Environmental Quality:
Monitoring and Analysis

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Lecture No. 29
Monitoring methods for Air PM - Part 2

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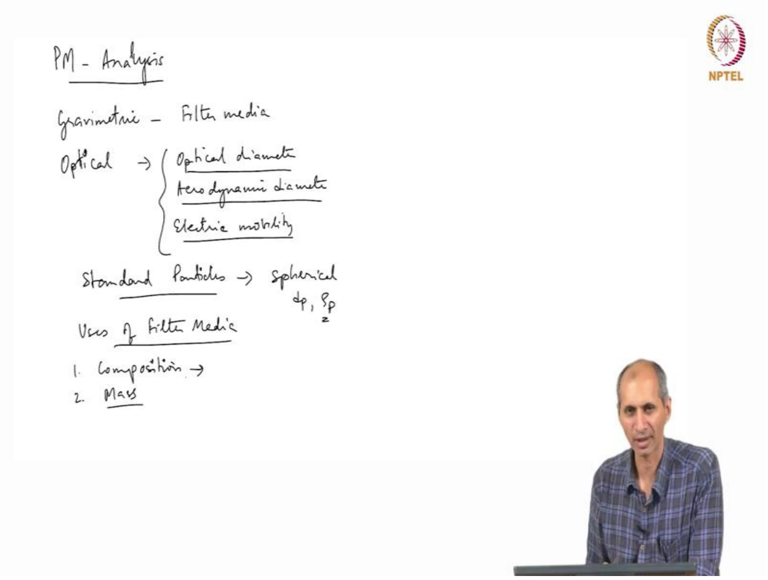

PM - Analysis

Gravimetric - Filter media

Optical → Optical diameter
Aerodynamic diameter
Electric mobility

Standard Particles → Spherical
d_p, ρ_p

Uses of Filter Media

1. Composition →
2. Mass

So we will continue from where we left yesterday we are looking at the analysis of PM. Look at different methods of measurement, quantification for the entire range. So, one of the, we were looking at gravimetric measurements which involved a collection on a filter media versus other techniques which are things like optical techniques include both images have the optical diameter or by the aerodynamic method.

So optical methods both the AV, APS which is around particle sizer is also an optical method because, it uses lasers to track the particles. The other method also uses a laser to measure scattering to scatter of particle and measured the angle of scattering and all that both are optical methods but they give you different information one gives you optical diameter, aerodynamic diameter.

Then we also looked at something called as electrical mobility which is a DMA electrical mobility diameter the different sizes at different phases. So, these all these 3 are not the same. So, if you want to compare these 3 data sets you have to do an experiment with the same kind of particle and then, see if the diameter are the same, the correlation between these 3. So one has to be careful about this. Generally they are nearby, but they are not equal exactly comparable.

So, something which you say is 10 microns, aerodynamic diameter may not be 10 microns in an optical and their behavior may be different. So, if you are looking at PM 10 from a respiratory point of view, the PM 10 that you get from a particle optical diameters may not match exactly with your PM there will be some variation and you have to find out what that correlation is based on very carefully planned experiments.

So, again as with any other analytical method that we are looking at, we need standards. We are looking at optical diameter versus particle error I mean we need standards here are standard particles. Standard particles means the standard which means there are particles that are known to be of a specific size and a specific clip. So, standard particles typically, I would like to have standard particles as spherical of a certain physical diameter.

You know specific physical diameter and density. If I know this is the definition of aerodynamic diameter is the mobility of an equivalent particle, spherical particle of a certain diameter and density is 1 gram so, you choose a material which for the density is close to 1 gram and that is the standard. So, based on that we defined the other whatever. So, we define the optical diameter what is the difference between optical diameter and the electrical mobility diameter and the APS the aerodynamic diameter how close it is in terms of that.

So, the instrument is you calibrate the instrument using standard particles like this and then compare it with the same thing. You do it with other instruments and say what is that giving whatever this is other instruments seeing. So you make a correlation like this the simplest way is to get these 3 instruments and run it at the same location if you did not have a standard and then compare the particle size distribution or the numbers that you are getting in what supposed to be PM 10 one instrument is getting other instruments giving PM 10.

How does it vary? He says in this memory reference, there will be a difference and this is usual that is normal. So you have to use this data carefully. You cannot just blindly use one classification for the other. So, we are also talking about the advantages of using a filter the purpose of using filters one is composition, one of the main things is composition. Second, this is mass see mass is a very fundamental quantity.

People want to see particles, if I show them a filter paper, whereby that the sample that you have collected is dirty, this is the mass is this is the atmosphere, people will believe it. What I mean by people is, you have to make decisions based on your ambient monitoring based on you are going to make policy decisions, which means that you have to explain to some regulator somewhere that this is happening, and therefore, this means some process may have to be controlled.

Everything costs money. So, there is this big link that we talked about in the beginning of this course, to economics and social policy and all that. So you need to show if I show them optical scattering and diameter that nobody will believe it is a black box, it says, I did not know what you are punching you are you are doing some. You are doing some programming and you are showing some numbers. I did not believe anything that you are saying.

So physical mass shows that is there? Even though it does not give you full information it does not gives you a very staggered information. It gives you a time average information but it is still there physical evidence that something is there. So that is one of the main advantages why a mass base detector is still used. But as we go deeper into the problem this mass does have limitations severe limitations.

And we would like to go ahead and understand more about the physical processes happening in their environment we would like to have more real time and distribution based instruments for you can imagine if I use an SMPS, which is the DMA and particle CPC that we discuss, how much information can you get from a single sample for one day at a road site, you can get a lot of information you can get tons of information.

You can do data analysis on that, all kinds of inferences can be made. So composition of filter media is a very efficient thing so, we would like to see what these particles are.

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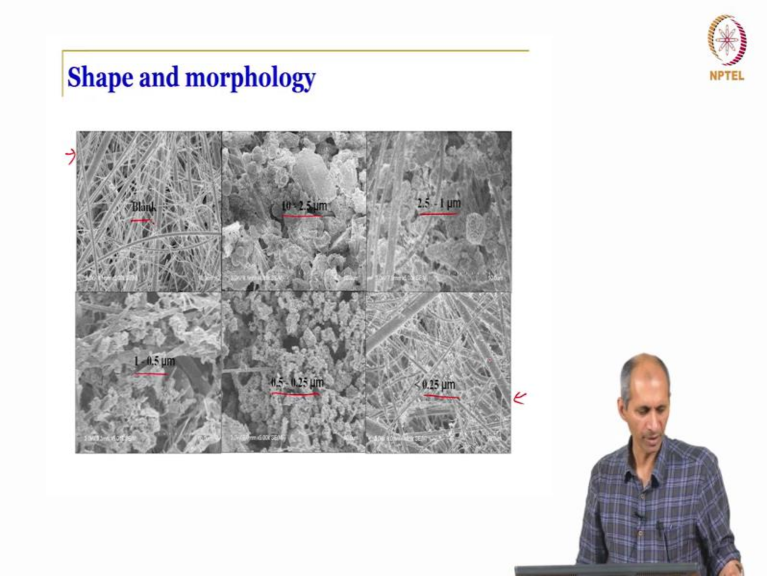

Shape and morphology

So, one of the ways in which we do that is by looking at composition one shape and morphology. Shape and morphology you can look at shape and morphology by using microscopy. So, this is a these are images from scanning electron microscope of particulate matter. So the first image here, this one is blank this is image of a filter. Filter media looks like this it has you can see a scale here. Not sure you can see it very well the scale going from here to here.

I cannot see it is about 10 micron, something around that, number 10 micron. So, you can see that the filter size itself is quite small in order of microns. And then particles are all kinds of shapes and sizes you can see, this is from a cascade impact from an impactor in which this is 10 to 2.5 microns, 2.5 to 1 microns, 1 to 0.25 and point less than 0.25, you can see that particle size is generally decreasing as you are going down the order.

You can see here the particles are very small and they are stuck on the finish. There is not much difference between this image and this image, the first image and the last image, the blank and this one. But you can see particles are still there they are stuck on the fiber. And this is one of the important things that you need to remember that particles even though the opening of the filters is much larger than the particle size particles can still get trapped on a filter by initial impaction and interceptions.

The filtration work like it does not work by straining what we call a straining is where particle size is smaller than the particle that is training that is like a you know your tea strainer or no this does not work like that if you were to do straining nothing, no filtration at this level will work. So, it they rely on you look at a filter, this is a few microns thick fiber and the filter is about 100 microns thick. So you have about 10 layers of filters. So this particle has to go just to change direction.

And the process it will hit and it will stick onto the fiber and the small particles stick on the fiber. So you can see that you can see at the edge of all of these fibers you can see the same phenomenon that you see in your house. If you have a mesh mosquito mesh something you will have dust that is collected on the mesh is very small, much smaller than that the opening thus there is the same principle it is wind blowing across it will get trapped along the on the sides and so on so you have physical particles.

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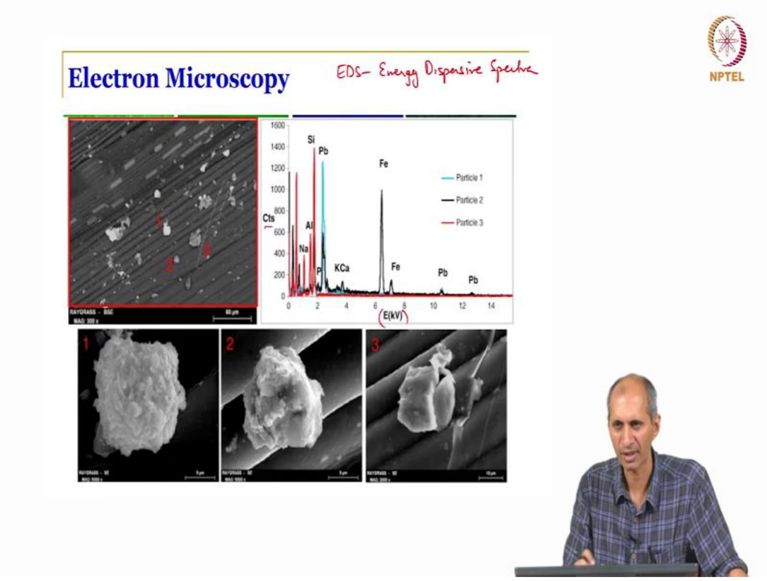

Electron Microscopy

EDS– Energy Dispersive Spectra

You can also based on the electron microscope the electron microscope also has a tool that is called as the energy dispersive spectra this is called the EDS so, I can go and probe go deeper into the distinct angling focus on one particle and I can so, electron microscopy very briefly works in this manner if you hit in microscopy the resolution of particles depends on a wavelength in wavelength depends on energy E is equal to C by lambda.

For visible optical visible light as a wavelength limitation. So, therefore, the resolution also is dependent reduced not goes beyond the point. So, you want to have higher resolution you need higher energy and electrons, the energy that electrons have are much higher and therefore, it corresponds to a resolution wavelength resolution is much higher. So, the way it works is this electrons hit the particle and some part of the, because of the density of the particle, some electrons are bounced back, they are scattered.

And they are collected by a detector that is sitting at an angle and as electrons are hitting each portion of this it is scattered and the scatters creates an image. So, the energy of the electrons that is going out creates an image of that particular spot and so, image if it cannot go very deep, it will be a weak scatter if it cannot go very deep, which means it is bounced back immediately it will be a bright scatter. So, based on that you can get the basis of the shape of the particle.

And corresponding to this energy that is coming out there is a wavelength corresponding to the radiation that is coming out scattering there is a wavelength energy curve and a wavelength. And so, we talked about it the few classes ago in emission thing atomic emission spectroscopy and one more some other topic, I did not know what to call right now, this gives a characteristic this thing signal this is called as energy.

So, this is this relates to the atomic structure of the element and there is an energy that is coming out and based on that you can find out what this particle is, this is very critical information because this is like a signature of the particle. So, you have particle if you collect particulate matter, say in a roadside environment and you go and do this kind of analysis and new elemental analysis, you can get very nice information of what is going to go to a very specific environment, say indoor air.

And you are seeing, say only carbon, nothing else there. So you can know that there is some carbon source in the air in this particular location and so on. So you can get a fair amount of information. But the downside to this is this particle is I know about 10 microns or 5 microns. How do I know there are millions of particles in this small sample I have, I am not sure if all of this is the same. So you cannot, you can give get some idea about this.

But you cannot use this anywhere. It is very difficult to use this for this you need a little more macroscopic data and average data for a large number of particles. You need to have elemental compositions. So people did not use a lot of this in the analysis.

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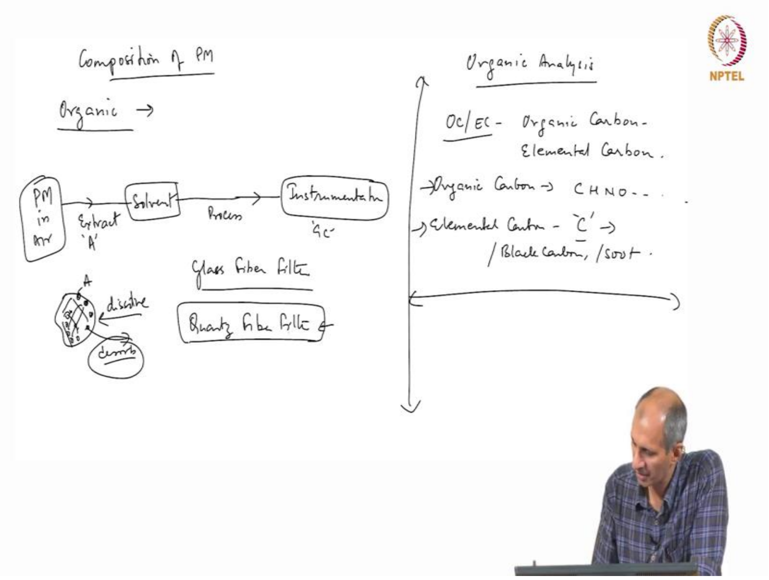

So that PM so we want to do the composition of PM you have 2 options again you can do so, you can look at organic or inorganic. So we are looking at organic you know the instruments that are used for organic we saw that already in terms of the water, if you want to look at organic chemicals, there are a set of instrumentation that you can use starting from the GC or LC or any of those instrumentations we want to use.

So, which we already know the instrumentation and we know that is PM in air, this is your source particles are coming from here. So, it needs to PM from the PM in air you need to pull out extract the you have to extract this component A into a suitable solvent and then we can process the solvent for the sample for the instrument, so, depending on GC takes a solvent like hexane or dichloromethane or something, you have to pull the PM, you have to pull the constituents where are the constituents of PM.

So, let us say particle is there is particle itself maybe an organic particle, which means that you have to dissolve the entire particle into a solvent. So, that is one option. Second option is if the particle is organic material is absorbed on other particles and you have to pull these particles out, you have to dissolve or desorb. Desorption also can be considered dissolution either way. So, this if A is stuck here; or the entire thing is A either way is possible.

So, what may happen sometimes is you may have a particle of sand silt or clay on which some organic matter may be organic absorbed sticking organic carbon humic material or you may have a standalone particle which is only carbon that happens in case of combustion sources only a small particle that is there in atmosphere is entirely carbon organic, it is made of either unburned fuel or any byproducts or carbon soot, elemental carbon, these are all possible.

So, any of these things is possible. So, when you are looking at these, the GC instrumentation like GC, it is very unlikely. So, GC will look at compounds which have some structure and some GC we saw how it measures with FID and all that. So, typically, it is mostly this category for carbons compounds which are organic compounds which are absorbed on something or they are some they have a composition.

And not just carbon, not just elemental carbon elemental carbon will not dissolve in many of these things it will stay as elemental carbon. So, here again there is a distinction. So, if you want to pull out look at composition of some of these things, if they are absorbed on something else, they will nicely show up in something like the GC or VLC but if it is pure carbon, it may not show up there, it will not dissolve in anything, it will sit there and it is elemental.

So, solid particle by itself pure carbon. So, so, for that you need to have a different approach of measuring it. So, there are tools for doing that are different. So, I will just classify it I am not going to discuss in detail so, when you do organic analysis for PM we do what is called us OC, EC analysis is called organic carbon, elemental carbon. What we mean by organic carbon is the carbon that is, part of CH, NO and so on.

So it is compound is any compound that we have seen in the list of organic chemicals. Elemental carbon is just carbon. This carbon, nothing else soot. We also call it is also called as black carbon. It is also called a soot various names for this elemental carbon. Organic carbon and elemental carbon are generally associated with different sources in the environment. So, there is an instrument which will measure the organic carbon elemental carbon pretty much on the same lines as what a GC works, but it is very dedicated to this.

So, the organic carbon elemental carbon instrument we will get to that in a minute. The other kind of this is that is all this is 2 of them.

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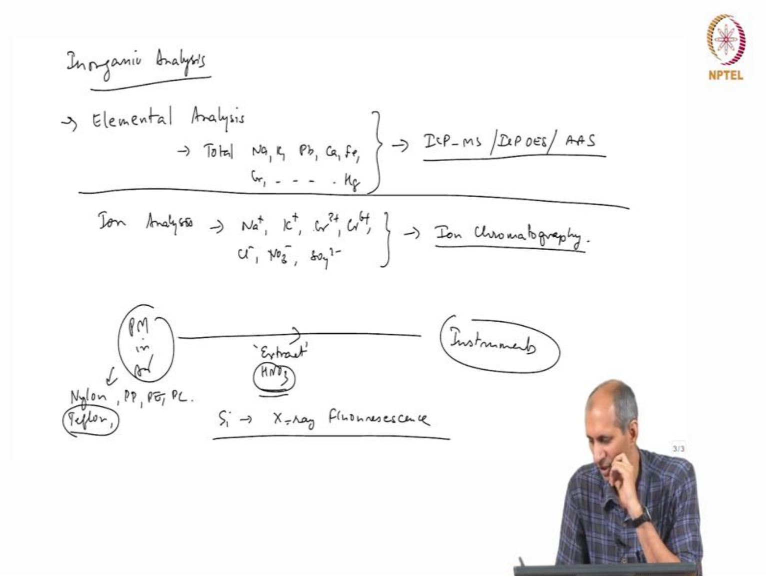

Inorganic Analysis

→ Elemental Analysis
→ Total Na, K, Pb, Ca, Fe, Cr, - - - . Hg } → ICP_MS / ICP OES / AAS

Ion Analysis → Na^+, K^+, Cr^{3+}, Cr^{6+}, Cl^-, NO_3^-, SO_4^{2-} } → Ion Chromatography.

PM in [illegible] → Instruments
'Extract'
HNO_3

Nylon, PP, PE, PC.
Teflon,

Si → X-ray Fluorescence

3/3

The other kind of analysis that you have is inorganic analysis. So, in organic analysis, you can do 2 kind of things you can do elemental analysis or you can do ions can you can get what is present in the on the particle by either of these methods. Both of these gives you different information you can combine this information so, it gives to know a full picture of you do both of them. So, element analysis will give you for example, it will give you a total sodium potassium, lead calcium ion, chromium.

So, you are doing all these methods that I have discussed last week. So, in that bunch of this mercury and everything, so, there are different methods for this there are different this is total, ion analysis specifically looks at ions. Ions means this is an NA+, K+, CR 3+, CR 6+, CL-, NO

3-, SO 4-, cations and anions separately element analysis you can do using an ICP – MS, ICP - OES as we discussed last week or the atomic absorption spectroscopy the instruments available this we use a technique called us ion chromatography.

So, the difference between these 2 approaches ICP - OES all of this stuff everything is done in the in terms of this is total everything is completely ion chromatography is just the ions. Now, 1 limitation of the elemental analysis is that it related to how you do the element analysis. So, like in the previous figure, you have the instruments and you have the PM in air to take it from here to here, you need to extract it into something you cannot directly put it.

What will you extract with in the case of organics our material, we want to extract organic compound from particulate matter. Just like what we do for water or soil solids, we extract it using an organic solvent. So the procedure there, here, this is for the organic the procedure here is to take the filter paper and you extract everything. And the only way you saw the SEM image, the filter paper and the particulate matter, you cannot separate it very well.

It is several layers deep. It is very difficult for me to pull out all the particulate matter so I am well better if I am doing mass balance. If I say in a filter paper, I have x micrograms of particles. I would like to do a mass balance on that I would like to know how much of this x micrograms corresponds to carbon or some element so I need to capture everything. I did not want to disturb it so I take the filter vapor and extract it as it is.

If I am extracting an organic solvent what is the possible interference that can happen in your analysis extraction extracting organic solvent the filter material itself may dissolve or depending on what the filter is made of it may leach out. So, what do you prefer? Like what we did for sampling what do you prefer? Is this filter paper material for organic analysis? You go back to our discussion on liquid water analysis of elements in water.

What did we discuss their terms of for organic analysis the water sample is preferably collected in glass. So, the preferable filter matrix is also glass. So, we use glass fiber filter your glass fiber filters, but glass fiber filters also contains a binder sometimes even though it is fully glass sometimes you just have glass fibers it is very brittle it will break very easily. So, there is another one called is quartz fiber filter.

You can have glass regular glass low grade glass can weave it into fibers and you can do that you can also have quartz fiber which is very high grade less the difference in quartz can withstand very high temperatures you can go up to 1000 degrees it will not disintegrate and stay as it is so, quartz is very high temperature this thing glass fiber filter may have a binder in it which can leach out when you do this so the preferred filter matrix is quartz for organic.

So nothing will happen if you put any organic solvent there is only glass there and there is no other binder. So it will, but last because of this quartz fiber filter, very brittle, quartz fiber not very preferred for mass measurement, because you take a filter and putting into a filter by that time some corner edge of the filter material go away. So, you will get an incorrect mass measurement, so we did not use quartz for that.

On the other hand, if you are doing metal analysis, what is the filter? What is the extraction medium that we generally use? We have not discussed it, what do we extract metals with? Generally all elements from high school chemistry what is the material used for extraction of metals, metal elements what solvent what liquid can we use and how acid which is acid that has dissolved everything on HNO3, so all nitrates are supposed to be soluble.

So, the generic solvent is HNO3, but sometimes you also add other acids along with it sometimes you depending on what the matrix is so, in general you can go and see the actual method for specific elements you have specific combinations of acids, but HNO3 is by and large the basis, so you used so for extraction of metals from soil, sediment and soil, which is a very dense matrix, a lot of material, we use concentrated on HNO3.

But the filter paper has only a few micrograms of you did not need to use concentrated HNO3 in amount of metals here is very small and it is a very mild process. So we generally did not use concentration so you can use the diluted HNO3 you know, 310 percent, the specification is given. So it is extracted and separate whether the acid extract is taken away, so, when you use

HNO3 will one element that will not dissolve in HNO3 you know which one is one element which will not dissolve in HNO3.

You required hydrofluoric acid for that, which is a very dangerous substance we did not use hydrochloric acid often in use hydrochloric acid you have to a separate lab separate conditions for all that which element can only be removed by hydrofluoric acid, dissolved hydrochloric acid any guess anybody it is a major constituent of particulate matter in atmosphere led to using the semiconductor industry a lot hydrofluoric acid used in semiconductor industry for this reason silicon.

Silicon is a big portion of crustal material re suspended, road dust, soil, silt, clay, all of them have silicon you cannot measure silicon by extract silicon, this method. So, in all these methods, you will see a footnote there that you cannot use silicon, you cannot measure you can measure silicon in the ICP, but the extraction will not contain silicon. So, you will see silicon in the data, but extraction will not tolerate hydrochloric acid.

You also have to understand that if you use hydrofluoric acid to extract you cannot put it into the ICP, it will destroy the ICP. ICP glass comprehension all that it will create a problem there. So, we did not silicon is generally not analyzed in these methods, but you need a non-invasive method a different kind of method. And you already seen that one of the methods that is used for silicon is what is called us X ray fluorescence.

Which is the same principle as the EDS direct energy dispersive spectra, you hit X rays and silicon will give a characteristic wavelength as the emission, you measure that so, the filter paper itself you have all elements you can use X ray fluorescence to get all elements infra using ICP it has problems because there are all spectroscopy have problems in terms of the extraction method is very simple because there is no problem about how what is the depth of the sample everything, it will take away everything, it will remove everything.

It is a Brute force method, it does not have any you did not have to be very precise with that knowledge. So the point we are making is if you want to do extraction with nitric acid, what is the filter bit paper that you need to use? You cannot use glass, because glass is elemental. A glass is a bunch of zip you can use quartz but quartz is again you know chill metal, we quartz is very expensive you did not want to use cost cheaper material for filter, what can you use for elemental analysis metals.

Same way what we use in for water metals in water, we use plastic bottles, you can use a plastic filter. So, you can use the filter paper that we use can be nylon, you get you get all kinds of polymer fibers. We have nylon, teflon, poly polypropylene, polyethylene, polycarbonate, all kinds of things. Teflon is preferred because teflon is considered to be inert, there is no binder, nothing, it is just teflon it is nothing. And it is the filter teflon filter paper is used for analysis of metals, at least in the X ray fluorescence and in ICP methods.

Definitely expensive so you can use a nylon if you want for some cases prefer teflon, you can also use teflon for mass measurement mass, because glass fiber is a very delicate fiber, it may tear and all that so the teflon can be used for PM actual, PM measurement, you are going to collect the sample take it and put it in a balance and take it out that actual full mass measurement. When we say mass measurements combined mass, PM mass, this what we are talking about is the composition analysis.

So in a given site, say outside this building, I want to get the full composition of everything. How many filters minimum number of filters I need to use. I cannot use the same filter for all analysis, which means I have to use multiple filters in the same at the same time.

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Multiple filters concurrently

QF → Org ~~etc~~

Teflon → Metals,

Teflon/Nylon → Ions

Speciation Sampler.

↓

SOURCE APPORTIONMENT

Ions extraction using water
(De-ionised)

So it is a bit of an inconvenience so you have to use if you get you have multiple concurrently multiple filters concurrently you can at least have quartz fiber for all the organic analysis. You have teflon for metals you have one more teflon or nylon for the ions, what is the extraction solvent for ions? For metals is acid organic is carbon organic solvents for ions, what is the solvent for ions? Water, you know, but is there a specific nature of the water that we want to use? Can we use tap water, we are used deionized water.

Because the extraction ion analysis using water we use what is called as Deionized. Why do we use water that is as deionized as possible? So, it is not possible to get zero absolutely, but very, very low amounts of deionization. There is a process called ion exchange which removes all ions and adds to the extent possible it makes it neutral and sensitive in this use case. So, again the same rules of blank minimum detection limit all apply depending on how so, this is a problem in metal analysis because metal analysis you are using solvents.

And you are exposed sample exposed to air there is always a chance that something from air will fall into the sample, which means you are false positives are likely to be higher. So, your minimum detection limit is likely to be higher. Shooting sensitivity is lower. Now, you cannot go to as low concentrations as possible because, for example, if you are deionized water, you cannot get deionization beyond a certain level.

So therefore, you cannot detect ions concentrations below a certain level, you always have to take that minimum detection limit and that is what it is there is nothing you can do about it unless you get so there is a lot of problems when you open a bottle of water, there is a lot of particles in the air they will all get in the time you are processing extracting and all that. So, you have run a method blank only with the deionized water.

Just to see what are the ions that are coming and if that is affecting your analysis method blanks become very important in metal analysis, we are doing aerosol, because the amount we are talking about aerosols are very small, you are talking about very large quantities little bit of error may not even show up but we are talking about very small quantities doing trace analysis, this becomes very critical.

So ion extraction is done using the network so you have at least 3 filters. One for each hand running success concurrently, which means that you need to have 3 EPM sampler or 3 of these sampler running concurrently. So, to do this there is what is called as the speciation sampler commercially available, so it is a multi-channel sampler. So you have multiple channels, they are all doing the same thing attached to one pump.

And the pump distributes flow in this 5 channels already that justify they are all the same flow so that the cutoff is the same. So you are you are measuring PM 2.5, all of them are measuring PM 2.5 at the same site, the intake is the same occasion. So you can I can get data on the course organic I can get organic, which includes OC, EC and everything and other things and on the metals, elements and ions.

Everything happens in the same site so I can get a good picture of course, there are statistical problems in this because, even though there are 3 different even though they are the same site 3 different filters, they all may not correspond to the same value, there is always a chance that they are slightly off. So, we have to do a lot of statistical replicates and find out what average and standard deviations and all that so, that is very important in this.

This is used in what we generally call as source apportionment. We will talk about this later, if you have time towards the end of the course, where essentially the source apportionment does is it tries to ascribe what is the contribution of different sources to pollutants in the atmosphere so, the source apportionment term is a general term it applies to anything it applies to water, soil, air, everything but in the air now, it is applied mostly to air.

Because the air is very complex medium and materials from different sources can come far away from the source and mix and therefore, it is important for us to find some way of doing it. So the information required for source apportionment comes from this kind of speciation analysis. For this we need to speciation sampler. Otherwise we have 3 samplers next to each other sampling 3 different species point we are trying to make is filter paper choice.

Depends on what you want to analyze cannot do one for all you can do one for all you it will be full of errors, you have to have a lot of control samples. For example, if I were to do extraction of metals using I will use only glass fiber filters for everything. I will have a lot of leaching extraction of other things. My blank filter paper signal will be maybe so huge that any trace I am getting there will be lost in it possibly.

So I have to do a lot of cleanup. And a lot of my MDLs will all be low and high and so on sensitivity of the method will go down so on, so because information like this is used in policy, making very careful about this, but if you want general information, just want to know what is there you can probably do it with one filter and then get an idea this is approximately these are the things which are there and therefore I will then refine my study.