Environmental Quality:
Monitoring and Analysis
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Lecture No. 23
Analysis Methods – Overall Methodology for Organics

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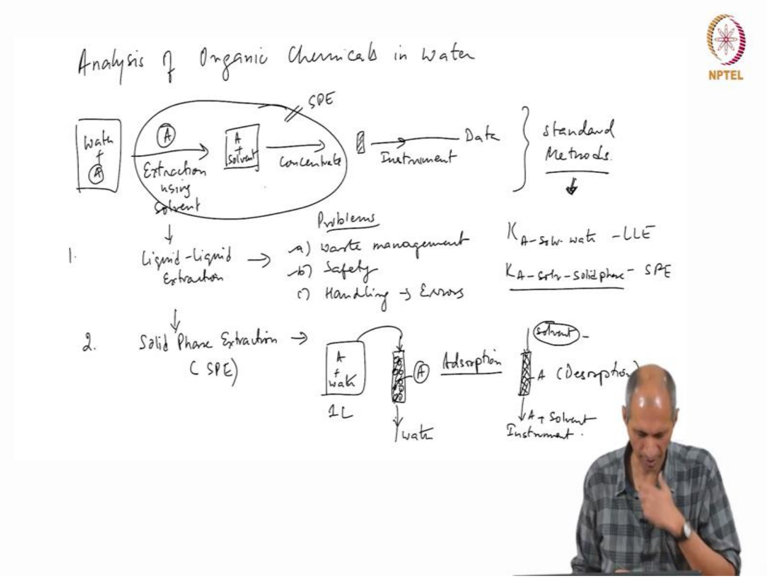

So, last class we were discussing the analysis. We have talked about this discussing the analysis of organic chemicals in, water. So, we looked at the process that we are looking at is say we have water, we have a water samples with a, we do we remove the A here, my extraction and then we also have another process A + solvent. And then we concentrate to make this a smaller volume and this goes into the instrument and legal instrument to get data concentration data on.

So, we discussed 1 method of this and we also looked at some standard methods, for we looked at standard methods for that are reported there are they are listed in the regulatory agencies for the analysis of different types of components in water. So, here, the 1 method that we use for extraction is what is called as liquid - liquid extraction. And this usually involves the adding of some amount of solvent to the water sample and then shaking it to extractions by whatever means you can bring the solvent.

And the water and contact so that there is efficient exchange of a between the water and the solvent. So the idea is to use a solvent that is a very good it has very good capacity to hold the solute that you are interested in so, that is a matter of experience and there are people who have collected this data and recommend so the standard methods that you are looking at will recommend a particular solvent for the analysis of solvent or solvent, several solvents that are applicable for the extraction of one class of chemicals A from the water.

And so we looked at some of the solids there is no point in me giving a list of solid by and large we have chlorinated organic solvents are very strong for any of these purposes, but they also have a problem they are themselves listed as hazardous chemicals. So, you have to worry about their disposal. And so, people always look at some alternative, but extraction is the main concern when people still use these chemicals they are not banned.

You just have to take care of their disposal properly, if you are using it. So, 1 option because this is a concern for using a liquid solvent, there are several problems in using liquid - liquid extraction 1 is the concerns the problems, 1 is the waste management. Second is safety itself for while doing this, while in the process of extracting and concentration. What do I mean by concentration is your evaporating solvent which means solvent is coming out.

And it is potentially released into the environment then the analyst themselves can get exposed to the solvent. So, we have to be careful about doing all that. So, in the standard methods, if you are doing liquid - liquid extraction, you will also see the safety the methods that you have to follow for safety safe handling of this thing which includes the concentration to be done inside what is called as a fumarole. So, I will not go into details of it so, I suggest you will be reading some of these methods in detail so, we will read some of it there and them.

So, there are 2 issues here risk management safety and third is the amount of handling can lead to a lot of errors. So, you are manually taking sample extracting taking out solvent concentrating it and taking it to instrument all this can also lead to additional errors in sample loss in the process. So, in order to circumvent all of this there is another method that people use now is called us solid phase extraction.

This cuts the problem in a little bit it does not remove the problem completely. But what this means is solid phase extraction means, instead of using a solvent to extract were using this A + water we are sending the entire thing into a solid sending the entire thing into a solid vapors water into solid the water comes out. The A is retained on the column solid column so, essentially what we are doing is we are doing another mass transfer process is called as adsorption.

We are absorbing all A from the water onto the solid phase which is usually a packed column and all the A is retained here in in the solid phase. So, what we do is we say if you are processing 1 liter of water a large quantity when you send it through the solid phase and whatever quantity of a that is there in the water gets retained on this on this small solid column and the water is all gone orders goes through there is no solvent involved here.

And this safety issues are lesser then you take this solid phase this which contains A is inside here. You have to take it out to bring it to the instrument again which means that I have to remove the A from here, A has to be removed from here in and then go to the instrument for analysis. There are very few methods that people have especially at the organics that we are interested in the direct analysis of a on a solid phase is not possible.

It is not easy methods do not exist for it as of now so, you should have to avoid out of the solid phases. So, you have to extract it somehow so, this process is called as desorption use desorption to get it out. So, depending on for water usually the instrument that we are going to be using is typically takes a liquid some solvent. So, 1 way is to send a solvent now, this solvent interaction with chemical with reference to water is very different from his interactions reference to the solid.

So, we are talking about here the partition in this case liquid - liquid extraction are talking about a partition constant of a between the solvent and water in a liquid - liquid extraction in the case of the desorption we are talking about the solvent and the solid phase SP. So, desorption you have to select a solvent because now the organic the solids that is there on the SP column itself is must be able to take its properties are very similar to that of the solvent.

You are using in the first place which means that if you are using other solvent to take it out of SP it must be really strong. So, the partitioning of the chemical from the solid phase to the solvent or must be really, good really. So there are recommendations for selection of solvents for a particular class of chemicals in from a particular solid. So there is adsorption and desorption, this is mass transfer and the equilibrium of a chemical between 2 phases in these kind of systems.

So, what we are effectively doing is 1 example is say you have 1 liter of sample it goes into a small cartridge, which contains maybe a few 100 milligrams or maybe a gram few grams of the solid and all is there then you take a small amount of solvent, maybe 10 ml of solvent and these all will bring it out all the A and now comes into the this solvent. So, you are essentially doing the same thing what you did what you did in this.

This zone is equivalent to what we are doing in the SP except that we are not using a solvent we are not using liquid - liquid extraction, we are using the solid phase extraction.

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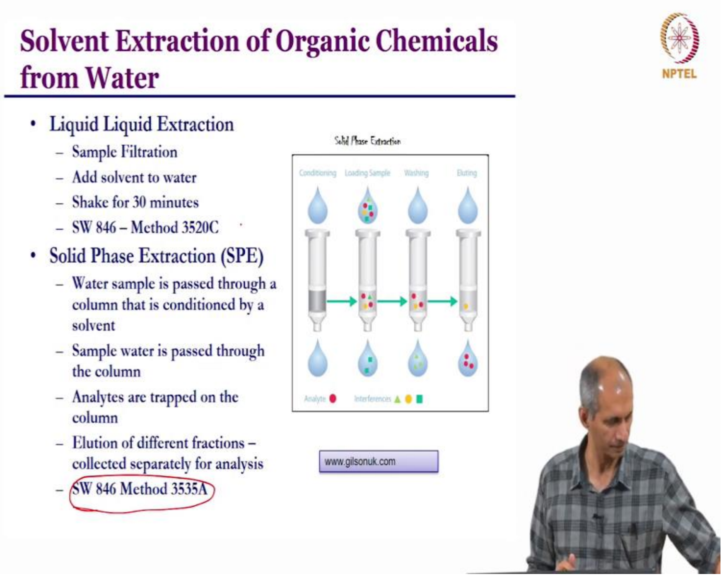

Solvent Extraction of Organic Chemicals from Water

- Liquid Liquid Extraction
  - Sample Filtration
  - Add solvent to water
  - Shake for 30 minutes
  - SW 846 – Method 3520C
- Solid Phase Extraction (SPE)
  - Water sample is passed through a column that is conditioned by a solvent
  - Sample water is passed through the column
  - Analytes are trapped on the column
  - Elution of different fractions – collected separately for analysis
  - SW 846 Method 3535A

So, then I have an image showing that this is a solid phase extraction. So, essentially what we do is we have a cartridge which has a solid and this cartridge then allows material to be sent through and the analytes is received initially restored here and then we eluted. And there is a method for that there is a standard method for that also. So, yesterday we talked about solid ways standard methods, one of them was for solid waste.

So, there is a large number of methods which talk about different extraction methods there are standard order for extraction, so, you can do the quality control for extraction, how much is the recovery efficiency how much is the laws during for different groups of compounds with different kinds of methods and all that. So, what you will get in the method you will get very specific instructions as to what is the flow rate?

You need to use what is the time that you need to have what is the purity of solvents all that how much of solvent you should use and what is the mass of SP you should use and same in liquid - liquid extraction also you have for a given volume of water, what is the solvent volume you should use, how long should you shake, how should you shake it what is rpm and all that all those instructions are given you can modify it whichever way you want, for wherever you have enough sufficient justification for doing it.

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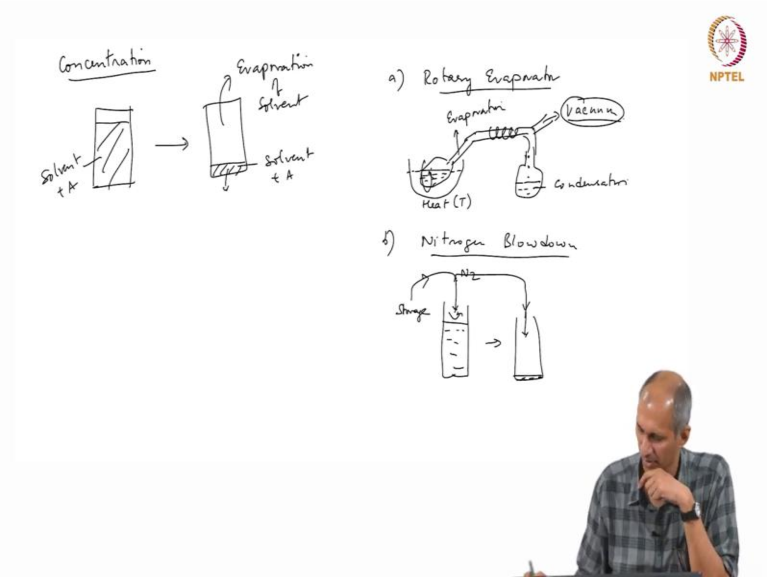

So, the concentration, the next step is a concentration step. Sometimes when you when you extract you extract a large volume of solvent is sometimes possible that you only can use 20 or 30 ml or sometimes even larger. So, in order to reduce this volume concentration essentially means you are reducing the volume, solvent volume is going from this to this, which means that the solvent is evaporating reducing the volume of solvent assuming and hoping that.

All the A that is in the system really is retained in this second set also. So, that concentration is higher in this case. And 2 ways of doing it, 1 is if you have a very large amount of solvent, you can use equipment that is used for it, we can use what is called as a rotary evaporator. Rotary evaporator essentially is a system where you have and I will show you a picture in a minute. But essentially what we do is we have a sample is kept inside a container.

And this is kept inside a heating for a particular temperature heating bath or something and then the vapor that comes out is condensed and collected. But here we are also applying this vaporization, evaporations and condensation to collect to recover this we use vacuum. So, at a particular temperature by using a certain vacuum, you are influencing the equivalent to boiling except we do not boil it we do not increase temperature we change the pressure we reduce the pressure.

And through evaporation occurs at a lower temperature. So, it at room temperatures you have certain amounts of vacuum you need to apply for certain solvents. So, there is a listing of that. So at 35 degrees, this is a vacuum apply solvent different solvents will based on the vacuum they will evaporate. So this is rotated there is it is called rotary evaporator because this is rotated, there is this portion is rotated.

And so that and it keeps coming down the level keeps coming down. So beyond a certain volume, you cannot reduce this. So if you are 100 ml of solvent, you can reduce it to a 5 ml of so beyond that the effect of vacuum is not felt by then if you go up condense and come back to straight away. It would not you cannot reduce it all the way but it is a very good. This, thing we will use it for various reasons, but in environmental sciences we do it for concentration.

The advantage of this method is you also can recover the solvent. Now, hope you are the solvent is a different question you may have to check that because there are multiple things few things will go out, several things will go but it is like distillation which means that it is the basis of evaporation the separation on basis of the volatility of that particular there are influencing volatility by applying different vacuum, this is a more sophisticated way of doing it and it is used for large volumes.

But for small volumes that say this is only 10 ml or 5 ml as in the case of SP your volume of what did you extract from the SP column is 10 ml or 6 ml or something like that. But you still want to reduce it you can use it you can use rotary evaporator it is too much. So we use what is called as a nitrogen blowdown is very straightforward, very simple sample is placed here. And you have nitrogen flow of nitrogen on the surface. So it is essentially evaporating just like that.

So it is very precise. So you have a needle that is supplying nitrogen from nitrogen cylinder storage and evaporation so you can keep on bringing this needle inside as the level keeps going down. So this will go down nitrogen flow of nitrogen is nitrogen because it is inert. That is the reason why we use nitrogen. It would not react and it also would not cause other problems in the system. The commercially available nitrogen load on system but it is nothing.

There is no special specific, this is what it means so our instrument that you can do it and all automated manner and all that all that but essentially it is developed evaporation. So the quality control issues here are during evaporation you will lose some you will lose some of your interest depending on what volatility of that also, while you are doing naphthalene analysis comparing has reasonable volatility.

A solvent 1 of the main problems is; what do you call as co evaporation effect for hexane if say dichloromethane hexane is a solvent, very volatile solvent. The reason we choose a particular solvent in for extraction is that if the solvent does high vapor pressure, high volatility, it is easy for us to come to concentrate. If you take a solvent, which is not easy to evaporate, you cannot concentrate it easily. You have to expend a lot of energy to evaporate.

And in the process, you may lose a lot of the chemical itself. So you always have to worry about quality control recovery of stuff have to analyte main chemical is critical here for sometimes you will have a lot of losses. So, losses can occur by way of incomplete extraction during the extraction process, it also can be lost during this process. So, what you recover in the instrument is lesser than what is there an original sample for these reasons, all these possible reasons. These are 2 possible ways in which we do nitrogen blowdown for solid samples, if you are doing solid samples.

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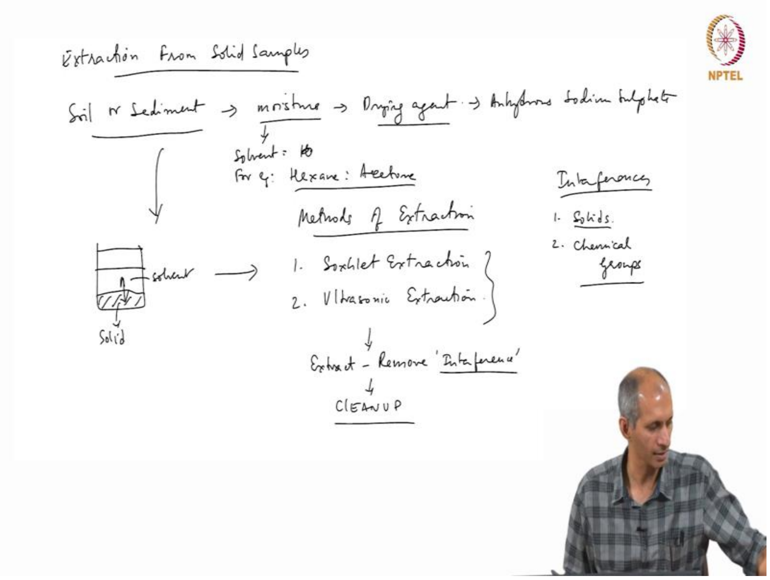

Extraction From Solid Samples

Soil or Sediment → moisture → Drying agent → Anhydrous Sodium Sulphate

Solvent :
For eg: Hexane : Acetone

Methods of Extraction

1. Soxhlet Extraction
2. Ultrasonic Extraction

Extract – Remove 'Interference'

CLEANUP

Interferences

1. Solids.
2. Chemical groups

We will talk about the extraction extracting solid samples. Solid samples or more complex matrices for you need something more rigorous. You can do liquid - liquid extraction, that kind of things you can ask solvent and mix it but 1 of the main problems is salt solid do not let us say because of sediment or soil or sediment contain the moisture you do not mix very well you are adding an organic salt and water is there it would not mix. So, you need to the solvent must be sufficiently mixture where it can allow water that is one way of doing so sometimes people use solvent is a mixture.

So for example we have a mixture of hexane and acetone. Both of them are good organic solvent but one of them is soluble in water. One of them mixes with water well the other one does not hexane does not mix well with water. But you still need a phase by acetone and hexane mix well. The water we will get into a little bit of acetone and all that all that will happen but it is not important for the but what it what this will help is that the solvent and the solid matrix can mix well we need good mass transfer that is one second is they will also add we also add a drying agent.

So, there is moisture we add a drying agent something like we have we add anhydrous sodium sulphate not for himself which will absorb moisture, pick up the moisture, it will absorb moisture and this this sample will become more powdery and very easy for us to do mass transfer shaking. So when you do when you have soil or sediment, so essentially what we do is we take some sample solid sample then we add the solvent then we have to bring these 2 in contact with each other and pull out the A that is sitting.

So, originally various a chemical sitting on the solid this is with the organic matter or some such phase or it is sitting as bulk phase to phase. So, you have to pull out pull it out into this and it is it is a solid matrix. So, by doing all this moisture reduction and drying agent, it becomes particles that are easily you can mix it well with the solvent and therefore, extraction efficiency is higher. But in some cases, so, one way of doing this is to you can just mix it mixing itself is not sometimes enough.

So, people the methods of extraction one more, one older method is what is called let us the Soxhlet extraction. This is an old it is a very old method and this is used to extract all kinds of solid matrices, anything sludge soil sediment from anything any solid, big chunk whatever you want.

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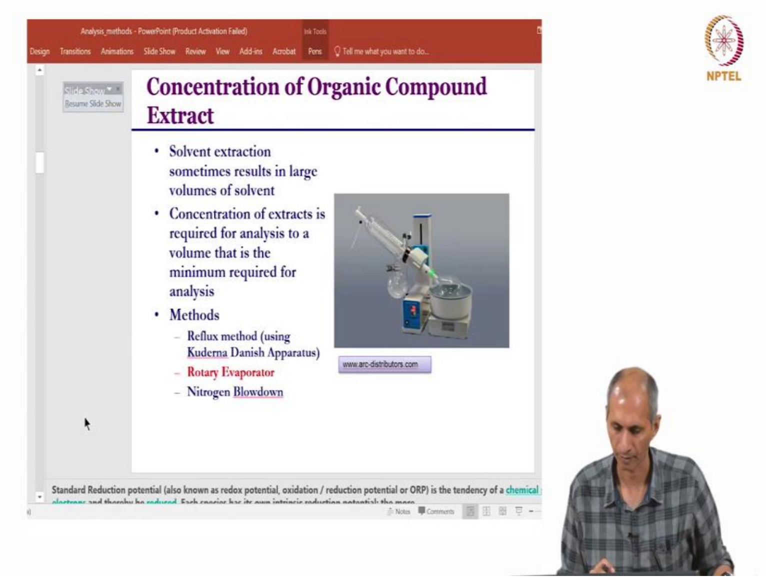

Concentration of Organic Compound Extract

- Solvent extraction sometimes results in large volumes of solvent
- Concentration of extracts is required for analysis to a volume that is the minimum required for analysis
- Methods
  - Reflux method (using Kuderna Danish Apparatus)
  - Rotary Evaporator
  - Nitrogen Blowdown

Standard Reduction potential (also known as redox potential, oxidation / reduction potential or ORP) is the tendency of a chemical

The Rotary evaporator as I showed you.

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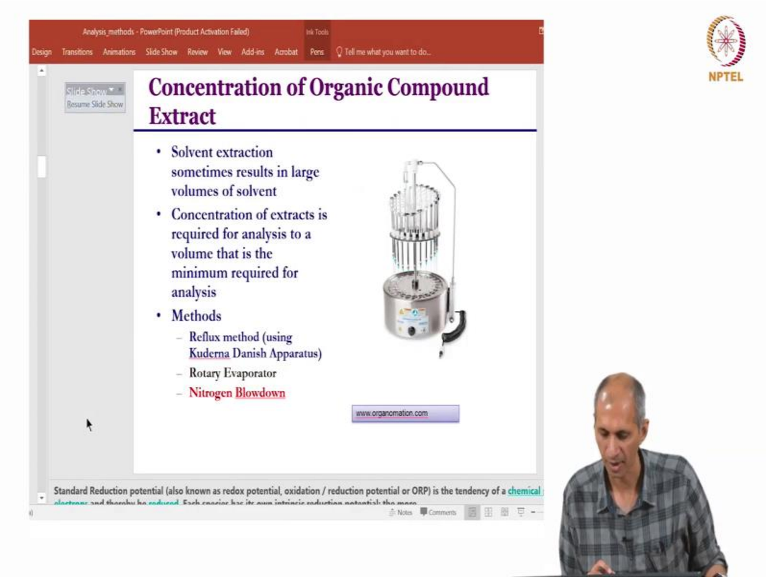

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Standard Reduction potential (also known as redox potential, oxidation / reduction potential or ORP) is the tendency of a chemical

This is a nitrogen system, which we looked at.

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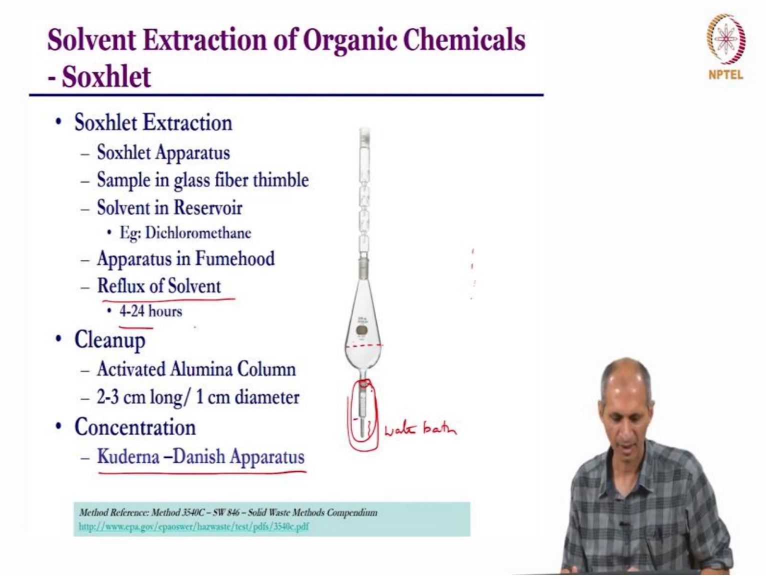

Solvent Extraction of Organic Chemicals - Soxhlet

- Soxhlet Extraction
  - Soxhlet Apparatus
  - Sample in glass fiber thimble
  - Solvent in Reservoir
    - Eg: Dichloromethane
  - Apparatus in Fumehood
  - Reflux of Solvent
    - 4-24 hours
- Cleanup
  - Activated Alumina Column
  - 2-3 cm long/ 1 cm diameter
- Concentration
  - Kuderna –Danish Apparatus

Method Reference: Method 3540C – SW 846 – Solid Waste Methods Compendium
http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3540c.pdf

This is what is called the Soxhlet apparatus. What we do is in this, there is this small thing that you see here on the right hand side. This small thing is a thimble here this is a sample holder sample holder like a cup. You one of the other things in extraction that you solid extraction is like liquid extraction after you finish the extraction you have to separate the solid and the extract you solid. So here what they use is this symbol is what called as symbol is a filter.

It is already the filters, it is made of filter material, you put the solid into that and you then it has to be brought in contact with the solvent. So, this is apparatus the solvent is placed here, this is a solvent. So this solvent is placed on a heating bath and it is kept at close to its boiling point. It starts boiling, it goes up. It goes up here you see this condensation is condensing. This thing goes up and goes up condensers and drops down into the thimble.

So it is dropping added boiling point close to its boiling point, very close to his boiling point. So it is hot. So it is a hot extraction and it drops down it is now in contact with the solid and it fills up. So, when it fills up this outer layer also fills up when it reaches this level there is you see a small system here, it goes beyond that and it creates a suction effect and the entire liquid level. The entire liquid solvent that is there in this chamber is now transferred back into the main reservoir.

So this happens in cycles, it takes about a 30 minutes for the boiling to happen and drops into this thing. And it fills up when it fills up everything empties. So it is like 1 cycle of extraction you are extracting, if at that temperature with a certain volume of solvent for 45 minutes, and then you do another one and then you do another one so you can look at it. It is called the reflex of solvent and it is done for 4 to 24 hours depending on how hard the matrix is, so what is very rigorous, very harsh extractions, it high temperature.

And the solvent that you are using, and it is, very time consuming, and it is also expensive, expensive in a sense in terms of energy and all that it is a bit laborious, but once you pack it in, it is done, it keeps going, it keeps going round and round. So, you will get at the end of the process, the extract is here, this is the extract, you take out everything and the extract is taken for further processing.

So, in this method, you need a large amount of solvent you cannot do it 20 ml and 30 ml you may need 150 ml or so because it asks evaporate and go on still needs something must be there here. So in this kind of situations we have to use rotary evaporator or some such if you do not have a rotary evaporator there is another option that is instrument that is used it is called this one.

So this is placed inside a water bath this is again reflects the idea when is it evaporate it basically, but it does not evaporate very rapidly.

What it does is it evaporates the sample is placed here you see this the sample the initial sample level, maybe here, in the bottom you have a small attachment which is like a test tube and as you can see the graduations you can see, these graduations are much smaller graduations here are much smaller than here. So you can reduce it to about 1 ml this is about 1 ml and 250 ml is somewhere here and you are boiling it so it goes up.

You can see that these do not allow the sample just go escape, they go up and they condense they fall back they go up condense fall back some of it escapes the pressure becomes enough to keep escaping. This is a very old technique is to prevent reduce the loss of analyte because 1 of the problems I was talking about if you rapidly evaporate for concentration is whatever solvent will evaporate at the boiling point.

Rate of evaporation so fast that it will take a lot of other things and go with it evaporation lack and loss will occur a lot of losses. So, this was seen as a way of reducing it a little bit. But this is a very time consuming method and it will also again not entirely reduce it to whatever one you will reduce it to some volume here. The same problem as a rotary evaporator which you cannot reduce it below a certain volume.

So but the idea is once you get it inside this tube, you can take this tube and do the nitrogen, reduce it to whatever what small volume you want.

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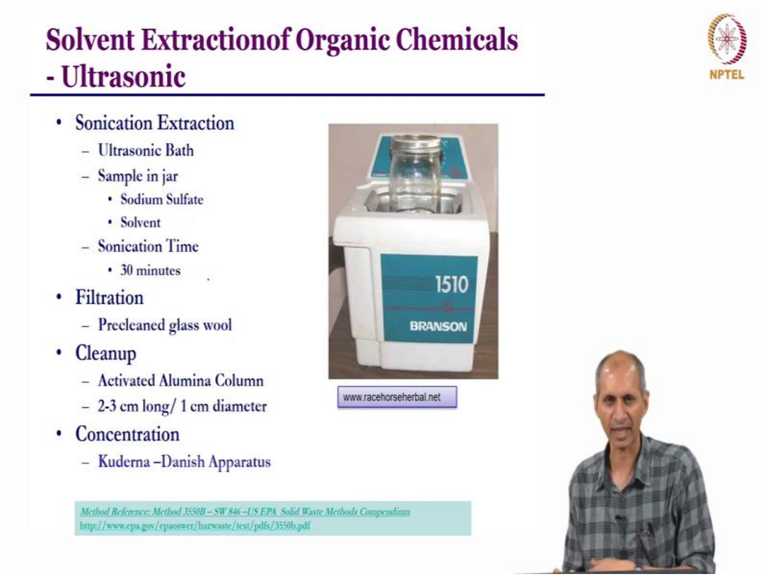

Solvent Extractionof Organic Chemicals - Ultrasonic

- Sonication Extraction
  - Ultrasonic Bath
  - Sample in jar
    - Sodium Sulfate
    - Solvent
  - Sonication Time
    - 30 minutes
- Filtration
  - Precleaned glass wool
- Cleanup
  - Activated Alumina Column
  - 2-3 cm long/ 1 cm diameter
- Concentration
  - Kuderna –Danish Apparatus

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Method Reference: Method 3550B – SW 846 –US EPA Solid Waste Methods Compendium
http://www.epa.gov/epaoswer/hazwaste/test/pdfs/3550b.pdf

So far for solids, the other option that we have it is a more recent method is using ultrasonic. But soxhlet extraction is a very painful and long process to do. So, the new method was developed what is called ultrasonic extraction. Ultrasonic extraction is takes a sample and you add all the whatever moisture reducing sodium sulfate and the solvent in it, mix it well and put in it but what does the ultrasonic but what it does is it at that frequency that is suggested it breaks particles and it makes more.

So, this ultrasonic have different enhancement of mass transfer effects and also it breaks particles. So, both these things allow it to be effective as extraction methods. In both these methods, Once you get an extract once you get the extract in solid phase extraction from solid samples like soil this it will contain a lot of things it will contain organic matter it can contain a lot of so your extract typically looks if you are extracting from soil the extract will look the solvent is color exactly look yellow or sometimes in brown, dark brown in color, which means it is contains a lot of other things, some of which may be of interest, some of which may not be.

So we were discussing this the other day we will call this as an interference, whether it is an interference are not determined by you depending on what you want to analyze. But if you do not want the interference, so it contains the extract to remove what we call as interferences. You have to filter sample process sample. So, we do what is called as a cleanup before we go any further so, one of the main interferences is solid itself.

Because we are not even though we use a filter symbol, the filter material or even an ultrasonic extraction we there is no filter you are you still have to filter it. So, one way of doing this filtration is interferences, possible interferences. One is solid with other certain chemical groups that we are talking about so there are cleanup methods to remove different types of different types of interferences whatever you want. So, essentially it looks like this.

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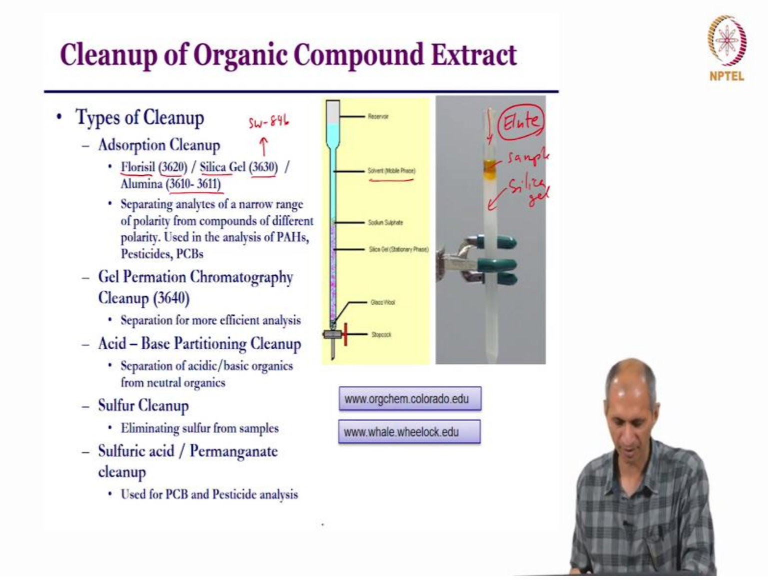

Cleanup of Organic Compound Extract

- Types of Cleanup
  - Adsorption Cleanup
    - Florisil (3620) / Silica Gel (3630) / Alumina (3610- 3611)
    - Separating analytes of a narrow range of polarity from compounds of different polarity. Used in the analysis of PAHs, Pesticides, PCBs
  - Gel Permation Chromatography Cleanup (3640)
    - Separation for more efficient analysis
  - Acid – Base Partitioning Cleanup
    - Separation of acidic/basic organics from neutral organics
  - Sulfur Cleanup
    - Eliminating sulfur from samples
  - Sulfuric acid / Permanganate cleanup
    - Used for PCB and Pesticide analysis

SW-846

www.orgchem.colorado.edu

www.whale.wheelock.edu

So, type of cleanup you have an adoption we have cleanup for these are all standard methods the numbers you see here 3620 are shot solid waste 846 method numbers you know solid waste is SW-846 as yesterday's last class we saw this solid waste 846 methods and these, are the type of material that is used for the cleanup for example, you have silica gel cleanup, alumina cleanup, florisil cleanup their different materials.

So, what happens here is it is like a filter, it is just a belt, your sample is added in the top and allowed to go through this column and it is a filter, it retains anything that you or do not want and depending on what you know. So some of the basic things so it looks like this on the right hand side, you can see in this case, this is the is a silica gel column. Silica gel is not the silica gel that you use in the lab here, but it is the silica gel is used for this particular process.

And it is not just the solid, you can see that it is the gel and it becomes like this when you saturate it with solvent, if you add solvent, it becomes a liquid solid gel. And on top of it, you add the sample, this is a sample, you can see and the sample goes through and you have to if you just keep the sample, it is not enough you have to elude the sample. And this term of illusion is very specific illusion is a term that is used in chromatography.

And this we will come to chromatography in the next topic. So we are doing what is called less column chromatography here in some sense, but if you are just a filter that we are using that is filtration, but in the case of silica gel, it also does what is called us chromatography liquid chromatography. So, the oldest form of chromatography which means that you have you should have a mobile phase here you can see that there is a mobile phase it is moving through when you add this here.

And we will discuss chromatography after this to understand more so, basically you must have a continuous flow of this going through. So, you have various kinds of cleanup procedures you for cleaning up Sulphur cleaning up acid base, all kinds of things. So, depending on where your sample is what you expect to be as a significant interference we remove many of these things. Come back to this. Any questions on this so far, the terms of what we are doing.