Environmental Quality: Monitoring and Analysis
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Lecture – 16
Environmental Analysis: Quality Control – Part 3

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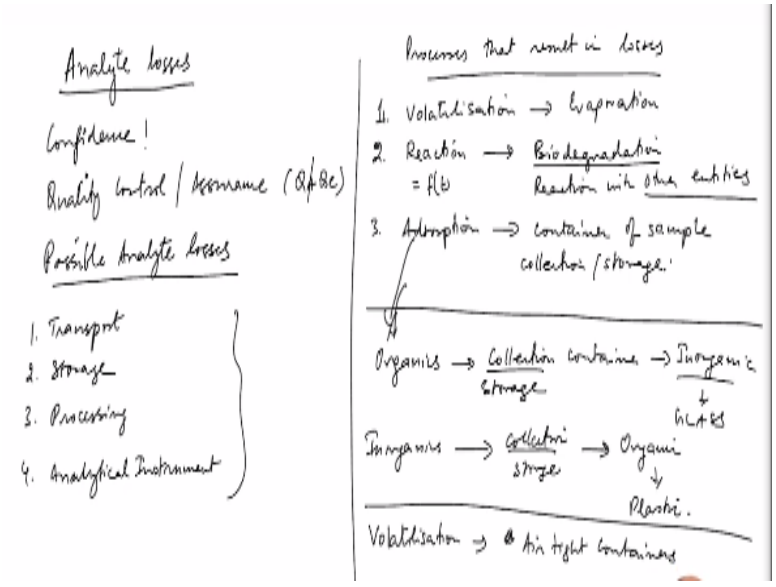

In the last class, we had discussed the analysis method for organic compound from water and we went to the sequence of the extraction process and the analytical instrumentation. One of the concerns in chemical analysis for environmental samples is the issue of analyte losses. This is important from the point of view of the confidence people have in the measurement and because this is also subject litigation, the analysis that people do are used for important decisions, and therefore people would like to have some kind of confidence in terms of the accuracy of the results.

Therefore, the burden of the quality control and assurance lies with the analyst and the chemical analyst. So, there are a large number of procedures that are built into the analytical procedures. If you look at a standard method that as we are discussed, this quality control and this Q/QC procedures are inbuilt into the system. So, in terms of analyte losses, we look at what are the possible analyte losses, where do this occur? So, the possible analyte losses occur first in the transportation of the sample.

Second, which occur in the storage, then in processing, the fourth in the analytical instrument itself or the chemical analysis instrument part of it. So, if you look at these things, we first take it one by one. We look at transport. Transport for example if you are taking a water sample from somewhere, you are collecting the water samples, various kinds of errors can occur during the transport and the entire all of these categories, there are certain number of processes that can result in the analyte losses.

So, we will rewrite this in terms of, and these are common processes that result in losses. One of the main first things is volatilization, which is evaporation of the sample, evaporation of the analyte from the water sample or the filter or anything. So, whatever we are going to discuss here applies to analysis of all matrices whether it be water or A sample using sorbent or a filter or using extraction often analyte from a sludge or soil and it is common for all of them. So you just have to adapt it based on that.

Volatilization essentially is evaporation, we will come back to it little bit, how to assess it. The second part of it is reaction. This reaction could be many things. Reaction could be biodegradation, it could be reaction with other entities in the system which is things which are already present in the sample, they have started reacting and over a period of time they will react. So when we say reaction, the reaction is a function of time.

So, if you collect the sample at a certain time and then you wait till a certain amount of time to analyze them, there is a likelihood that the analyte that you are interested has been starting to react and even if the reaction is slow, you will lose some part of it due to reaction, this is a big concern, especially biodegradation. This biodegradation is one of the primary concerns. This reaction with other entities is what generally we have to take care of this because sometimes analysis itself is a problem and then we have first of all briefly in the other discussion, but we will again go iterate again in this discussion.

Third one is adsorption. So, the adsorption occurs through any solid surface during the processing, collection and processing, and one of the solid surfaces that you can generally see is solid surfaces we are looking at adsorption is the container itself, container of sample collection and storage. Again, adsorption is a kinetic process. It means that if you look at the adsorption, the way adsorption occurs, the volatilization reaction occurs they are all kinetic processes until there is an equilibrium.

So, they will reach a point where they will not happen anymore, these process would not happen anymore, but till that point there is continuous loss and, and therefore this influences the value of the analysis depending on how far it is from the time of collection. So, this is one of the big things. So, when you look at the design of the sample collection and the analysis processes, to reduce these 3 things, we keep this in mind when we are designing processes for sample collection. So, for example we are looking at organics.

There is a general theory that rule of thumb that organics like to bind with other organics. Therefore, the collection vessel, this collection and storage containers should be inorganic. In other words, the one of the most common inorganic containers is glass. So, if you are handling organics, then typically it is glass containers and similarly if you are handling inorganics, the storage and collection is organic, typically, which means a lot of times this is plastic. So there is no adsorption, it will take care of adsorption, the other things are something else.

So if there is reactions happening, then that is something you need to take care. So you need to find out what is your analyte and if it will react, okay. So there are also ways of finding all of these things. So, I am just describing the initial processes here. So this takes care of adsorption. For volatilization, it is very obvious for volatilization you need to have airtight containers, which means that the container that you bring from the sampling site to the lab for storage should be airtight which means that there is no increase, there is no chance of loss. So, let me explain this a little bit.

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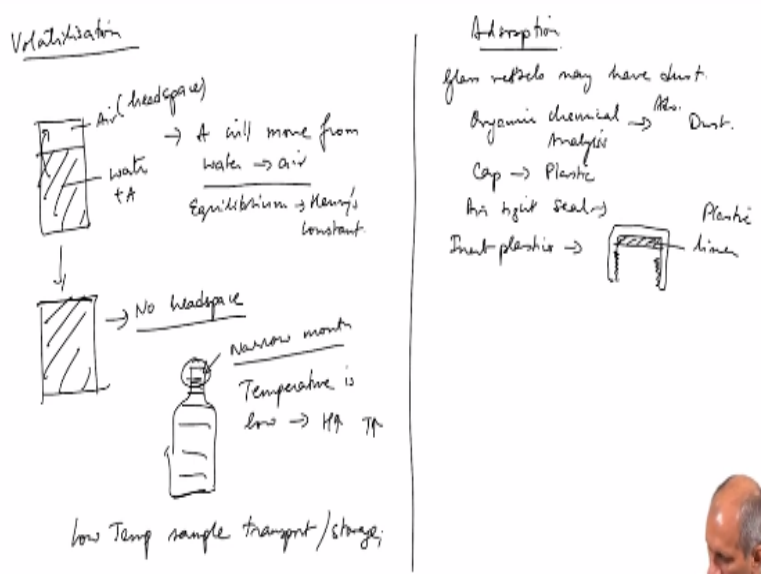

When we are talking about volatilization, what we are really looking at is this. Let us say a sample is exposed to, this is water plus A, this is air. So if I take water from a river or a lake or any such place and fill this container, there is a certain amount of air in contact with it. So, the A will move or transport and it will move until there is equilibrium and this equilibrium is related to the Henry's constant. So, this is a very volatile compounds sitting in the water. If there is air space, it will move up.

So, the general tendency is to reduce this, your sample collection is done. So, this is also called as headspace. The sample collection is done with no headspace, yeah. So, this takes care of volatilization. Second part is even if there is no headspace, there is also chance that this container, so what all typical type of containers that we have, all containers need an opening which typically you have a bottle like this, a jar.

So, the openings are usually narrow mouth, even if it is full, you do not need that you have a very narrow opening, so the evaporation itself is very small, so that narrow mouth bottles are usually taken care of yeah and then also the temperature is low. The temperature is low because Henry's constant is a function of temperature and this constant increases with increase in temperature. Therefore, you keep the temperature down, Henry's constant likely to be low okay.

In addition keeping the temperature low for sample storage and sample transportation sometimes, it will also reduce biodegradation if there is happening. So, all reaction all biodegradation typically is low when at low temperature. So, this is generally the rule of

thumb that sample storage and collection is happening at low temperature, sample transport and storage yeah. When we talk about adsorption, one of the main things that even if you use a glass vessel, sometimes they may be adsorption, glass vessels may have dust and the dust can be organic.

So, if you are looking at an organic chemical analysis, an adsorption occurs on the dust and the cap of the vessel, so you have this kind of cap, the cap is usually made of plastic. The reason it is made of plastic is we need a an airtight seal and to get an airtight seal, usually it is you can get an airtight seal only if you have some kind of a washer or something like that and that is usually these materials are plastic or polymers and so there is a chance of, so one must take care that if do not want any loss by adsorption, you must use a clean glassware as well as use very small amount of plastic are as far as possible use an inert plastic.

So, inert plastics means that these plastics do not interact with anything. So, there will be adsorption where adsorption is minimized to a large extent. So, there are many plastics that are available that people make these caps with, the lining of the caps, so the inner lining of the caps. The inner lining of the cap is this portion, where this is the screwing mechanism, the screw cap mechanism is here. So, this is a plastic cap and the inner lining, there is a lining, there is a plastic liner.

So, this plastic liner is to an extent made. You also have aluminum liners and all that, but their problem is that they may not be very tight, so people are trying to make containers that are as best as possible. Your samples in the sample transportation and storage, there is a possibility that the bottle will get upturn. If you do not want to do it at all, you do not want one to take care, absolutely there is no contact.

Then one can ensure that the bottles are not turned and they are upright throughout and that one can take care, but a lot of times one is not sure whether this is possible you know sometimes sample storage and sample transportation not possible to keep bottles upright and it will happen. So, this is all to take care of those kinds of issues as well, okay.

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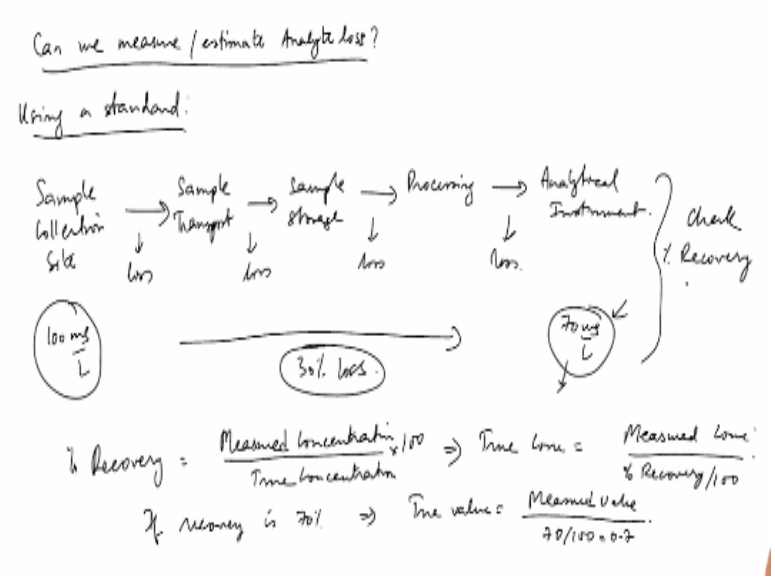

So, we know that there are these losses. So, when you do an analysis, how do you check? How do you check for these losses? We ask this question, can we measure our estimate analyte loss? And the answer is yes and we do it the same way we do, since this is type of measuring the accuracy of the sample, the only way we can check accuracy is by using a standard. So, one of the 2 things, so when you are doing analyte loss, we are assuming that that there is a certain amount of material and that is going out of the system.

So the only way to do that is you know what is there in the sample originally and then you find out what you can recover. So, we measure, this is a sequence of sampling. So we get sample, collection site, this is a recap of what we do, sample processing and analysis and the analyte goes through all of these stages and therefore, each stage there is a loss, there can be a loss, especially when we are doing extraction by solvent and all and then we are concentrating the solvent, we can have a lot of volatile loss because some of these solvents are volatile.

They meant to be volatile because you need to concentrate, they must be easy to evaporate. During evaporation, they will also release some of these chemicals, the analyte also may go along with it. So, it is fair to expect that there is a fair amount of loss. So, if I put 100 milligrams per liter of a sample. If the analyte contains another concentration in the sample is 100 milligram per liter for say, and by the time you come to the analytical instrument, and the instrument reading gives 70 milligrams per liter.

All it means is that there is a 30% loss in the system, yeah. There 30% loss in the system, if you do not measure this that there is 30% loss, you will assume that 70 is correct number. So, you are underestimating a pollutant concentration. From an environmental analysis point of view, this is not a good thing, underestimating the pollutant concentration is not safe, and therefore one would rather overestimate it because it is still conservative, but underestimation is a problem. So, we would like to measure it.

So, the easy one way is to check the loss, so is to check the recovery efficiency, the percentage is recovery. So, we define recovery as measured the concentration by true concentration. This is the recovery, percent recovery is into 100. This implies that the true concentration equals measured concentration divided by percent recovery by 100, yeah. So for example, in this case if recovery is 70%, there was a true concentration. The true value is measured value divided by 70 by 100, 0.7 okay. Usually, this is the calculation one does.

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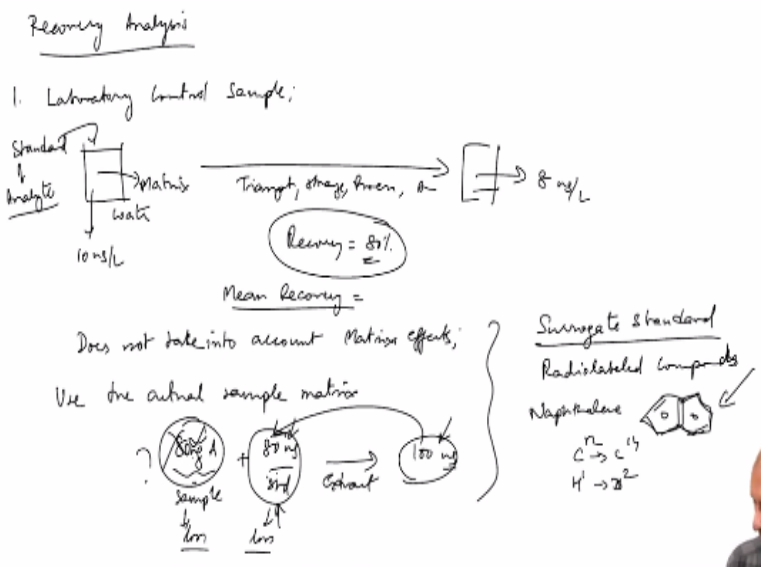

So how does one calculate measured recovery? One method that is available is by doing what is called as a laboratory control sample. What we do here is we take the matrix, so in this case let us take the case of water. We take water, we add a known amount standard into this and let it go through the entire sample storage. So we add it and we take it through the transport, storage, processing and analysis. So we know what we are adding, let us say that we are adding so that this concentration is known for us, say it is 10 nanograms per liter or something like that and then we run it into the instrument.

Finally, we get a concentration of 8 nanograms per liter okay. We calculate what is the concentration in the extract based on the GC as we discussed in the previous class. So, we know now that the recovery is 80% okay. Now, we assume that this recovery applies to all analysis were done in the same manner, same method, so you are not changing the method or not changing the time it takes when recovery is assumed to be the same or we do it several times and we have an average, we have a mean recovery and then we apply it to all samples as a correction factors for the analysis that we do.

There is a problem and this is not accepted, this is the easier way to do it, because you can take the standard of the analyte itself and do it, and so it is exactly the recovery of that particular compound. However, the general criticism or the drawback of this is that it does not take into account what is called as matrix effects. What we mean by this is that the water itself, say we are taking samples from a lake, the lake water may contain other constituents that may influence the analysis, that may influence the way in which extraction is done and the way influence the concentration.

So by doing a laboratory control sample, we do not take into account all of these. So, we need to take this matrix of effect, which we need to use the same type of water, how do we make the same type of water, very difficult and we get into more trouble by trying to replicate that that control. So, the second option that you have is use the actual sample, sample matrix, but this leads to a problem that if you use the same sample matrix, then how are we going to, if you add the standard of this particular analyte into the water, you do not know what exactly is present in the beginning.

So for example, let us say I have 80 nanograms of A that is already there in the sample to which I add 80 nanograms of the standard. I extract and I end up with say 100 nanograms the final extract. I have no idea of knowing if it is 100, then of course I have a problem, it is greater than 80, which is a standard addition. So I do not know how much of this loss, there is a loss from here and there is also a loss of this and I do not know which one because I do not know this number.

If I know this number, I can find out yes, because I do not know this number, I do not know how much of this loss is coming from here and here. Therefore, I cannot do that, but it is the same compound or compound may be there. So this can work if the standard that you add is

not present in the sample, okay. Now, you have no a priori, no way of finding out, but you have already some guess that what you are looking for. So it is a very tough situation because it is difficult for us to find a compound that is not the analyte, but it is close to the analyte okay.

This is where we get to the definition of what is called as a surrogate standard. A surrogate standard is usually a compound that is very similar to the analyte of interest, but it is not analyte of interest, and so in the analytical instrument that we are using, this shows up around its characteristics similar to it, most of the time we are using chromatography. So, it shows up in the chromatogram, but not at the same point at the analyte, but it shows likely off especially in methods like GCMS okay.

So, what we are looking at is typically things like radio labeled compounds. For example, if we are looking at naphthalene, yeah, so there are 2 benzene rings. The radiolabel part is either replacing it is either replacing one C12 by C14 or replacing one H by deuterium 2 some such thing. So, one atom is replaced by an isotope and so these isotopes are not part of, they are not present in the environment and they also show up a signal that is slightly different from the non radiolabeled naphthalene.

So, this being the case, if this is the case, then one of the things that we know is we are able to distinguish between in these 2 cases which is the sample. The sample is you get a signal of naphthalene, we have some value of naphthalene, but we know the value of the radiolabel standard that was injected and radiolabel standard that was extracted. So, we use the extraction efficiency or the recovery efficiency of the surrogate standard and apply it to all compounds and run A batch.

The reason I am saying this apply to all compounds is surrogates standards are expensive, therefore if you are analyzing 100 compounds in a series in a water sample, we cannot, it is difficult for us to buy 100 surrogate standards, it is prohibitively expensive. So there is one surrogate for a set of compounds and we apply that and then for the next set, we buy another surrogate standard and we apply that. So it is not the best way to do it, but it is close.

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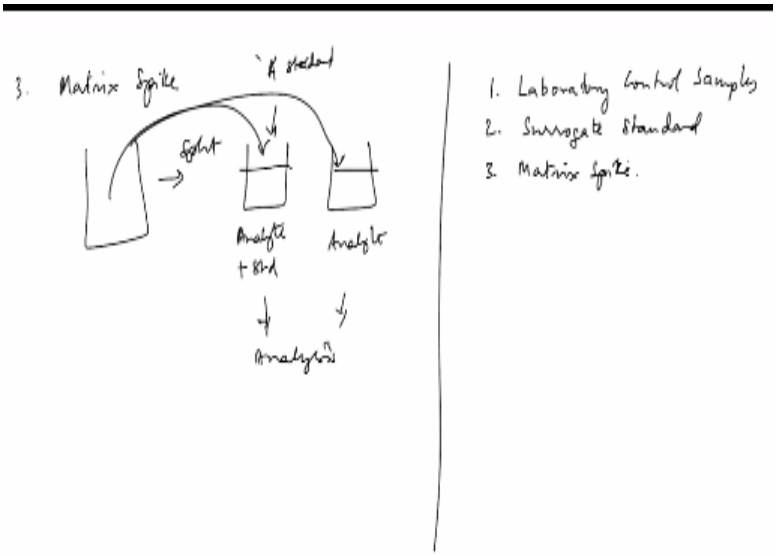

The third method is called as a matrix spike. In this, we take a sample, we split into 2 smaller samples. Into one, I add a normal standard. I add the analyte A standard. This is not a surrogate. The other, I do not add the standard. So this has analyte plus standard, here only analyte, and both of these samples go through the analysis and then the difference between these two, yeah. So difference between these two will reflect the efficiency of the extraction of one of the standard that you have added, okay.

So what this does is this is a better way than using a surrogate. The only problem here is again that you are splitting the sample and that is additional analysis, one additional analysis that you have to do. So you have to work out the overall cost of doing it but you do not have to do it often, you do it once in a while just to check if there are matrix effects on this. So, these are the 3 methods. You have laboratory control samples, the standard addition, you have a surrogate and we have the matrix spike.

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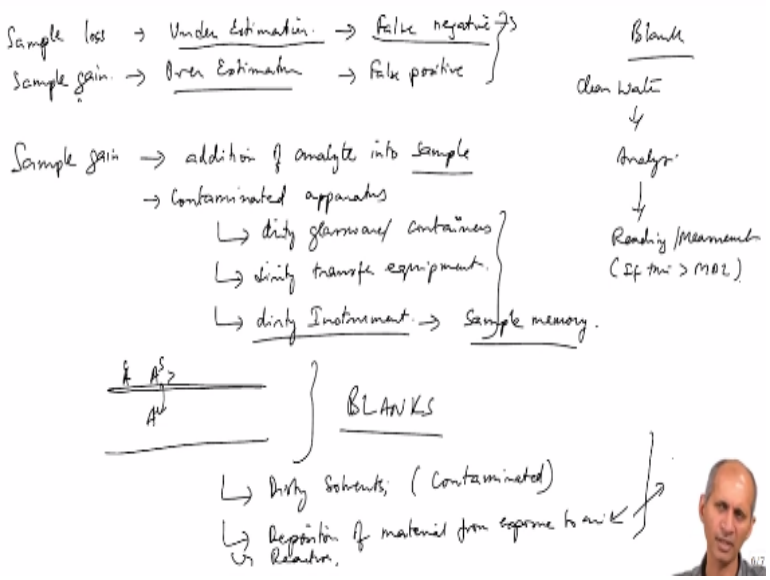

Sometimes, we are talking about sample losses. There is also another aspect to sample losses lead to underestimation, which is usually falls under the category of false negative, but there is also another case of false positives, which means that what we are calling us false negative is not just whether it is not a true false answer. We are saying false negative essentially means there is an underestimation. It is another way of representing a false negative that is you are assuming that something is not there when it is there.

So, you are neglecting that missing component. Similarly, you have false positive, which means you are overestimating and this can happen if you have sample gain. So, sample gain it seems not intuitive because sample will lose, where can you gain sample from since mass cannot be created from nothing. So there are a few instances where you get sample gain and the sample gain happens, the sample gain we are talking about mean by addition of the analyte from somewhere.

Addition of analyte in the sample, not at the collection site but somewhere else by an artificial mean. So, how does this happen? This happens by several means. One is the most common contaminated apparatus. This is a very general case. Contaminated apparatus very simply it means dirty glassware or containers, dirty transfer equipment. So, for example, during the analysis and extraction, you transfer, a lot of that transfers that is happening.

In that, there could be you use a pipette for higher concentration and dip into a lower this thing and that is contamination, it can transfer material from higher concentration to the lower concentration, that is a problem, yeah. Dirty instrument, this is a very common way of

things happening. Dirty instrument means the analytical instrument is not lost its previous samples. So I inject a sample into a gas chromatography instrument and it retains some of these chemical from one analysis and that is sample loss for one sample, but for the next sample, it is sample gain.

So both these things can occur this kind of instrument loss, in the case of an instrument thing. So this is usually called a sample memory for instruments. So there is a lot of very strange things that happen because when you have sample loss, all of these adsorption and volatilization all of these are happening driven by equilibrium which means that material always move from a region of high concentration to low concentration.

So, if the analyte is in a matrix, in a medium that has a higher concentration than the one which is in contact with, it will try to go and adsorb there, but if you have a sample with a lower concentration than whatever is contamination, so therefore there is a channel in which the analyte is adsorbed. If this concentration on the solid is greater than the concentration in the liquid, then transfer will occur in this direction, which means it will release chemicals into your sample, so that is a false positive.

Your concentration is being gained by this. So, how do you check for this? The checking for this is why we use what is called as blanks and we have discussed this in other lecture, but the blanks analysis is very important, every time we do an analysis, we need do blank and this blank can also, dirty glassware and apparatus, we also have the other category of dirty solvents. What we mean by dirty is contaminated that is a correct word for it because in the lab where a lot of analytical work is happening, there is always the possibility of cross-contamination and this is a very real way to do it.

So, you need a reference for clean matrix for doing a blank which means that I need to do the entire analysis. So, blank analysis usually will occur where I need to do the entire analysis. I take clean water and go through the analysis through the entire thing and I get a reading or a measurement. If this is greater than 0, which means that system is contaminated, you cannot do any further analysis until this becomes close to 0 or insignificant, below detection limit. In other words, the correct word is greater than the minimum detection limit okay.

So, this is I think to summarize we need to estimate recovery for losses, we need to do blank analysis for sample gains. Sample gain can also happen by contamination of the sample itself. For example, the contamination of sample we are looking at dirty glassware. We are also looking at things like deposition. This does not happen to all sample, deposition of material from exposure to air, can also happen the reaction but that very rare, they usually do not. It is a rare coincidence where the analyte you are interested in is coming from reaction of other things present in the system and leading to this.

So that is usually very uncommon, but this deposition of material exposure to air is common and is important in some cases, especially when the component that you are looking for interested is there in the environment and most commonly this deposition of material from exposure to air is most common in the analysis of elements, metals elements. Because there is a lot of dust which is for example, you analyzing soil or water from a lake or a river. There is also a lot of material is there ambient environment which can deposit in and that will give you wrong reading in that case.

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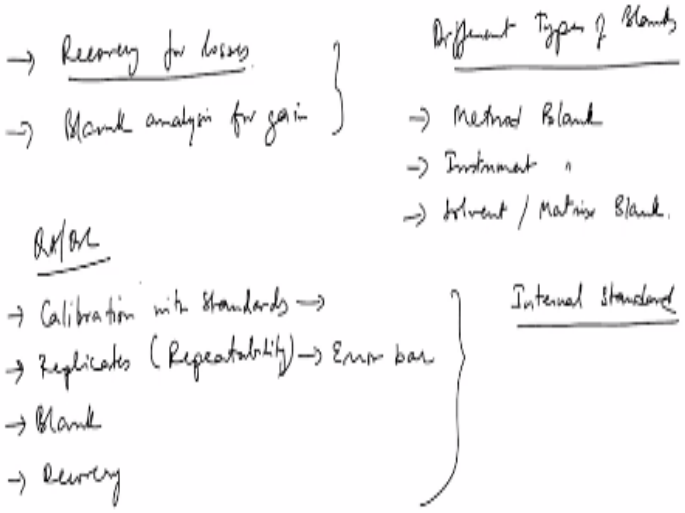

So, to summarize this recovery for losses is blank analysis for this thing. There are different kinds of blanks. There is a method blank. These are all methods of troubleshooting. There is a method blank that essentially tells you if along the way there is any contamination is happening, yeah. There is an instrument blank which tells you only analytical instrument is causing a release which is causing an addition. Then there is a solvent or the matrix blank.

These are all troubleshooting methods in which you see some sample, you see some additional thing, blank that is not clean, then you try to find out which part of the process is dirty and then find out okay. Similarly, even for the losses, you can run the standard, you can run it, you can do different kinds of recoveries, you can do the introduction of the chemical all the way back at the sample or you can introduce at different places to check if where the significant loss happening, so that you can correct for that is possible, especially if the loss is very big.

So, in general, the summary of the QA/QC procedures, the first and foremost we need calibration with standards. Then we need what we call us replicates for repeatability. Now this is repeatability of the entire process, which means samples, we must take sample replicate that will indicate several things. Sample replicates indicate the heterogeneity of the sample itself. This also indicates if your analysis procedure is consistent. So every time you do it, you should get similar results.

So that is the repeatability of it which means you have more confidence in your research. Usually this is expressed as the calibration with the standard which will give you the indication of the true value and how far it is from where. Repeatability is expressed as error bar, the people look at error bars and then tell you how close the values are, that is one thing. Then we have to do a blank, a series of blank. So, every time you start an analysis, you start with the blank and then you start with a standard.

Then we have, we do a recovery with many of this thing, yeah. In some cases we also use what is called as an internal standard. It is not done in a lot of methods, done in only a few minutes where the way the instrument processes the sample analyte is a bit, there is a lot of uncertainty in that and therefore in order to track what the instrument is doing and it changes as samples are being processed. So this happens in a few instruments like the ICP, MS.

So this internal standard we are not going to discuss it in detail, but all it means is that just like the surrogate, we add one internal standard to every sample and we track the ratio of the internal standard to the actual analyte so that we know whatever loss is happening to the internal standard is applicable to the analyte of your interest also. So, I think this covers the major QA/QC portion for chemical analysis and this applies for everything.

So, if you go and look at a standard method, there is a large section on QA/QC, which covers all of this and gives recommendations as to which surrogates standard to use, which internal standard to use, and people have done a lot of work on different methods, analytical methods, and this analytical methods works for all matrices, it is not just for water or air or filters or sediment or sludge, it works for everything. If you are developing a new method also you need to look at quality control procedures to incorporate all of these things.