Environmental Quality:
Monitoring and Analysis
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Lecture No. 29
Monitoring methods for Air PM - Part 2

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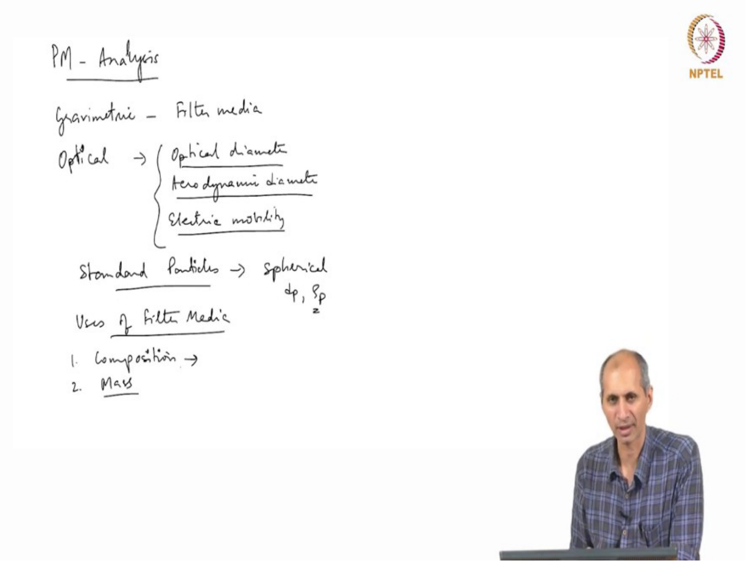

PM - Analysis

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. We looked at different methods of measurement, quantification for the entire range. So, we were looking at gravimetric measurements which involved a collection on a filter media versus other techniques which are things like optical techniques. Optical techniques include both measurement of the optical diameter or by the aerodynamic method. So optical methods both the AV, APS which is aerodynamic 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, other one gives you aerodynamic diameter. Then we also looked at something called as electrical mobility which is a DMA. The electrical mobility diameter is different sizes at different phases. So, 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 diameters are the same, there should be 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 an 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 aerodynamic diameter, I mean we need standards here are standard particles. Standard particle means there are particles that are known to be of a specific size. 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. The definition of aerodynamic diameter is the mobility of an equivalent spherical particle of a certain diameter and density of 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, you calibrate the instrument using standard particles like this and then the same thing you do it with other instruments and see what is that giving. Whatever, this says n what is the other instruments saying. 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 don't have a standard and then compare the particle size distribution or the numbers that you are getting, what supposed to be PM 10 one instrument is getting other instruments giving PM 10. How does it vary? There may be difference, there will be a difference and 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 is mass. Mass is a very fundamental quantity. People want to see particles, if I show them a filter paper, that the sample that you have collected is dirty, this is the mass in 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 that 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. If I show them optical scattering and diameter then nobody will believe it is like a black box, they say, I don’t know what you are punching. You are doing some programming and you are showing some numbers. I don’t believe anything that you are saying. So physical mass shows that it is there. Even though it does not give you full information, it 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 base detector have 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. So you can imagine if I use an SMPS, which is the DMA and particle CPC that we discussed, how much information can you get from a single sample for one day at a road side, 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.

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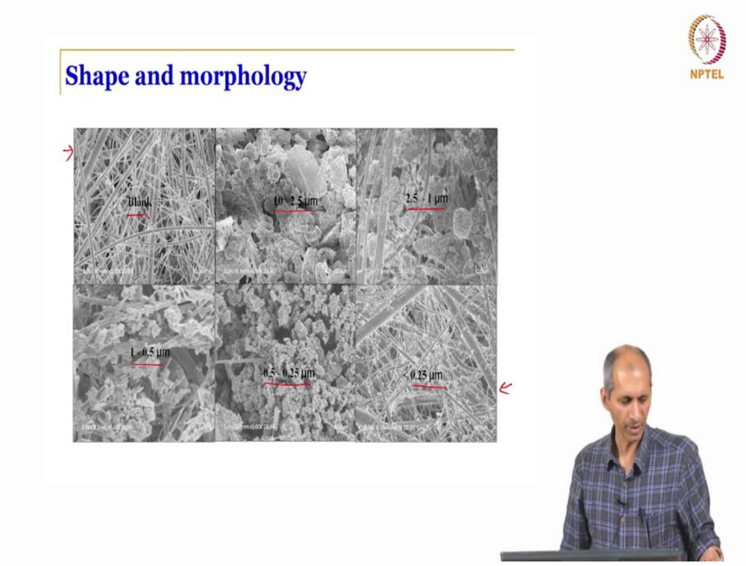

Shape and morphology

So composition of filter media is a very important thing so, we would like to see what these particles are. So, one of the ways in which we do that is by looking at composition, shape and morphology. You can look at shape and morphology by using microscopy. So, 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, it is about 10 microns. 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 impactor, from an impactor in which this is 10 to 2.5 microns, 2.5 to 1 microns, 1 to 0.25 and 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 filter. 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 inertial 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 straining that is like a tea strainer or some of these. It does not work like that if you were to do straining, no filtration at this level will work. So, if 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, it has 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 at the edge of all of these fibers, you can see the same phenomenon that you see in your house. If you have a mosquito mesh something you will have dust that is collected on the mesh is very small, much smaller than that the opening that is there, is the same principle it is wind blowing across it will get trapped along the on the sides.

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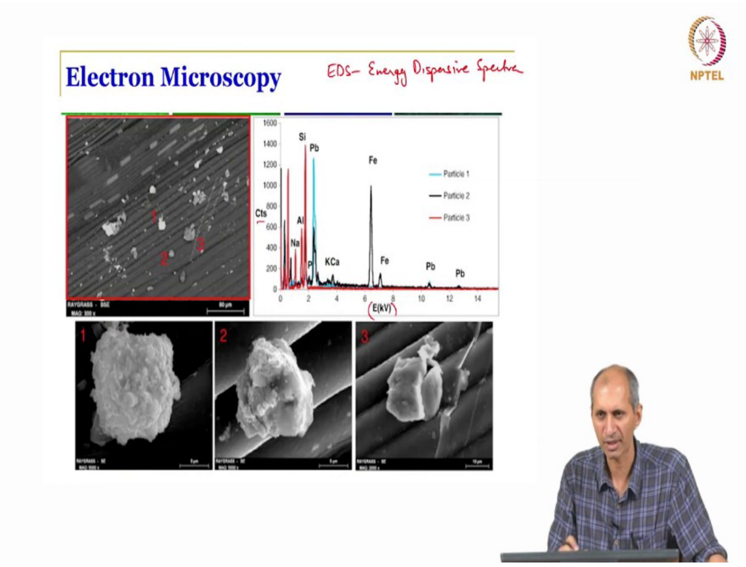

Electron Microscopy

EDS– Energy Dispersive Spectra

Electron microscope, also has a tool that is called as the energy dispersive spectra, the EDS so, I can go deeper and focus on one particle and so, electron microscopy very briefly works in this manner, in general microscopy the resolution of particles depends on a wavelength, and wavelength depends on energy.

$$E = \frac{hC}{\lambda}$$

Visible light has 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 the energy that electrons have are much higher and therefore, it corresponds to a wavelength resolution that is much higher. So, the way it works is this, electrons hit the particle and because of the density of the particle, some electrons are bounced back, they are scattered and collected by a detector that is sitting at an angle and as electrons are hitting each portion of this it is scattered and the scatter 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 can 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 the radiation that is coming out scattering there is a wavelength energy curve and a wavelength. We talked about it the few classes ago in atomic emission spectroscopy and one more some other topic, this gives a characteristic signal, this is called as energy. So, 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, if you collect particulate matter, say in a roadside environment and you go and do this kind of analysis, a few elemental analyses, you can get very nice information of what is going on and if you 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 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 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, an average data for a large number of particles. You need to have elemental compositions. So people don’t use a lot of this in the analysis.

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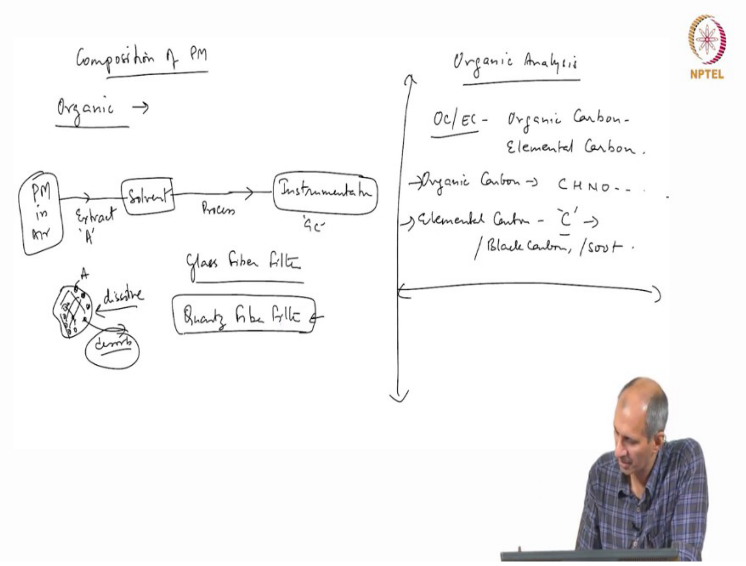

So we want to do the composition of PM, you have 2 options again you can look at organic or inorganic. So we are looking at organic you know the instruments that are used for organic we saw that already in terms of the water, if you want to look at organic chemicals, there are a set of instrumentation that you can use starting from the GC or LC or any of those instrumentation. So, which we already know the instrumentation. We know that PM is in air and we need to pull out, we have to extract this component A into a suitable solvent and then we can process the solvent for the instrument. So, GC takes a solvent like hexane or dichloromethane or something, you have to pull the PM or constituents, where are the constituents/PM?

So, let us say particle is there, this 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 organic material is adsorbed on other particles and when you have to pull these particles out, you have to dissolve or desorb. Desorption also can be considered as dissolution either way. So, 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 adsorbed, sticking, organic carbon or 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 or 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 instrumentations like GC, it is very unlikely, GC will look at compounds which have some structure and we saw how it measures with FID and all that. So, typically, it is mostly this category, compounds which are organic compounds which are adsorbed on something or they have some composition. And 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 adsorbed on something else, they will nicely show up in something like the GC or LC but if it is pure carbon, it may not show up there because it will not dissolve in anything, it will sit there and it is elemental.

So, solid particle by itself pure carbon. So, for that you need to have a different approach of measuring it. So, there are tools for doing that which 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 CHNO and so on. So it 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.

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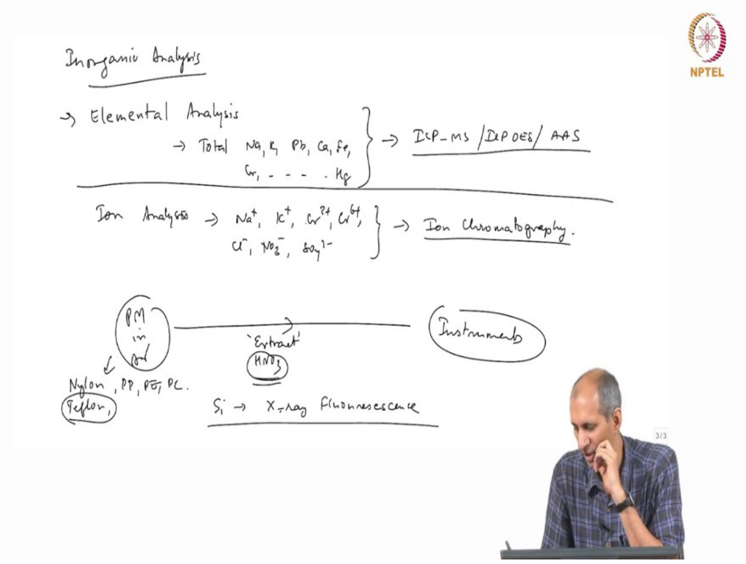

Inorganic Analysis

→ 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.

The other kind of analysis that you have is inorganic analysis. So, inorganic analysis, you can do 2 kind of things you can do elemental analysis or you can do ions, you can get what is present on the particle by either of these methods. Both of these gives you different information you can combine this information so, it gives a full picture if you do both of them. So, element analysis will give you for example, it will give you a total sodium, potassium, lead, calcium, iron, chromium. So, you are doing all these methods that I have discussed last week. Ion analysis specifically looks at ions. Ions means Na^+, K^+, Cr^{3+}, Cr^{6+}, Cl^-, NO^{3-}, SO_4^{2-}, there are 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 as ion chromatography.

So, the difference between these two approaches is ICP-MS, ICP-OES, AAS all of this does is everything, ion chromatography is just the ions. Now, one 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 sample to instrument, you need to extract it into something you cannot directly put it. What will you extract with? in the case of organics we extract just like what we do for water or soil solids, we extract it using an organic solvent. So the procedure here is to take the filter paper and you extract everything. 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. 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 don't want to disturb it so I take the filter paper and extract it as it is. If I am extracting with an organic solvent what is the possible interference that can happen in your analysis extraction? you are extracting this in an 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 there, 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, but glass fiber filters also contain a binder sometimes even though it is fully glass, if you just have glass fibers it is very brittle it will break very easily. So, there is another one called as quartz fiber filter. You can have regular glass, low grade glass, you can weave it into fibers and you can do that. You can also have quartz fiber which is very high grade glass. The difference is 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 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 and there is no other binder. But because quartz fiber filter is very brittle, it is 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 tear and go away. So, you will get an incorrect mass measurement, so we don't use quartz for that.

On the other hand, if you are doing metal analysis, what is the extraction medium that we generally use? We have not discussed it, what do we extract metals with? Generally, from high school chemistry what is the material used for extraction of metals, what solvent, what liquid can we use and how? An acid, which is the acid that has capacity to dissolve everything, HNO_3, so all nitrates are supposed to be soluble. So, the generic solvent is HNO_3, but sometimes you also add other acids along with it 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 HNO_3 is by and large the basis, so for extraction of metals from sediment and soil, which is a very dense matrix, a lot of material, we use concentrated on HNO_3. But the filter paper has only a few micrograms of it, you don't need to use concentrated HNO_3. The amount of metals here is very small and it is a very mild process. So we generally don't use concentration so you can use the diluted HNO_3 10 percent, 20 percent, the specification is given. So it is extracted and separated so that the acid extract is taken away. So, when you use HNO_3 there is one element that will not dissolve in it, you know which one is that? You required hydrofluoric acid for that, which is a very dangerous substance we don't use hydrofluoric acid often, when you use hydrofluoric acid you have to a separate lab, separate conditions for all that. Which element can only be removed by hydrofluoric acid? Any guesses? It is a major constituent of particulate matter in atmosphere, it is used in the semiconductor industry a lot. Hydrofluoric acid is used in semiconductor industry for this reason, silicon. Silicon is a big portion of crustal material, right? Re-suspended road dust, soil, silt, clay, all of them have silicon, you cannot measure silicon by extraction, this method. So, in all these methods, you will see a footnote there that you cannot use silicon. You can measure silicon in the ICP, but the extraction will not contain silicon. So, you will see silicon in the data, but extraction cannot be done.

You also have to understand that if you use hydrofluoric acid to extract it will destroy the ICP. ICP has glass components and all that it will create a problem there. So, 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 as X ray fluorescence which is on the same principle as the EDS, 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 instead of doing ICP, but it has problems. All spectroscopies have problems. The extraction method is very simple because there is no problem about what is the depth of the sample everything, it will take away everything, it will remove everything. It is a brute force method, you don't have to be very precise with it and all that. 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. You can use quartz but quartz is again very expensive so you don't want to use. What cheaper material can you use as filter, for elemental analysis metals? Same way what we use in for metals in water, we use plastic bottles, you can use a plastic filter. So, the filter paper that we use can be nylon, you get all kinds of polymer fibers. We have nylon, teflon, polypropylene, polyethylene, polycarbonate, all kinds of things. Teflon is preferred because it is considered to be inert, there is no binder, nothing, it is just teflon. So, teflon filter paper is used for analysis of metals, at least in the X ray fluorescence and in ICP methods. Teflon is expensive so you can use a nylon if you want for some cases, but prefer Teflon. You can also use Teflon for mass measurement, because glass fiber is a very delicate fiber, it may tear and all that so the Teflon can be used for actual PM measurement. You are going to collect the sample, take it and put it in a balance and take it out that is full mass measurement. When we say mass measurements it's 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. What is the minimum number of filters I need to use? I can't use the same filter for all analysis, which means I have to use multiple filters at the same time.

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Multiple filters concurrently

QF → Org ~~ata~~

Teflon → Metals,

Teflon/Nylon → Ions

Speciation Sampler.

↓

SOURCE APPORTIONMENT

Ions extraction using wate

(De-ionised)

So it is a bit of an inconvenience, you have 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 it is acid, for organic it is organic solvents, what is the solvent for ions? Water, you know, water is enough for ions. But is there a specific nature of the water that we want to use? Can we use tap water, we use deionized water because the extraction ion analysis using water we use what is called as Deionized water. We use water that is as deionized as possible. So, it is not possible to get zero absolutely, but very, very low amounts of ions. There is a process called ion exchange which removes all ions and to the extent possible it makes it neutral and sensitive in this 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. It means 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's what it is there is nothing you can do about it. 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. So, 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 deionized water.

so you have at least 3 filters. One for each and they are running 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 flow rate is adjusted so they are all the same flow so that the cutoff is the same. So if 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 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 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. What 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 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 you cannot do one for all, you can do one for all but 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 and I were to use only glass fiber filters for everything. I will have a lot of leaching, extraction of other things. My blank filter paper signal 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, you 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.