Atomic and Molecular Absorption Spectrometry for Pollution Monitoring

Dr. J R Mudakavi
Department of Chemical Engineering
Indian Institute of Science, Bangalore

Lecture - 27
Status of spectrophotometry vis a vis environment

Greetings to you, it is a pleasure to be back again. And I want to tell you that we have completed the instrumentation part of spectrophotometry, and nephelometry, turbidimetry, fluorescence, and luminescence methods etcetera. We have completed the theoretical aspects of the molecular absorption mechanisms; we have also developed particular tricks to use the instruments more comfortably and to their full potential.

Now, we are entering the second phase of this course that is the molecular absorption spectrometry for the environmental pollutants for pollution monitoring. And regarding this, before we proceed further, I want to tell you that spectrophotometry is not limited to only a few parameters nearly 99 percent of the analytical work whether it is chemical, inorganic, organic, biochemical and any type of air environment, water environment, algal, botanical, geological and say geological, so many parameters, sciences use spectrophotometry as one of their main analytical technique to determine a variety of parameters which respond to reaction with colours with chemical reagents producing colours.

That is it follows automatically because spectrophotometry, fluorescence, nephelometry, turbidimetry, they are all mechanisms to measure the colour basically and sometimes turbidity etcetera. So, what we are concerned here in this course is regarding the environmental pollutants. So, therefore, I will be concentrating mostly on status of spectrophotometry vis-a-vis environment that too the environment what I have chosen is the aqueous environment that is water bodies, effluents and any other process chemicals that need to be monitored for their parameters. So, what is important in these experiments is for you to understand the chemical aspects of the chemical analysis basically.

So, if you want to determine a particular parameter or an element let us say fluoride, you should know under what conditions fluoride in a given solution will react with a reagent

to produce a coloured substances, and how specific or sensitivity for fluoride alone, and if there are any other chemicals present along with the fluoride as a concomitant, then what are the actual effects of these elements - foreign substances on this sensitivity or on the quality of determination of fluoride. Same thing applies to all other parameters like aluminum, zinc, boron, molybdenum and many other parameters that are fixed for water quality management. We will take a look at what are the different parameters we normally look for in the aqueous environment.

By aqueous environment, what I specifically mean is the drinking water as well as effluents. My focus is mostly on drinking water and to lesser extent process waters and effluents, but the methods the analytical reagents, quality of this sensitivity all remain the same whether it is for environment aqueous water, or process water effluents or any other thing that remains the same essentially. So, it is important for us to learn a lot of chemistry before we apply the spectrophotometric technique for the determination of metals ions cations and anions and other substances present in the water. So, before we proceed, we have to make sure that the method is full proof, method works, how sensitive is the method etcetera; and what are the interfering concomitants substances present in the sample.

Therefore, it is very, very important for us to know the parameters, how to control or how to modify a given existing system for particular application. For example, if I tell you that when I started my research on platinum and palladium in trace concentrations, I was asked to go to the library and find out how many what are the current reagents used for palladium. Then I was shocked I spent about three months in the library at IIT Madras going through various journals, and chemical abstracts to find out what are the different ways of determining palladium and platinum. To my utter shock, I found out that there were about 256 methods for the determination of palladium in different matrices. So, it was very disappointing for me to know that before I start my research, there are already people who are engaged in the determination of palladium and more than 256 methods are there already existing.

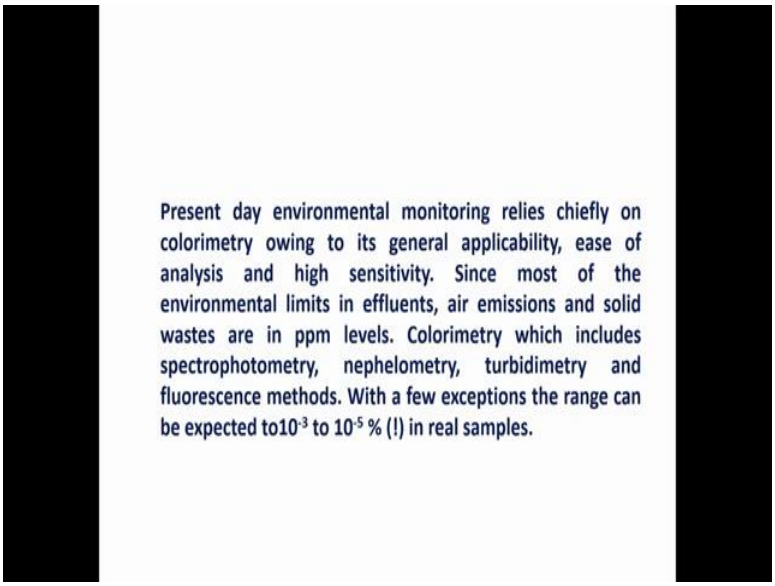
So, what to do suppose I find out one more method would it not be just another addition to the existing plethora of analytical methods would somebody else what are the possibilities of using my method for their determination etcetera say it is a very fairy sort of disappointing scenario. But then my teacher - my guide Prof. T.V Ramakrishna told

me that you just find out, think, why there are 256 methods for the determination of palladium. Very interesting thought sir, I told, and then I started thinking why there would be so many methods required for a particular analysis, the answer did not come to me immediately. But after a few days of thinking I came to the conclusion, I studied the methods each one in detail, and I came to the conclusion that not one single method is applicable in all matrices. So, that itself was a great revelation to me, because the given method if it is applicable for all circumstances, then it is a wonderful universal method.

Unfortunately, molecular spectroscopy or any spectroscopic technique for that matter cannot be so specific. So, I started looking at what are the merits and demerits of a spectrophotometer and spectrophotometric method for a particular parameter, in my case palladium. And then I found out that there was a need for me to evaluate each and every method with respect to sensitivity, selectivity, and then sandal sensitivity, and then evaluate the interferences and then apply in actual situations to show the potential of the method. Therefore, it is very, very important for us to know a little more chemistry with respect to spectrophotometric methods especially with the existing matrices etcetera.

So, I have collected some of my thoughts in the next 20 or so slides, afterwards even these 24 slides or they require a little bit of discussion and understanding, but I have tried to put them in slides. We will go through slides one by one, and then I will also explain to you what are the different things, we look for in a particular spectrophotometric methods. So, here it goes.

(Refer Slide Time: 10:41)



The present day environmental monitoring relies chiefly on colorimetry owing to its general applicability ease of analysis and high sensitivity. Since, most of the environmental limits in the effluents, air emissions and solid wastes are in parts per million levels. Colorimetry including spectrophotometry, nephelometry, turbidimetry and fluorescence methods, they are all applicable with a few modifications. And the sensitivity of each method can range from 10 raise to minus 3 to 10 raise to minus 5 percent in real samples. So, I what I want you to know especially in this situation is the sensitivity range itself decides whether you should go for spectrophotometry or not.

Suppose a substance contains a particular analyte in 1 percent or 10 percent, may be 99 percent, and then is the use of spectrophotometry justified in that situation. So, it is a matter to be thought very seriously because spectrophotometry as we understand is a relative technique, it is not an absolute technique. That means, if I say spectrophotometry method gives me so much percentage of the sample or so much quantity of the substance present, it does not tell me how much of the material can be recovered. So, it is all a basically still a theoretical level which needs to be corroborated by other chemical techniques for example, gravometry, and volumetry.

So, if I want to win cobalt from a given ore, I may use a spectrophotometry method to estimate how much of cobalt is there, but it does not tell me how much of cobalt can be collected from the ore as a metal. For that I need to go to basic chemical techniques that

are gravometry and volumetry. From gravometry, we know how to precipitate the ore leaving all other concomitants in the solution, filter it, dry it, get the precipitate, convert it into metal that is the another branch of chemistry or another branch of science itself known as metallurgy. But a spectrophotometric method can be a great help in determining how much of the pollutant is there.

So, we are talking about the sensitivity. So, according to the previous slide what we can say is if the substance exists in concentration of 10 raise to minus 3 to 10 raise to minus 5 percent that is 0.000001 percent then I can comfortably go for spectrophotometry. Because, if it is in higher concentration what I have to do I have to dilute the sample first I have to dissolve it and then it is too much concentration for me. So, I have to dilute bring it to 10 raise to minus 3 to 10 raise to minus 5 percent level then go for determination. Suppose the sample you are you want to estimate is gold, so that is present in 1 or 2 ppm in the ore that means, to get 1 gram of gold from the ore you need to process 1 tonne of the ore that contains mud, silica, and iron, aluminum and so many other materials that the earth crust consists of out of that only 1 ppm - 1 microgram per gram is the platinum or gold.

Therefore, is a spectrophotometric method justified in going for gravimetry or molecular spectrometry? Obviously, if it is in ppm level then it has to be spectrophotometry of course, compared to gravimetry. Of course, there are other methods of determining the same gold or platinum in 1 ppm, but here we are discussing only spectrophotometry. So, I am sticking to spectrophotometry. Therefore, what is important is we have to know the approximate concentration of the substance in a given sample and it should be in the range of ten raise to minus 3 to ten raise to minus 5 percent, so that is important for us.

So, what are the procedural requirements? The procedural requirement is when you have only 1 ppm of the substance in 1 tonne in 1 tonne of the material then the concomitants can play a very important role. So, great care must be taken to present gross contamination of the sample through the analysis. What do we mean that we have to take great care to present the gross contamination? So, what we are essentially talking about is in the final analysis, the gold or any other sample platinum or whatever it is which is present in 1 ppm must be converted into some sort of coloured substance which is specific to gold. But there are 10 raise to 6 grams 1 tonne almost material extra that is present in the sample. So, a contamination there may be several other metals which may

give you similar colour for example, water what we use itself may be a coloured a little bit. So, the contamination is a great important aspect in spectrophotometric analysis and we have to guard against the contamination under all circumstances. .

So, where can contamination come from, contamination come from laboratory reagents itself may be a, it may not be a 100 percent pure substance. So, the water what you use for dissolution, digestion etcetera to bring the sample into solution that itself may lead to contamination. And then for example, if you are using in a typical laboratory, you may be using a iron stand that may be corroded and that corroded iron particles will may fall into the solution without your knowledge you do not know when it happens. So, from the ring stand, it can come from if you are using a nickel crucible to dissolve particular substance part of nickel may also dissolve in that.

So, it may present a contamination of nickel from the laboratory where and I will use a pair of tongs, we use copper heating plates, we use zinc, zinc will come from burner heads, and then pesilon motor, some quite often to dissolve the substance, we have to powder it. So, we use pesilon motor to bring it to particular particle size and then dissolve it.

And sometimes if the material is very large we use a mechanical grinder using ball miller or something like that and then in the laboratory itself. There are other sources of contamination for example, mercury from spillech it may come for somebody may break a thermometer and mercury might be spilled. And as you know mercury is having about 0.31 percent as a present in the vapor pressure at room temperature. So, if you are operating something which will react with mercury, it may react with mercury to give you another coloured substance.

See in spectrophotometry, the purity of the colour must come only from the analyte. Any any other concomitant material present giving some other colour may add an additional absorbance unless if you are not aware it may definitely lead to higher absorbance. So, higher absorbance means so long as you are using spectrophotometry you will be ending up with a higher concentration.

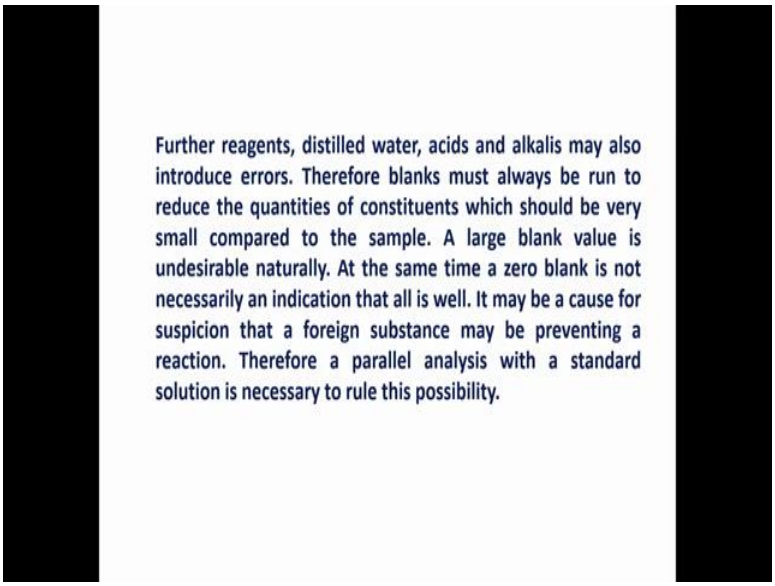
Sometimes it so happens that an interferent may not permit your substance your analyte to react in that case you get lower absorbance that also is not acceptable. So, we have to guard against contamination at all levels, from all angles, and from the operators

personal characteristics also, for example, our fingers you know quite often our fingers are contaminated with aluminum and iron, aluminum is the most only present material everywhere almost including the laboratory air, you may not be aware, but it happens. So, there may be other metals.

(Refer Slide Time: 21:39)

And sometimes filter papers what we use they also may be containing particular elements. So, I can simply concentrate I can simply say that even common laboratory processes can become sources of contamination and we have to be very, very careful with respect to contamination from different laboratory sources. So, whatever I have told so far I have concentrated; I am presenting in this slide.

(Refer Slide Time: 22:11)



And then we will when we proceed further, you will be surprised to note that further reagents, distilled water, acids and alkalis they may also introduce error. So, you have to use very high grade chemicals especially what is known as analar reagents or guaranteed reagents, sometimes even the solvents are have to be sort of spectrographic grade the HPCL grade or something like that which are highly purified. Therefore, we must always run a blank that means, all other substances what we have to do is whenever you want to do a spectrophotometric method you have to have a sample another as blank.

So, the blank, assume this is blank, this is the sample only difference between the blank and sample is the analyte. So, all the matrix components acids, alkalis, and fusion materials filter paper everything should be same with respect to blank and sample. So, it is very very important to have a blank. Why, because the colour contribution from the blank represents all other concomitant interferences. So, if we run a blank, the blank will have certain colour, sample will have certain colour plus your analyte. So, the only the analyte colour will be distinguished, so that is the idea of running a blank. So, we have a blank.

Now, assume that the blank also has a very high absorbance value. So, does it mean that it is interfering? The answer is no, because blank gets cancelled from the total absorbance of the sample plus blank. Now then what is the problem you may ask the problem is if the blank is having very high absorbance it may prevent your analyte from

reacting because it may have a higher affinity towards the organic reagent. So, what happens your sample gets masked. So, when the sample gets masked that means, you are not getting the correct absorbance at all. So, a high blank you must always worry that why I am getting so high blank at all. So, if the high blank is there, you must consider methods to reduce the blank value.

So, how do you determine the blank value, you measure the blank against water pure water. So, the blank if it is very high, I must consider the surroundings in the laboratory as well as in the matrix. Surroundings in the laboratory I have already identified that it could be water, it could be acid, it could be nickel crucible, it could be filter paper, it could be laboratory rings, it could be burner so many things. Now, I have established that whenever there is a high blank there could be possibility of getting wrong information, now that is established.

Think of another situation where they have blank is 0, there is no blank at absorbance, does it mean that the method is correct? If I do not have any absorbance from the blank does it mean that everything is well, all is well? The answer is no, because it may be a cause for suspicion for us that a foreign substance may be preventing the reaction of our analyte also. So, we have to be very, very careful, high blank is definitely an indication of the contamination, but a zero blank does not necessarily indicate that all is well. It only can mean that a foreign substance may be preventing a reaction.

Therefore, a parallel analysis with a standard solution is necessary to rule out this possibility. What I do is whenever I want to analyze a sample, I have to run a blank, I have to run a standard, and then I have to run my sample also. So, after subtracting the blank, when the sample and analyte are showing the same absorbance with a experimental error of course, then only it means we do not have a problem blank problem. So, much I want to tell you about the blank. So, it is important for us to understand the significance of the blanks, especially in spectrophotometric procedures.

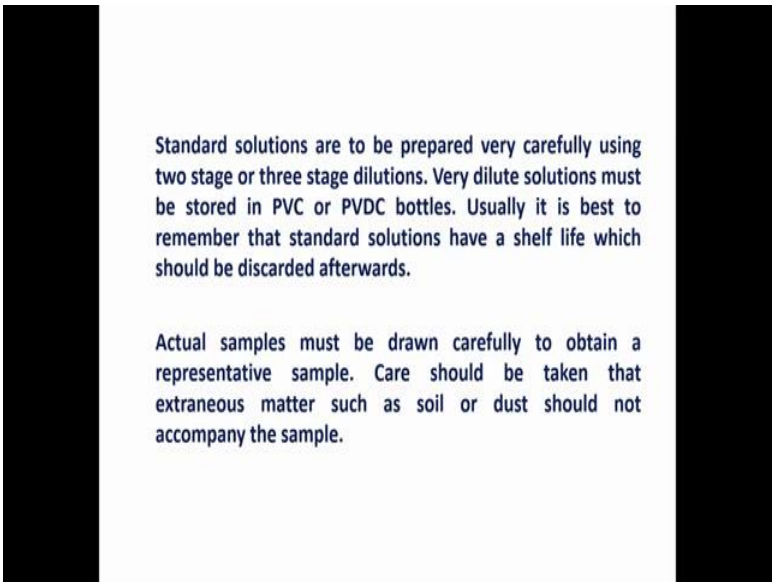
Now standard solutions, we have to prepare very carefully using two stages or three stage dilutions. For example, I want to tell you that most of the spectrophotometric procedures work between 1 to 10 ppm, 1 to 5 ppm, 1 to 100 ppm some of them very rarely they work in milligram level. For example, if you want to determine copper, copper itself is a coloured substance. So, a milligram concentration of copper will give

you some amount of blue absorbance, and you can measure, if the solution is very pure. But if the substance is in ppm level solution parts per million or sub ppm level, then you need to have the standard solutions also in ppm level suppose 1 to 5 ppm is your range your sample should be between 1 and 5 ppm right. So, how do you prepare a 1 to 5 ppm solution?

The point is the standard solutions need to prepared from pure chemicals known as NLR standards NLR chemicals. So, suppose it is not possible for you to prepare 1 ppm of solution that means, you have to take 1 microgram per ml. So, if you want to prepare 100 ml of the standard solution you need to weigh hundred micrograms your laboratory does not have the facility to measure 100 microgram to weigh you do not have a balance to weigh 100 micrograms. So, what do we do? The answer is very simple you prepare 1 percent solution or 0.01 percent solution. So, whenever you prepare one percent solution or 1 gram mole or 1000 ppm the weighing quantity becomes a few grams.

Suppose, you want to prepare one gram of copper you have to weigh copper sulphate 7 H 2 O, Cu SO 4 5 H 2 O that much molecular weight you have to calculate. So, to determine one molar one gram substance you can calculate how much of the substance to be weighed that will give you 1000 ppm. Now, that 1000 ppm solution you have to bring it to 1 ppm. How do you do that you have to dilute 1000 times correct, but you cannot take 1 ml and dilute to 1000 ml, second dilution to get 1 ppm, you will need huge glasswares, it is not possible. So, what we do is from 1000 ppm, we prepare 10 ml of may be 100 ml of 100 ppm, 10 times dilution, that 100 ppm solution we dilute it to 1 ppm, 2 ppm, 3 ppm like that. Therefore, it is important for us to dilute the sample in several stages to get to the parts per million level concentrations of the standards.

(Refer Slide Time: 31:31)



Now, there is another problem with very dilute solutions, if you use glassware the substance may get added or adsorbed on to the glassware, and it will not be in solution. Therefore, the container becomes very important for us where we store very, very dilute solutions. Normally, we use PVC bottles or PVDC bottles which are available in scientific laboratories, suppliers, and usually it is best to remember that the all standards have a self-life that means, which should be discarded afterwards. That means, if you want to prepare 100 ppm solution, whenever you can prepare dilute solution with that, but the longer you keep more of the substance will be adsorbed onto the walls of the container, and you will have problem with the standard preparation itself.

Therefore, it is very important for us to determine, what is the self-life and after the self-life is over you have to discard and prepare fresh solutions. So, it is a standard preparation and handling itself is a big aspect and actually what is important is samples must be drawn carefully to obtain a representative sample. So, the care should be taken that extraneous matter such as soil or dust or any other things should not accompany the sample. So, the there is more to come we will discuss them further now in the next class.

Thank you.