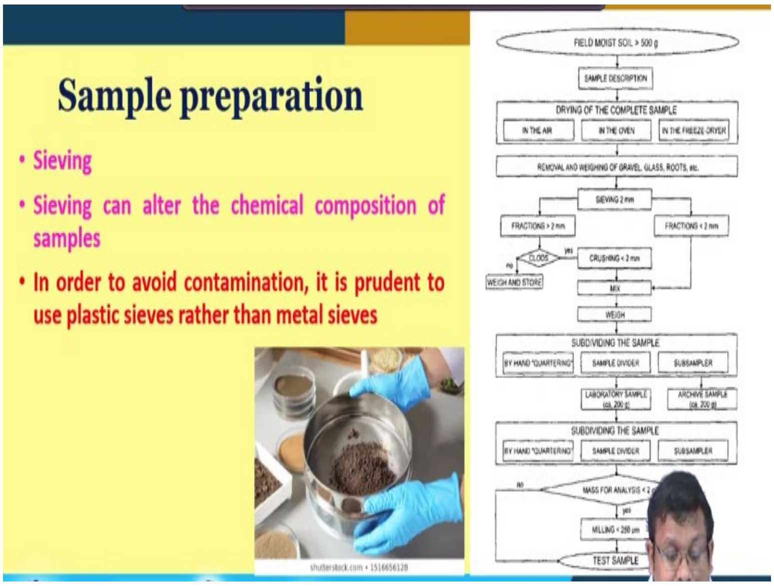
- Crushing and milling
- Generally < 2 mm
- According to ISO 11464, a 2 g subsample is large enough when its particle size is below 2 mm.
- Milling: test sample <2 g
- Size should be <250 µm

Now once you dry the samples, you remove the artifacts, then next step is crushing and milling. Now crushing and milling generally is done for keeping the particle size of less than 2 millimeter. Now according to ISO 11465, a 2 gram subsample is large enough when its particle size is below 2 millimeter. So when the particle size is below 2 millimeter, then 2 gram subsample is enough for doing the analysis.

However, milling is done when the test sample is less than 2 gram. So when there is a test sample which is less than 2 gram, then generally milling is done. Why milling is done, to further decrease the particle size and generally the size in the milling process goes below 250 micrometer. So here you can see this is a miller and this is used for milling the soils.

So, we have collected the soil, we have described the soils, then we have dried the soils and then we are doing the crushing.

(Refer Slide Time: 23:20)



Sample preparation

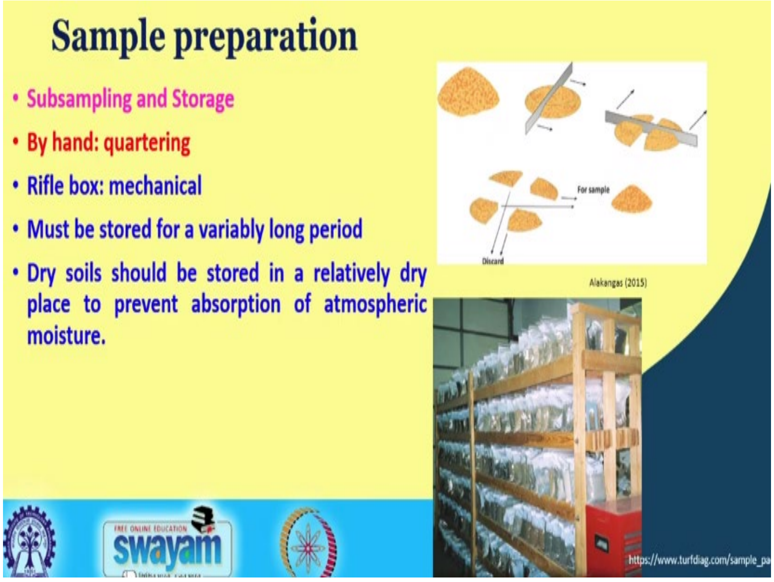
- Sieving
- Sieving can alter the chemical composition of samples
- In order to avoid contamination, it is prudent to use plastic sieves rather than metal sieves

shutterstock.com • 1516656128

After we crush the soil, then we are going to sieve the soil. Now sieving can alter the chemical composition of the samples also. Remember that in order to avoid the contamination, it is prudent to use plastic sieve rather than metal sieves, although metal sieves are more hardy than plastic sieves.

However, in case of plastic there is no chance of contamination from the metals which are present in the metal sieves. So, this is an important point when you should consider while sieving the samples.

(Refer Slide Time: 23:57)



Sample preparation

- Subsampling and Storage
- By hand: quartering
- Rifle box: mechanical
- Must be stored for a variably long period
- Dry soils should be stored in a relatively dry place to prevent absorption of atmospheric moisture.

Alakangas (2015)

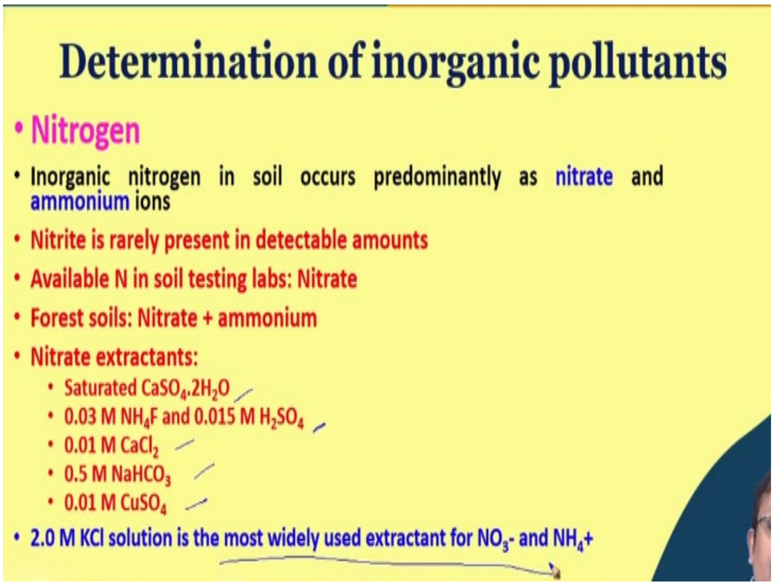
https://www.turfdiag.com/sample_pa

Now once you sieve the samples, you must have got enough samples. So store the samples for longer duration and to better utilization of the space for storing, you have to subsample the collected sample. Now for subsampling, generally we follow a method called quartering process. Now in the quartering process, you can see first we make a heap of the soil after we sieve them.

So it is forming a cone and after we form a cone, we generally make it four quadrants, so the opposite quadrants are basically discarded. As you can see here the opposite quadrants are basically discarded and by discarding the opposite quadrants, you keep the rest two quadrants and then mix them together. So by using this method, you can reduce the sample size for efficient storing.

And although this method is known as quartering process in case of mechanical subsampling you can use rifle boxes. So after you produce a subsample, you can store the sample for variable time period. Dry soil should be stored in a relatively dry place to prevent the absorption of atmospheric moisture. So after you do all these different processing, you can store the samples for longer duration of time for future analysis.

(Refer Slide Time: 25:47)



Determination of inorganic pollutants

- Nitrogen
- Inorganic nitrogen in soil occurs predominantly as nitrate and ammonium ions
- Nitrite is rarely present in detectable amounts
- Available N in soil testing labs: Nitrate
- Forest soils: Nitrate + ammonium
- Nitrate extractants:
  - Saturated $CaSO_4.2H_2O$
  - 0.03 M NH_4F and 0.015 M H_2SO_4
  - 0.01 M $CaCl_2$
  - 0.5 M $NaHCO_3$
  - 0.01 M $CuSO_4$
- 2.0 M KCl solution is the most widely used extractant for NO_3- and NH_4+

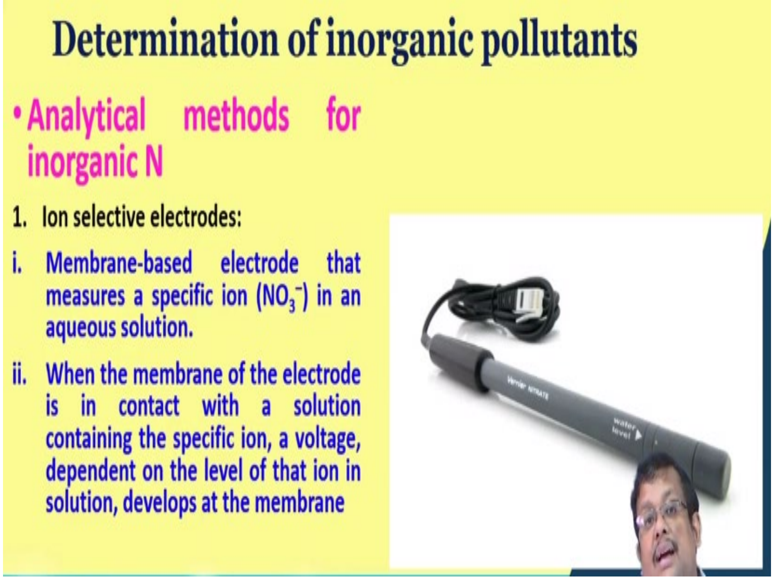
So we have covered the choices of techniques, criteria for the choices of the techniques and then sample preparation. Now let us start determination of different inorganic pollutants. So for discussing this, let us start with the nitrogen. Now, inorganic nitrogen in soil occurs predominantly as nitrate and ammonium ions. Now nitrite is generally very rarely present in detectable quantities.

Generally in the soil, nitrate and ammonium ions are present. Now for most of the soil testing laboratories when you talk about the available nitrogen, we generally test the nitrate concentration. However, in case of forest soils, the laboratories generally measure both the nitrate as well as ammonium ions also. Remember that for measurement of the concentration of a particular ion you have to add certain extractants.

Some of the extractants are for example in case of nitrates some of the extractants are for example saturated calcium sulphate 2H2O, then 0.03 molars ammonium fluoride and 0.015 molar H2SO4, 0.01 molar calcium chloride, 0.5 molar sodium bicarbonate, 0.01 molar copper sulfate. So, all these are generally used as an extractant for nitrate and 2 molar KCl solution is the most widely used extractant for nitrate and ammonium.

So, once you extract the ions from the soil using this extracting solution, you use different types of instruments for the measurement of this concentration of different ions.

(Refer Slide Time: 28:03)



Determination of inorganic pollutants

- Analytical methods for inorganic N

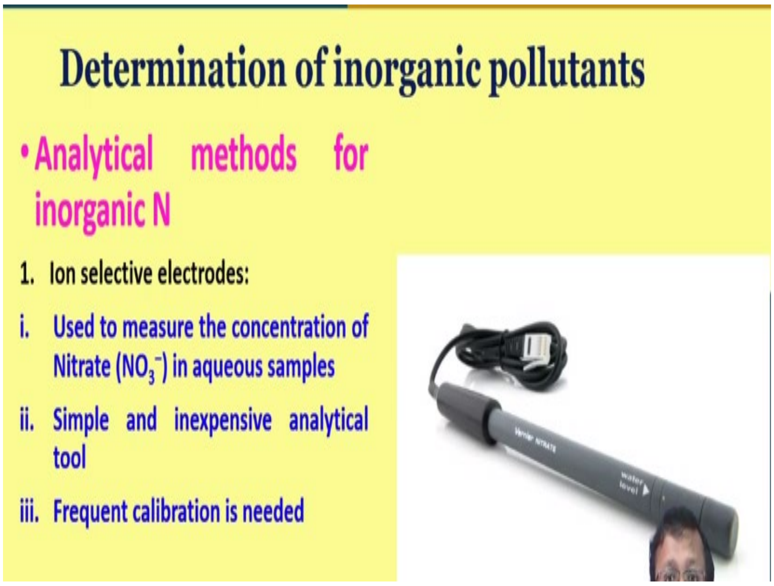
1. Ion selective electrodes:
   i. Membrane-based electrode that measures a specific ion (NO_3^-) in an aqueous solution.
   ii. When the membrane of the electrode is in contact with a solution containing the specific ion, a voltage, dependent on the level of that ion in solution, develops at the membrane

Now we are going to discuss about the analytical methods for inorganic nitrogen. The first tool which we generally use for determination of inorganic nitrogen in a particular ion is ion selective electrodes. Now, these ion selective electrodes are basically membrane-based electrode that measure a specific ion, for example nitrate in an aqueous solution.

So, after you extract that nitrate into an aqueous solution by using some extractant, then you can use this membrane-based electrode or ion selective electrode, we sometime call it ISE, to measure the specific ion concentration. Now when the membrane of the electrode is in contact with the solution containing the specific ion, a voltage, dependent on the level of that ion in solution develops in the membrane and that is why we can measure that ion concentration.

So this is basically the principle of this instrument or this tool. It is a membrane-based tool. So when we dip it, the membrane of the electrode come into contact with the solution containing the specific ion and then when it come into contact with the specific ion, a voltage gradient, voltage difference occurs depending on the concentration of the ions and develop across the membrane, so which can be further measured. So, this is the basic principle of this ion selective electrode.

(Refer Slide Time: 29:52)



Determination of inorganic pollutants

- Analytical methods for inorganic N

1. Ion selective electrodes:
   - i. Used to measure the concentration of Nitrate (NO_3^-) in aqueous samples
   - ii. Simple and inexpensive analytical tool
   - iii. Frequent calibration is needed

Now this ion selective electrode is used to measure the concentration of nitrate in aqueous samples and it is simple and inexpensive analytical tool. However, it requires frequent calibration. As I have mentioned that calibration is very, very necessary before you go for any analysis, so similarly in this case also frequent calibration is needed for this ion selective electrode.

So guys, let us wrap up our lecture here and we will start from here in our next lecture to see what are the other analytical instruments which are available for measurement of inorganic nitrogen and also we will discuss other instruments which we generally use for measurement of other inorganic pollutants in the soil. Let us wrap up our lecture. Let us meet in our second lecture of module 12. Thank you very much.