**Atomic and Molecular Absorption Spectrometry for Pollution Monitoring**

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

**Lecture – 28**
**Separations methods**

So, continuing our discussion on the specificity I have to tell you that the unfavorable ratio of the analyte to that of matrix components; as in the case of trace analysis.

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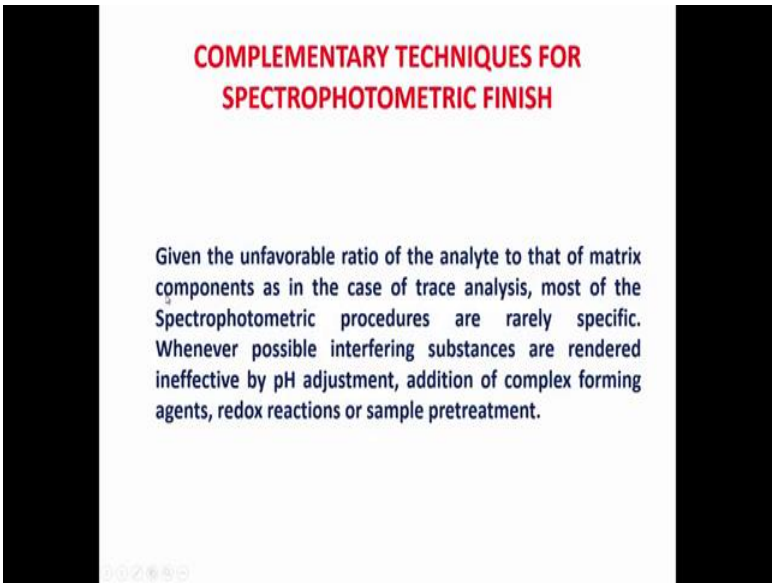


Most of the spectrophotometric procedures are rarely specific; that means, one reagent one analyte is never possible. We have to take it granted that there could be a single reagent may react with several parameters if present. It may give a different color or it may give a same color. So, it is unreasonable and unpractical to expect there is a one reagent for one analyte not at all possible.

So, whenever possible that; that means, there are no other materials present then one reagent one thing is possible. Suppose you want to determine a very pure quantity of, very pure zinc there would not be any other material. So, it becomes specific, but in a given matrix there may be you do not know may quite often we do not know what all it contains it is impossible to know everything. So, it may be possible sometimes to know what are the concomitants in that case we can take precautions. Now I have told you that

a substance a reagent can be made specific for a reagent under optimum conditions. And these things include pH adjustment and addition of complex forming agents; we can use redox reactions or sample pretreatment.

Now, coming back to this last sentence what you are seeing on your screen is the ray ahead for us to make a reaction specific. For example, if there are 2 or 3 substances with which the reagent a given reagent gives colored substances, we can optimize the pH at which it will react with each of the analyte.

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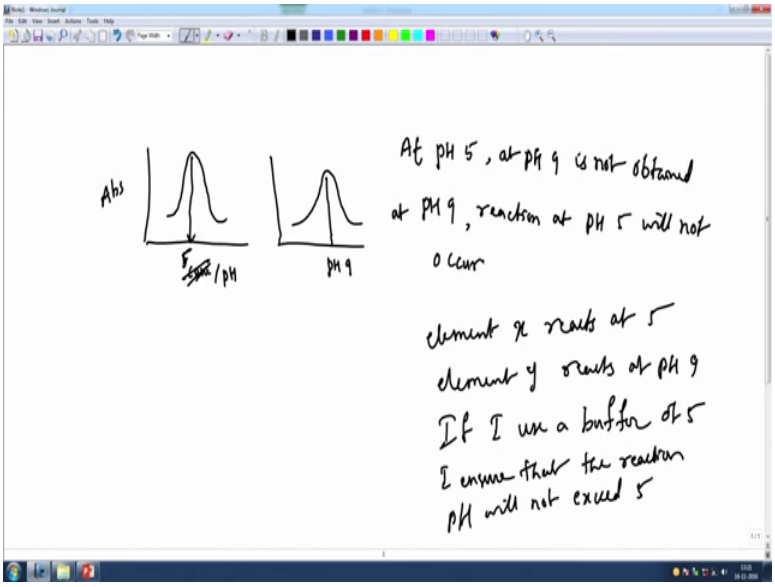


So, if I draw, if I plot absorbance versus concentration and pH. I may have a, forget about concentration, I may the substance may react with to give maximum absorbance at let us say about 4 5. Another substance if present it may also react, but it will give you a maximum reaction product at pH 9. Now by operating the reaction at pH 5, I can happily make sure that at pH 9 is not obtained. If I work at pH 5 pH 9 reaction will not occur or pH 9 if I maintain pH 5 reaction at pH 9, reaction at pH 5 will not occur. So, what I do essentially is I conduct a reaction at pH 5 or pH 9, because an element x element x reacts at pH 5. And element y reacts at pH 9. So, if I use a buffer of pH 5, I ensure that the reaction pH will not exceed 5. So, y will not interfere in pH 9. So, we are talking about the pH that is about the pH by using a buffer I make the reaction mixture to remain a perfect pH 5 or pH 4 pH 7 etcetera. So, the other reactions at different pH will not occur that is one way of making a reaction specific.

Another way is addition of complex forming agents, I can add. Suppose there are 2 substances reacting with the analyte at the same pH then what do we do 2 substances reacting at the same pH to give you same colored solutions. Then what I do is I add a complexing reagent suppose I have x and y, I complex yi leaving x in the solution. So, y will already been complexed. So, it may not react with the reagent with which I am dealing. Sometimes it is possible for me to use redox reactions. I can oxidize one of the components make it render harmless or not follow the color reactions. I can do a sample pretreatment. Sample pretreatment to eliminate one of the components y, for example, I want to determine xi have to eliminate y, I can do sample pretreatment and this sampled pretreatment takes several forms.

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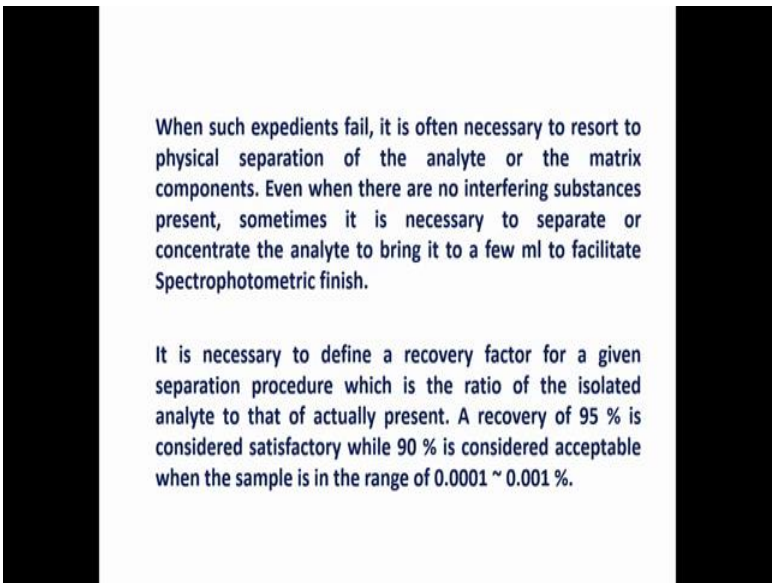


For example, take a look at this this it is necessary, I can do the extraction, I can do the physical separation I can do filtration and several other things I can do. So, when such separation itself is not possible our pH adjustment is not possible. Redox reaction is not possible and then the complex formation also is not possible. Then what happens is it is again we chemists have a different trick to sort out this problem.

So, what are the possibilities it is often necessary to resort physical separation, now itself of the analyte, I take out the analyte from the matrix, I have one ton of the ore containing 1 ppm of gold. So, I take out 1 ppm of gold from all of it leaving remaining one ton here and then I dissolve that 1 ppm and dissolve do the necessary analysis. That is known as

physical separation. Now how do I do the physical separation, there are lot of tricks we employ. When there are no interfering substances possible present sometimes it is necessary to separate or concentrate the analyte.

For example, if the substance is very dilute, I just evaporate take one liter and evaporate to 5 ml. So, I am concentrating. So, it will if the dilutant substance becomes more concentrated to bring it into within our measurable spectrophotometric finish. So, that is one way and sometimes whenever we do this we have to define a recovery factor. For example, how much you can recover from a separation procedure would it be hundred percent no, it will not be hundred percent it may be 95 percent it may be 90 percent it may be 85 percent. Then if you want to report the correct percentage of the substance you have to do the correction that you are that you are required 85 percent, but recovery percentage itself is 85. So, the actual substance would be 85 plus 15 percent which is not recovered it may be remain in the original matrix.

So, this correction factor becomes very important whenever you are dealing with very low concentrations of the substances. Usually a recovery of 95 percent is considered satisfactory in all spectrophotometric finish. For example, what do we do normally is whenever I develop a method spectrophotometric method, I take add an analyte. I know how much I have added from this spectrophotometric method I carry out the usual blank this that etcetera convert it into absorbance refer it to calibration curve, calculate how much I have how much is the concentration. So, I know what I have taken I know what is the response calculated. So, there is difference it may be 95 percent it may be 99 percent it may be 90 percent etcetera, because you would not get 100 percent theoretically at all.

So, whenever you do that is known as standard edition, I have already referred to the standard addition technique in the spectrophotometry topic when we are discussing an instrumentation. So, a 90 percent recovery is considered acceptable; that means, it is considered almost hundred percent accurate, when the sample is in the range of 0.0001 to 0.001 percent; that means, 10 ppm 1 ppm to 10 ppm level. If you get 90 percent recovery, we consider it as a fairly clean method there is no problem with the analysis.

But suppose you get 50 percent then; that means, it makes lot of difference we have to think why we are getting 50 percent when the satisfactory method is around 90 percent.

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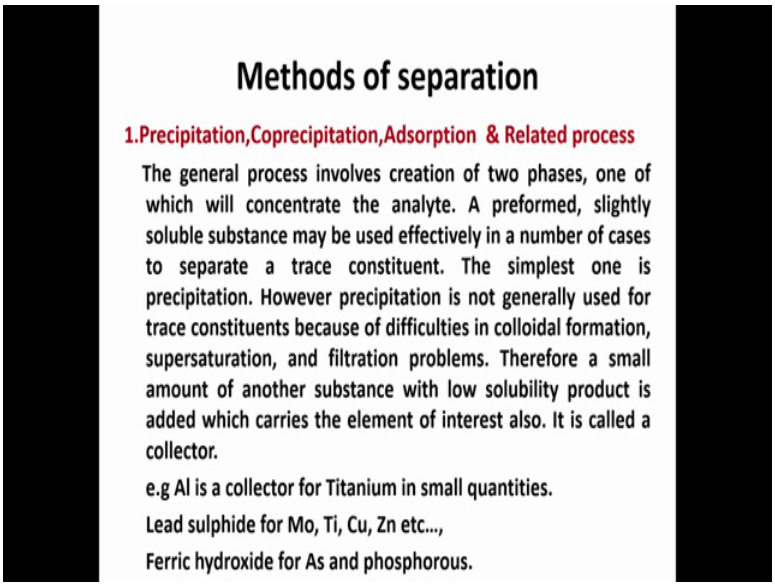


So, what are the different methods of separation we normally employ and these include precipitation co precipitation adsorption and related processes. So, these things for example, the general process what do we do, it involves creation of 2 faces one which will concentrate the analyte and the other one which will contain all the remaining matrix. A preformed slightly soluble substance may be used effectively in number of cases to separate a trace constituent. This theoretically while reading it may look somewhat complicated to you, but what is important is a soluble substance we just have to dissolve use a dissolve the sample leaving the other things undissolved. Then you filter it that is the way of concentration that is what we mean a preformed slightly soluble substance may be used effectively in a number of cases to separate a trace constituent.

The simplest one is precipitation. So, precipitation is not generally used for trace constituents because of difficulties in colloidal formation. For example, what happens is whenever you are trying to precipitate a very small quantity of the substance; the critical size of the precipitate may not be exceeded to make it visible like a precipitate. In that case we call it a colloidal solution it may look colored or it may not look colored, but the if the sample if the analyte is in ppm level 99 percent chances are that it will form an even if you had a precipitating reagent, it will form a colloidal solution.

For example, we all know from chemical history our chemical practice in PUC and college level, that if you take silver nitrate add sodium chloride silver chloride will

precipitate, but there is a limit to which silver chloride can be precipitated whatever is the amount of chloride you add. So, if it is 1 percent definitely you will get a precipitate if it is 0.1 percent you will still get a precipitate point 0 1 percent, you may get a precipitate 0.001 percent, we do not know. The precipitate may be there, but our eye is not sensitive enough to detect a precipitate. Sometimes the precipitate the reagent what we add is. So, high concentration that it may form a colloid, so colloids are not filterable. So, a colloidal formation is normally not possible not preferred. So, sometimes due to super saturation to precipitate I add more substance. And then what happens there may be a super saturation it may redissolve again. Then you do not have a problem at all. And sometimes it may lead to filtration problems.

Therefore, a small amount of another substance we add with low solubility product which carries the element of interest also; that means, I am adding another element which precipitates and along with that precipitate it will catch the analyte which is in very low concentration. So, that is known as carrier or a collector. So, collect what is a collector.

A collector is a substance that that is present in large concentration and precipitates while precipitating it will carry the analyte also. So, for example, I am showing you this slide that aluminum is a collector for titanium in small quantities. If you want to determine titanium what we say is add a little bit of aluminum hydroxide will precipitate, and titanium also will precipitate along with that, not as titanium hydroxide, but as titanium oxide, but along with aluminum hydroxide. So, aluminum is a collector and titanium remains is the analyte. Similarly, people have used. So, lead sulphide for molybdenum and titanium and copper zinc etcetera. This this kind of collector analysis collecting you know is a very common analysis technique in most of the spectrophotometry. Especially these are useful in geological samples and another well-known example is ferric hydroxide that is used as a collector for arsenic and phosphorous.

So, these the chemistry of these precipitations and collections is again a subject of special information, special chemistry many people are aware of it, but wherever whenever you come across a method normally that requires a collector the method may does make a mention standard method if you find it from google or standard methods a o s c methods etcetera, they will make a mention of these techniques. So, one has to be careful adsorption is again another process.

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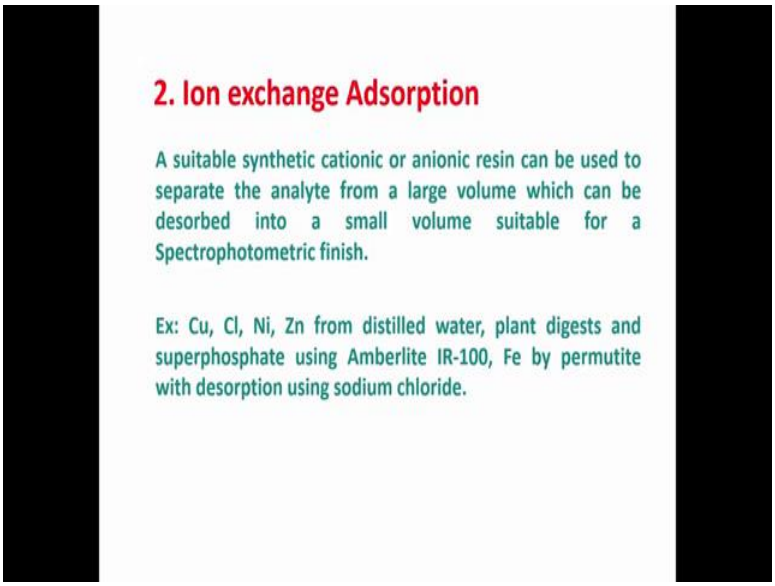


And other related processes are there. Then suppose again another possibility. That is, it is not possible to add the collector, you do not find a suitable collector, then what do you do other tricks, we go for what is the other trick that is ion exchange. So, what I do, I just take the sample put a little bit of ion exchanger shake it or pass it through a column. So, it can be cationic or it can be anionic resin that can be used to separate the anion from a large volume of the liquid sample or an effluent sample. So, it gets adsorbed on the ion exchange column and then you have to strip it, you have a very small quantity of the substance that is the anlayte for spectrophotmetric finish. So, ion exchange is a very wonderful technique for concentration of the analyte, when precipitation method fail quite often it becomes a preferred method compared to precipitation.

So, examples include copper and then chloride nickel zinc etcetera. These are from distilled water and plant digests and superphosphate, you know they are all used as in the routine samples, and all these things can be concentrated using amberlite IR 100, that is anion exchange ion exchange resin, amberlite IIR 100 is a cation exchange resin. And there are different categories of ion exchange resins which can be used for different elements and such data is also available in the standard textbooks, or in the standard methods.

Ion by permutite with desorption using sodium chloride is another method, for example, if you have ion in a given sample then the you can use a little bit of permutite that is

zeolite with desorption using you can check it ion will go along with the permutite then add a little bit of sodium chloride sodium will replace ion and ion will come back in a pure form for you to analyze separated from the other matrix elements. So, ion exchange adsorption is again a special technique very useful as an addendum for spectrophotometric finish.

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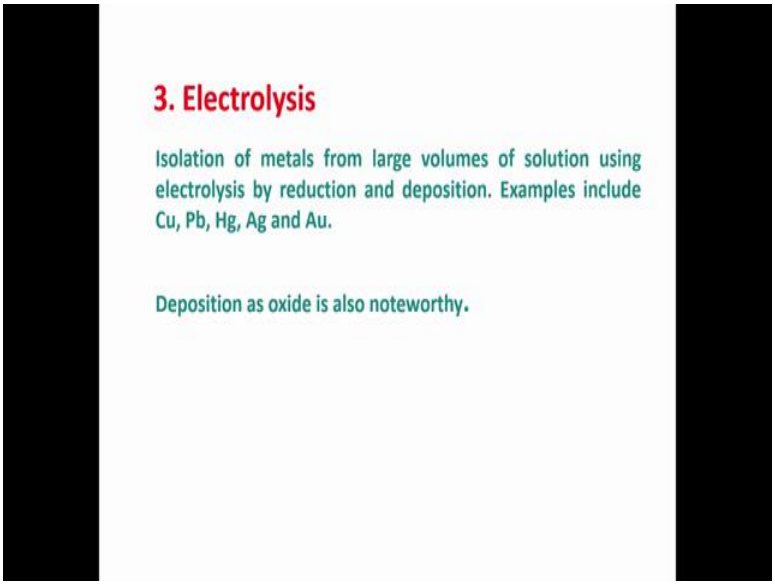


Now, electrolysis, another technique, what happens is suppose you want to determine copper or zinc. Then it is very simple all you got to do is bring everything in solution put a copper electrode and then collect all the copper do the electrolysis collect the copper and that carry out the analysis, very simple technique, but very effective, but not many laboratories do have this kind of accessories for specific purpose. Therefore, it is important for us to know the potential and if necessary apply it wherever necessary. So, the examples include copper lead mercury silver gold any element that can be quoted electrically that can be precipitated electrically on a cathode that should be useful to concentration. So, sometimes it may not be possible to determine element as such. Sometimes it may precipitate or it may deposit as oxide also that is also, acceptable because oxides can be stripped dissolved in assets and then with a normal spectrophotometric finish we normally end up having the spectrophotometric finish.

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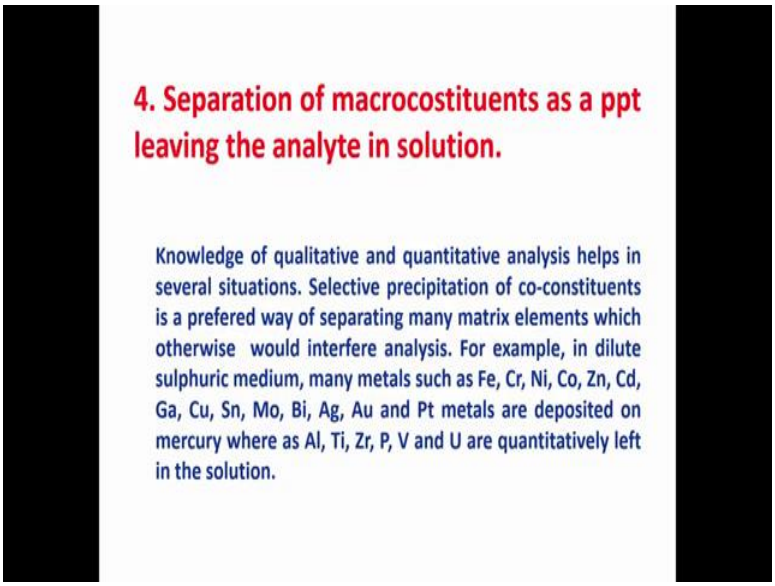


Now, another way is precipitate, macro constituents' knowledge of qualitative and quantitative analysis, what you did in high school and may be first year second year third year B.Sc. gravimetric as well as qualitative analysis tells us different ways of precipitating the whole matrix. For example, we can see in dilute sulphuric acid medium that is in the college experiments group 2 chemical analysis says add sulphuric acid, dilute sulphuric acid, medium ion, cobalt, nickel, nickel zinc, chromium cadmium all these metals are deposited on mercury.

Take a little bit of mercury add a little bit of sulphuric acid and all these metals will form amalgam, remaining metals will not form the amalgam you filter it and then you just wash it take out the amalgam and you have the evaporate the mercury, and then you have all the analyte element in a small volume for a regular routing spectrophotometric finish. And sometimes suppose you have in the sample aluminum titanium etcetera they do not form the amalgam. So, if you want to determine amalgam you should take the aqueous extract that will concentrate aluminum. If it is copper, if it is chromium, it is an amalgam portion. That you have to shake it with asset remove it from there and do the analysis. If it is aluminum titanium etcetera from the same solution, you just filter it remove the amalgam the remaining aqueous solution you can determine using the regular spectrophotometric finish.

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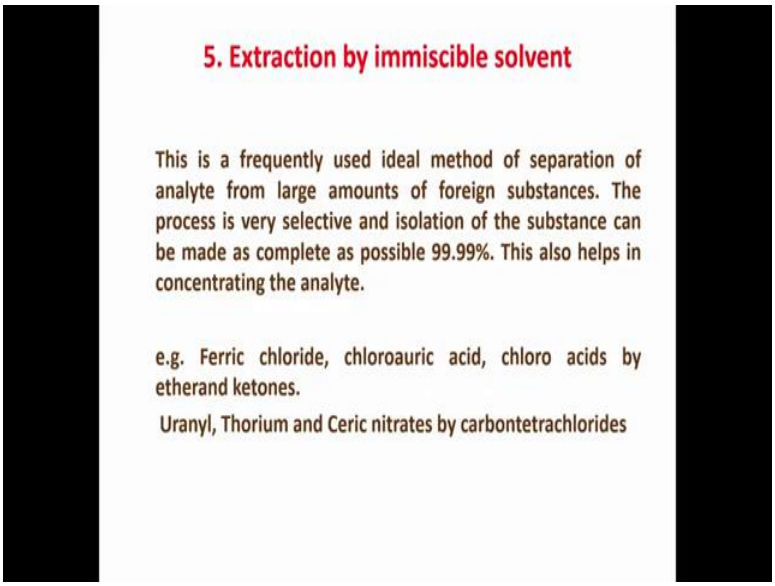


So, another technique, I have to give more emphasis to this technique, for you to appreciate because this is something to do with extraction, so a very important technique for extraction by animisible solvent. Very frequently used ideal method for separation of the analyte from large quantities of foreign substances the process is very selective.

Sometimes you know you may form a complex extract the complex in a small 5 ml volume from 100 ml 200 ml, 1 liter. You take one liter in a conical flask shake it with 5 ml of the substance everything comes in 5 ml of the organic substance, organic solvent and you can determine the process is very selective there are hundreds and thousands of papers where an analyte can be concentrated using a invisible solvent.

It is also a metallurgical process or the separation of the metals and several other substances and the beauty is the process can be made very selective because there is a large number of organic solvents which are specific to particular analyte. Sometimes the isolation can even exceed 99.99 percent. What more do you need? This also helps in concentrating the analysis as well as helps in analysis. For example, it is I can give you couple of very simple examples ferric chloride you know by ether and ketones ferric chloride can be concentrated, you have a large quantity of a substance containing ion you want to determine how much of ion is there.

For example, I can give you very practical example. For example, you know most of us know that apple contains quantities of iron. You know that palak what you eat every day

in your regular food it, contains iron you want to know how much of iron it contains. Now what you do you dissolve the palak or apple in a mash it a take an aqueous extract, but then aqueous extract will be 100 ml or 500 ml. So, concentration of iron will be very less. What I do? I take all the 5 hundred ml in a conical flask add 5 ml of ether. So, all the iron will get extracted into ether as ferric chloride. So, simple technique, wonderful technique actually, chloroauric acid and gold you just have to add hydrochloric acid it will form AuOCL 4 minus and that can be extracted by ethers and ketones. And chloro acids a lot of chloro acids organic substances can be extracted using all these extractance.

Similarly, uranium thorium and ceric nitrates they can be extracted by carbon tetrachloride very simple. So, there are actually in 90 more than 50 percent of the organic analytical procedures for most of the metal ions, they do have a solvent extraction as part of the standard procedure to determine to a spectrophotometric finish. There are 2 advantages that happen whenever you do solvent extraction. One is the analyte gets concentrated and the second is sensitivity of determination; that means, the detection limit gets reduced; that means, we can go down to very low concentrations and more accurately also very interesting technique.

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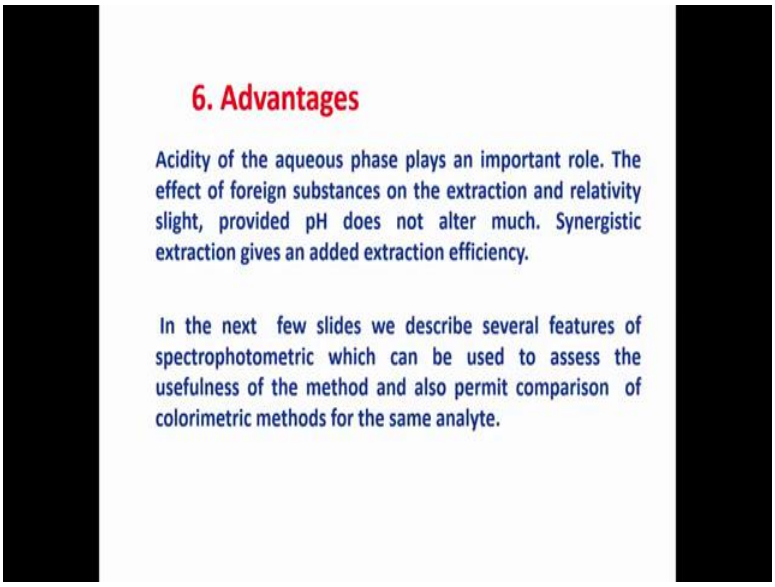


So, the advantage of this solvent extraction is that the acidity plays a very important role the effect of foreign substances on extraction and relativity is very slight. So, it can be pH independent provided pH does not alter much synergistic extraction also you can use.

So, what is synergistic extraction, if I make a statement that you can use synergistic extraction you may not understand, but I can if there are 2 substances instead of one extractant you use a second 2 extractants. Then what happens both extractants will try to extract the same sample and the extraction efficiency will be more.

Sometimes whenever you use 2 extractants, the combined extraction will be much more than the sum of their individual extraction. You understand? I use xi get 90 percent I use yiget 5 percent if I use x plus yiget instead of 95 percent I get 99 percent. This is known as synergistic effect. The synergistic effect I can give a small analogy, that if you are climbing a hill in a train, they put an engine on the front to pull and they put an engine at the back to push. So, it is something similar. So, one is pulling another is pushing. So, it is a synergistic effect, and which is more advantageous. So, synergistic extraction also gives you added extraction efficiency.

So, in the next few slides what I would like to do is describe several features of spectrophotometry, which can be used to assess the usefulness of the method. Again it permits is the comparison of colorimetric methods of the same analyte, because this brings me back to the starting of this todays class that is I had explained to you that there are more than hundred methods may be 1 or 2 analyte then how do you compare which is the one which is the ideal one.

So, in the next class what we will do is we will continue our discussion, about these aspects comparison and specific characteristics of spectrophotometry. And then we will go on to study the individual parameters.

Thank you very much. Have a nice day.