Atomic and Molecular Absorption Spectrometry for Pollution Monitoring

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Lecture – 26
Chemiluminiscence, principles

Continuing our discussion on the absorb matrix methods. We have discussed so far about the metallic about the atomic structure, and how the absorption bands occur because of the molecular bonding, and then we have also discussed the electromagnetic radiation and followed by spectrophotometry, what are the basic theory of spectrophotometry, followed by instrumentation for absorption methods to work out the absorption matrix methods. And then we have also discussed about the Beer-Lamberts law, relative concentration error followed by nephelometry and turbidimetry. And then we had a discussion regarding fluorescence, phosphorescence.

And now I want to talk to you about another related technique that is chemiluminescence. In chemiluminescence, the principle is same that is the radiation coming out of a chemical reaction in a colour form can be monitored. Here, the difference is the initial incident radiation is not very important; the chemical reaction itself will generate a compound which will give out particular colour. So, this method is known as chemiluminescence, this technique is known since quite a long time and but the application of chemiluminescence in analytical science is a very recent development. Normally, spectrophotometry, turbidimetry, fluorescence, nephelometry, and phosphorimetry and all these things are normally carried out in solutions.

But the main difference is chemiluminescence can happen in gaseous medium also as well as in liquid medium, aqueous medium also. So, but the essential principle is monitoring of colour produced in a chemical reaction. So, there is certain amount of overlapping of the techniques, but the instrumentation has to be entirely different and much more simpler because we do not need so many monochromators and things like that for chemiluminescence measurements.

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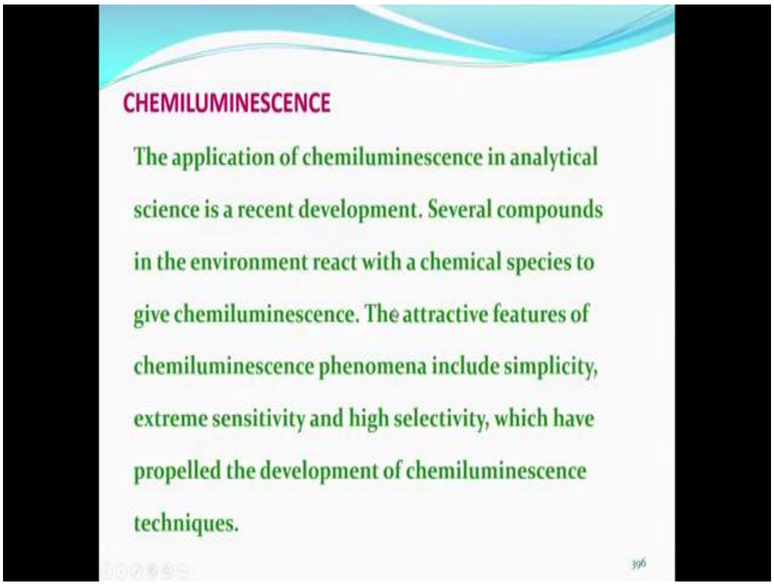

So, the application several compounds in the environment react with chemical species to give chemiluminescence. So, can we use this technique for the determination of the pollutants? Now, you will appreciate that there are different kinds of pollutants in the environment, one is air environment, one is liquid environment, and another is solid environment. And if we have a liquid environment, the basic idea is to bring the analyte into a coloured solution, coloured format by reacting with a chromophore, and then determining the substances.

But suppose I need to determine a substance like sulphur dioxide or nitrogen oxide that is in the air, so the attractive feature of chemiluminescence is that the reaction can be carried out in the; I can draw a small amount of air sample into a reactor, and then make it undergo the reaction. And this reaction can be monitored using the same monochromators, detectors and other things also. So, I can do it for the environment in the air as well as environment in a liquid form.

The beauty of this system is the simplicity. I just have to bring the reagents together let the reaction proceeds, and the moment reaction proceeds there will be certain amount of colour developing, and you can see virtually in your reactor if you allow particular reactions to take place according to chemiluminescence measurements. Then you can actually see the colour, but monitor it instrumentally to determine them at very low levels etcetera that is the beauty of spectrophotometry or any spectroscopic method that permits you to determine the substances in microgram, nanogram levels. So, the extreme sensitivity that you obtain normally in chemiluminescence is because of the specific chemical reaction with only known compounds; and other compounds do not react at all, they remain mute spectators to the event of chemiluminescence.

And same thing is true with respect to selectivity also. In selectivity what we normally look for is the reaction should be specific to a particular compound does not react with other compounds to give similar colours. Otherwise it will create in difficulty for isolating the desired radiation. So, because of these advantages they have propelled the development of chemiluminescence techniques nowadays we have chemiluminescence techniques for sulphur dioxide, (Refer Time: 06:47) etcetera which are air pollutants not in the liquid form. So, far we have been only talking about the liquid form, but now we may even talk about these things.

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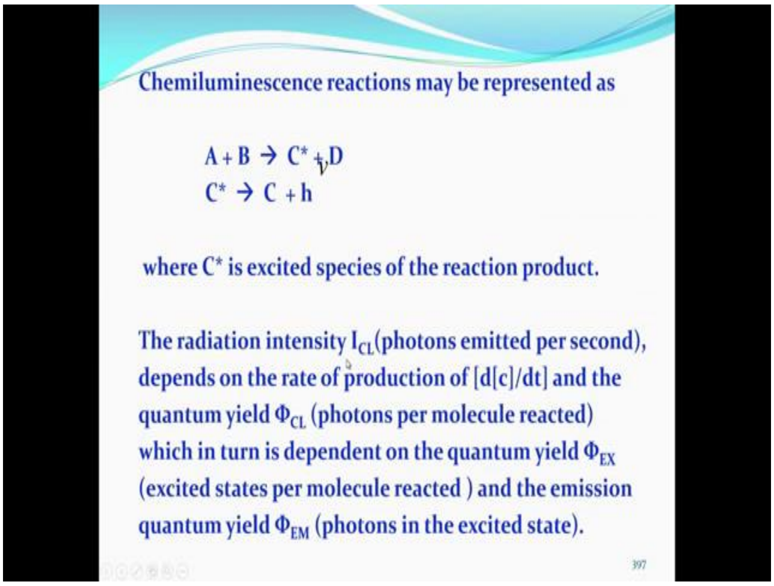

So, basically what is a chemical chemiluminescence reaction? You can see here, A reacts with another compound B that gives you a chemical C that is the excited species C, and it also gives out certain amount of radiation mu D. And this C star is the excited species which reverse to ground state allowing the radiation to come out. So, the radiation intensity - the I CL we write at that is photons emitted per second, it depends upon the rate of production of d c by dt. See, d c by dt is the rate of production and the quantum yield also is important because that is rate number of photons per molecule reacted which in turn again depends upon the quantum yield phi EX that is excited species of the per molecule reactant excited states per molecule reactant that is the fluorescence intensity and the emission quantum yield, that is photons in the excited state.

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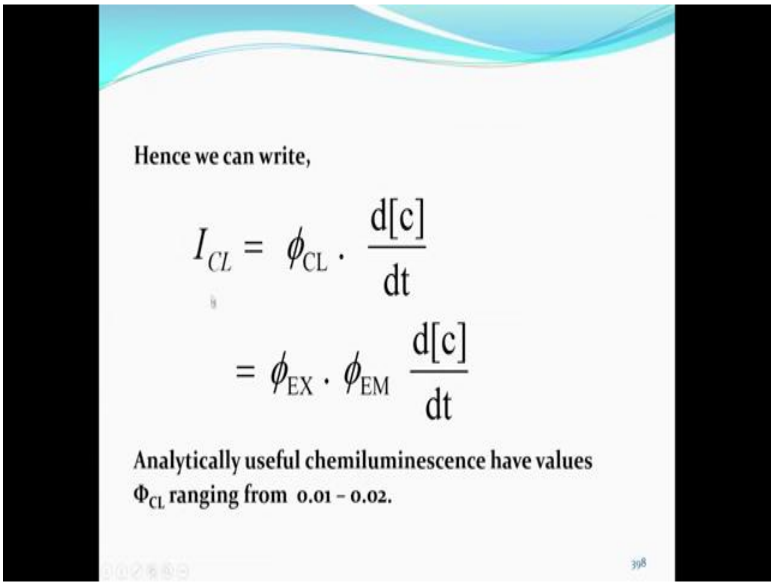

To put it mathematically what I normally write is I CL is equal to phi CL d c by dt. This phi CL is a product of two functions that is phi EX excited and emitted. So, analytically useful chemiluminescences have values ranging from for this phi CL ranging from 0.01 to 0.02 that is the proportionality constant. So, if I have that I can determine, I can relate the intensity to the concentration that is the whole logic.

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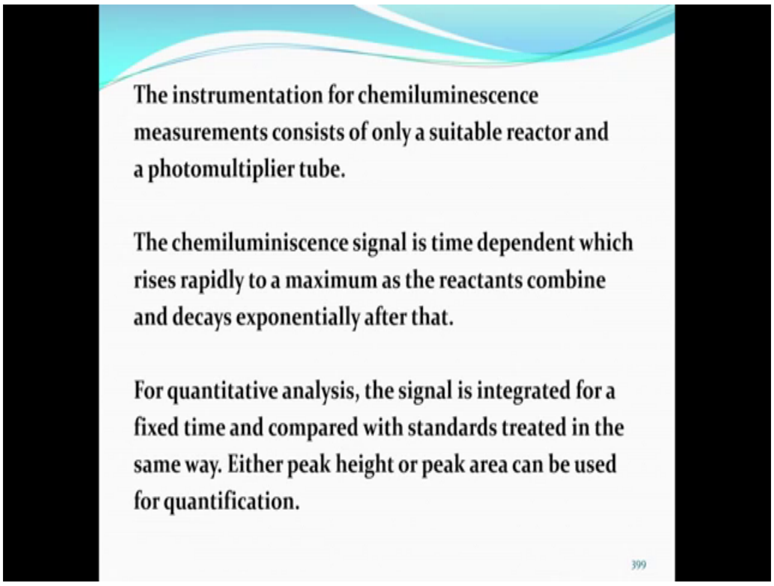

So, instrumentation consists only of a suitable reactor. All you have to do is design a suitable reactor, and select the radiations put a photomultiplier tube in front of it, and determine the current and correlate it to concentration. So, it is sometimes dependent which time dependent also, because all the reactions do not take place in the given reactor at the same time. So, it reacts each molecule has to react. So, if you are carrying out an air reaction in an air sample containing a chemiluminescence compound, it takes time for the reaction to start and proceed and reach a completion and then fall back on the equilibrium level. So, the chemiluminescence signals we have to understand that it is a time dependent reaction. So, it slowly raises to a maximum and then it falls as the reactants combine and once the reactants are consumed, there will be a decay like decay would be exponential after the event.

So, for quantitative analysis, the signal is integrated for a fixed time we have to fix the time and collect all the photons that are generated in the photomultiplier tubes and then integrate it have a certain number instead of the current or something like that. So, it is known as photon count, we can plot photon count versus concentration also. And the signal is integrated for a fixed time, time is important for us now, and it has we have compare it with a standard. Again we see more 99 percent of the spectroscopic methods, they are all relative. So, all your results would be as accurate as your standard. So, there is lot of chemistry, and then precaution, and then quality maintenance involved in the standard preparation, standard handling, and standard storage. So, all these things compared with if I have a full control over the standard my result will be more reliable.

So, either we can since the event itself is a very dynamic event that means, the initially there is no reaction, slowly there will be a reaction, it will reach a maximum and as the signal dies down it will come back to ground floor, it will come back to the base level. So, it is a dynamic signal. And once if it is a dynamic signal, I can always go for the peak height or peak area.

Normally, in 99 percent of the spectroscopic measurements peak height is used especially if the signal is very strong and very specific, but if the signal is weak and broader very broad then peak area is more important because the matrix components will affect the shape of the peak quite often. So, it is important for us to remember if the peak is sharp go for peak height; if the peak is broader, you should always go for peak area.

So, for quantification either one either one we can use or both will be equally good. I personally prefer peak area integration; because it can be done by the computer that is number one, and then it reflects the changes in the matrix with respect to the reagent as well as time. So, the difference between the starting event and ending event whatever is the excitation all the events will be covered in peak area, but not in the peak height. So, that is a very important consideration especially in spectroscopic reasoning quite often in ICP and atomic absorption the peaks are so sharp that area measurement makes does not make any difference at all. So, in that case one can go for a peak height determination.

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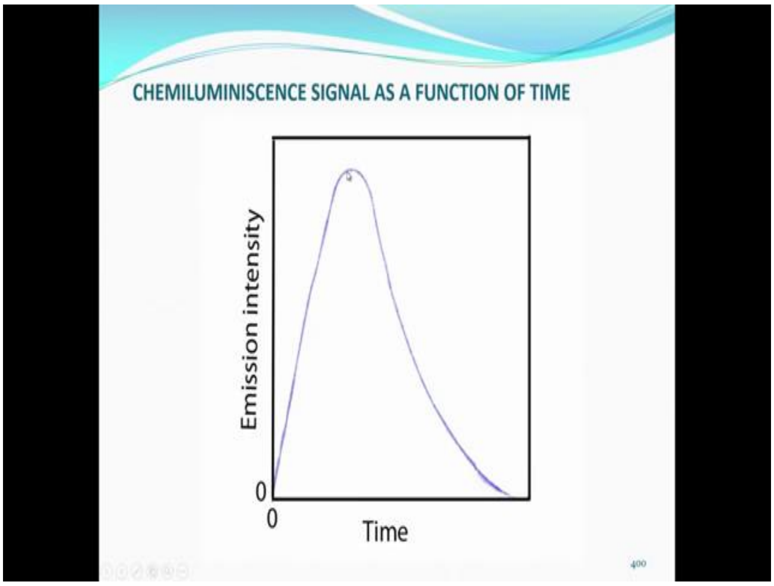

So, for example, look at this the signal, the chemiluminescence signal has a function of time, initially it will be zero and then slowly emission intensity will increase. Once it reaches with respect to particular time then this (Refer Time: 14:15) will come back to the ground state and then chemiluminescence will die down. So, in this case, you can see that the peak is quite broad and you can peak height also, you can use and peak area also you can use because the peak area does not have too much complications. It seems to be a fairly recent peak without much variation in the signal with respect to blank as well as sample. So, in this case, we can go for either for peak height or peak area.

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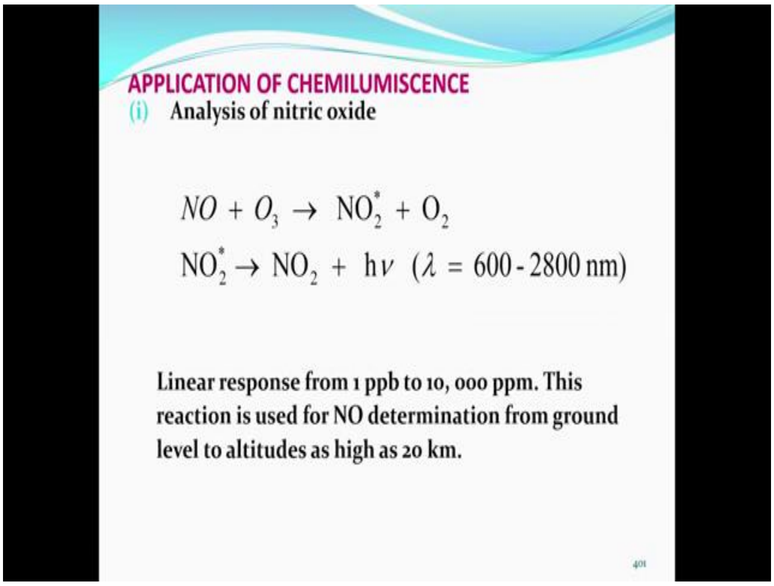

Now, I am not going into the instrumentation of the system because obviously, such instruments are 99 percent of the time they are all dedicated instruments. For example, if you want to determine nitric oxide in air, all you need is a box containing the reactor and the associated optics and detector. So, we have covered most of the things except the reactor, and reactor is a matter of design.

So, each manufacturer will have a different kind of design. What is important in chemiluminescence reaction is to bring the analyte and reagent together in a given space of either a flask or a reactor or a multiple slots in a in a given container, where reagents can be added, reagents can be subtracted or you can add buffer, you need a sample to draw the sample from air, you need a pump and other associated equipment. But all other things are a matter of detail rather than convenience. So, each manufacturer expects to produce a chemiluminescence system which is very specific to his leads. Again I have to emphasize here that there are no standards available for measurement of chemiluminescence.

So, what do we do, we take pure reagent or pure analyte itself, and note down the chemiluminescence value. It can be either peak height or peak area, but the delivery of the reagent, and allowing time and the reactor size, all these become important to note down the signal. So, the sensitivity of the system depends more on the design factors rather than the instrumental factors. So, 99 percent of the time you come across equipments chemiluminescence equipments which are dedicated instruments. For example, if you want to determine sodium nitric oxide in the air, Ii is a very common constituent coming from vehicles etcetera and also from atmospheric reactions whenever there is lightning, whenever there is lightning, there will be nitric oxide will be produced. So, in such cases, it is important for us to determine nitric oxide in the environment. So, the manufacturer will produce a dedicated instrument for the measurement of nitric oxide and for which the reactor design and everything is his.

So, the analysis of nitric oxide is one typical example. So, you can see the in the slide what I am showing you is this nitric oxide will react with ozone that means, in the reactor we have to supply ozone and draw nitric oxide from the environment through a pump or something like that. Allow it to react with ozone which will give you an excited species NO 2 that is nitrogen dioxide and that nitrogen dioxide excited species will decay into nitric oxide plus h mu. And the radiation is somewhere anywhere in this region. We can go for measurement using a filter or a monochromator or slate or anything like that depending, but anywhere in this range, you can go for that.

Because if you remember the peak seems to be quite broad in chemiluminescence, for example, you can see here the peak is quite broad and the wavelength need not be fixed at all, but you can fix it also and make the measurements. So, what is so special about this, the specialty is linear response is from 1 ppb parts per billion to 10,000 ppm. So, the order is approximately five nitrogen nitric oxide can be determined when to five order that is 0.1 molar, 0.01 molar point, 0.001 molar, 0.0001 like that you can go down to 0.00001 molar. And this is important. So, this reaction is used for nitric oxide determination from ground level to altitudes as high as 20 kilometers.

So, again this place is a some sort of a restriction that your equipment should be portable, and it should fly somewhere around up to 20 kilometer or you can you need to draw a signal from as high as 20 kilometer to the ground where the instrument is kept. That means, a sample needs to be drawn at that level, so that is the beauty of chemiluminescence especially nitric oxide.

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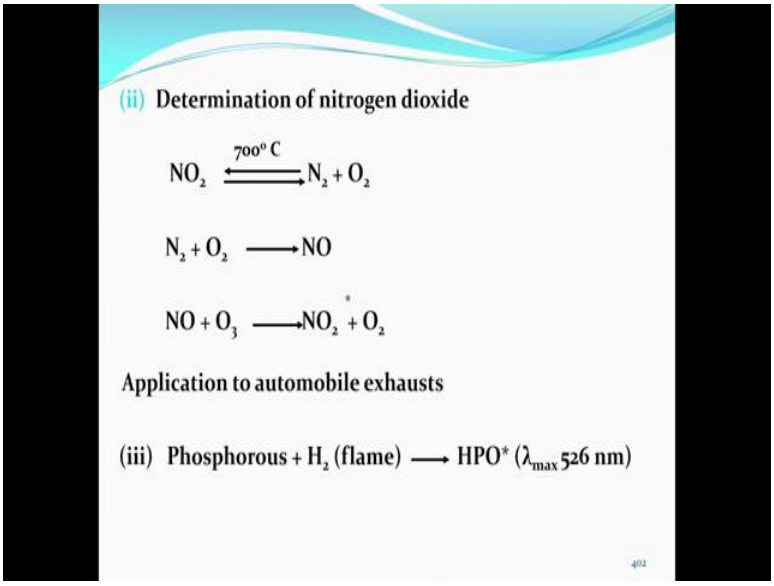

So, suppose I want to do in the nitrogen dioxide. So, nitrogen dioxide, it reacts around 700 degree to decompose to nitrogen and oxygen, it is a very common well-known reaction. So, but this nitrogen and oxygen can recombine to give you nitric oxide, and nitric oxide can react with ozone just like in the previous signal this nitric oxide and ozone ray same reaction scheme will continue. It will produce NO 2 excimer, NO 2 excimer will regenerate to NO 2 and then the NO 2 can be we do have some sort of wavelength to monitor.

Now, the nitrogen dioxide is important from the point of view of environmental pollution because nitrogen dioxide comes out from the vehicles on the road. So, obviously, here the instruments need not drawing a sample from anywhere except from the automobile exhaust. So, I need to have a sampling system from the exhaust into the chemical reactor that is a box and then the instrument. So, the here the determination becomes very, very simple because all I have to do is take the vehicle to the equipment, and then we finish the determination. Now, phosphorous is another element which burns in air hydrogen and that can give you HPO star ion and the lambda max is 526 nanometer that means, it gives out a radiation corresponding to 256 nanometer.

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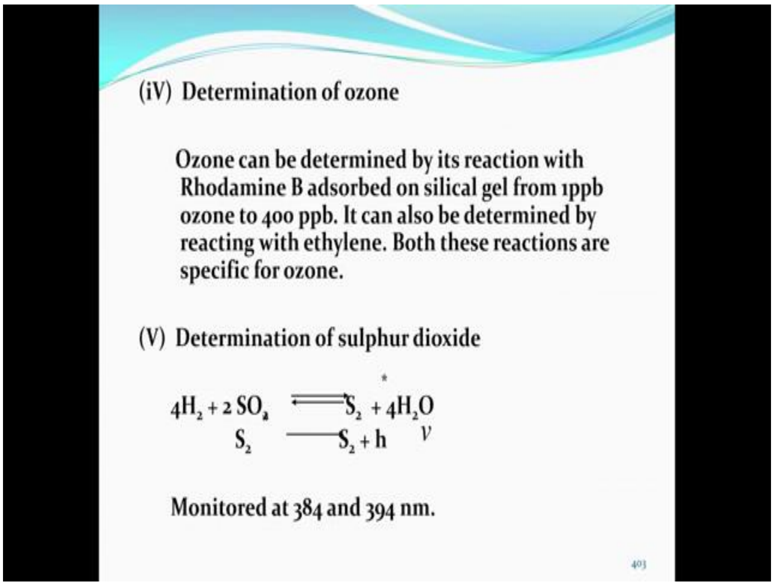

So, I can always go for the determination of phosphorous using that reaction. Now, if I can react with ozone and nitric oxide, can ozone itself be determined in a given environment? This is a question gains importance especially because ozone is a atmospheric contaminant, and it is also required to stop the radiation coming from the solar system. And you all of us know that chlorofluorocarbons and many other compounds, they do loose, they destroy the ozone layer in the environment. So, we can determine ozone, but on the underground ozone is again a very corroding chemical, and it is considered as pollutant especially in cities and towns around near the beaches.

So, ozone can be determined by its reaction with rhodamine B adsorbed on silica gel. What I do is I take silica gel put rhodamine B in that and then I allow it to react with ozone and the ozone range can be from 1 parts per billion to 400 parts per billion. Normally, the ozone content is only in the in the range of about 0.12 to 1 ppm or something like that, but it can be determined at higher levels. It can also be determined by reacting with ethylene both these reactions are almost specific for ozone nothing else can interfere in the determination.

So, there is a determination of sulphur dioxide, there is a specific dedicated equipment available for the determination of sulphur dioxide also. Now, I have not informed you the cost of such equipments especially the chemiluminescence equipments are very popular for the determination of ozone and then nitric oxide and nitrogen dioxide, sulphur dioxide etcetera the cost of this equipment varies from between 15 to 25 lakhs.

So, they are compare to spectrophotometer chemiluminescence equipments are quite costly, but the importance of these species in the environment makes it worthwhile to have it again I have to inform you that in India we do not produce chemiluminescence equipments. India is an under developed country as far as equipment monitoring, monitoring equipments and spectroscopic instruments are concerned 99 percent of the time we end up importing the chemical importing the instruments, but you are good at using that the using the equipments.

Now, that brings me to another application that is determination of sulphur dioxide that is the reaction I am presenting to you here that is 4 hydrogen molecules can react with 2 S) three molecules to give you a sulphur molecule and water. And sulphur molecule can excited sulphur molecule can get deactivated to sulphur and giving you a radiation of about 384 and 394, you can monitor the reaction at either wavelength and then sulphur dioxide can be determined again by chemiluminescence method.

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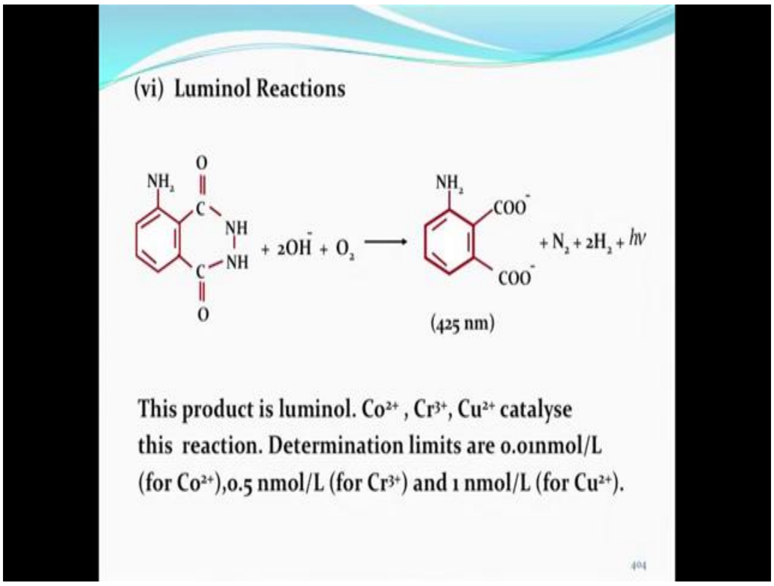

And then this is a very beautiful reaction that is luminol reaction. This luminol is a compound given here it is a an amino compound basically and fused ring with two amino groups and then 2 CO groups and it can react in the null cline medium I have written 2 OH minus here. And this alcline medium in this alcline medium atmospheric oxygen can be determined and the reaction is represented as this is NH 2 remains as it is. This group the NH-NH bond breaks and then we get COOH and COOH that is diacids aminobenzoic acid. Then the other reaction products are very simple products like nitrogen and hydrogen, but the reaction is accompanied by the emission of h mu. And the radiation corresponds to 425 nanometer this product is known as luminal CO 2, chromium and copper all these ions catalyze this reaction.

Especially whenever I am talking about catalyzation, catalysis of a reaction, we are talking of about microgram or nanogram level of the materials. So, determination limits are of the order of 0.01 nano moles per litre for carbon dioxide for cobalt and 0.5 nano moles per liter for chromium 3 and 1 nano moles per liter for Cu 2 plus. You can imagine what would be the laboratory conditions to work at this level the extreme precautions which I have been again and again emphasizing to teach you all these things are very important and we should be very careful whenever we are talking about determination especially quantitative determination using spectrophotometry or spectroscopy either way.

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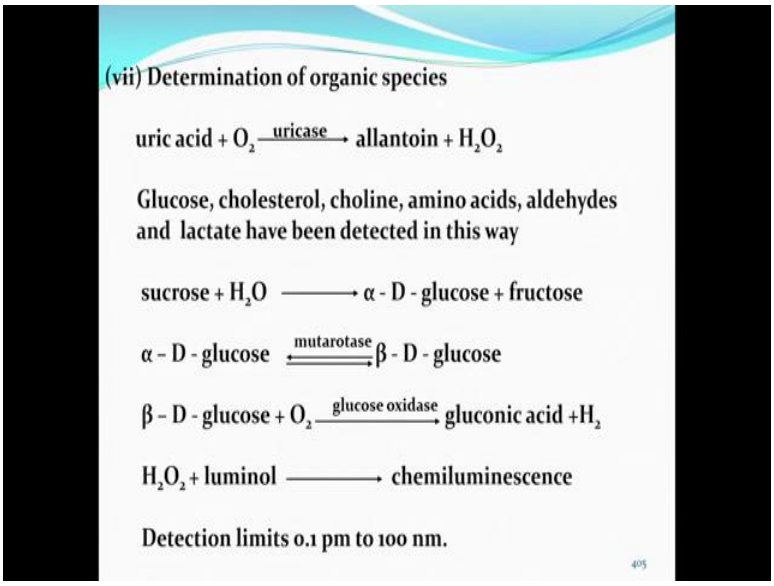

So, this brings me to another final presentation may be this is my final presentation today that is the determination of organic species. Several organic species like this uric acid. It is a part of urine, and uric acid can be reacted with oxygen to give uricase that is in that is in presence of urase enzyme and that gives a compound on a valentine and H 2 O 2 is produced. Glucose, cholesterol, choline, amino acids, aldehydes and lactate have been detected in this way, because many in many of these cases the reactant can change.

And in presence of these reagents sucrose and water alpha d glucose and alpha d glucose can mutarotase to beta d glucose beta d glucose can react with oxygen in presence of this glucose oxidase to give you gluconic acid. And H 2 O 2, now you have the gluconic acid you can just add H 2 O 2 and luminol that is the sequence that leading to chemiluminescence the detection limits. What we get is of about 0.1 pico grams, detection actually it should be pico gram 0.1 pico grams to 100 pico grams we can determine.

So, this brings us to the end of discussion about the spectrophotometric equipment, related techniques and the practice. Now, in the next four classes, I want to take you to through a procedure where we can use a method using the spectrophotometry or fluorescence or any other related technique for the determination of these things. That itself constitutes a separate sciences by itself because you will have to understand the chemical reactions and then possibly the other related terms with respect to analytical science will come into play. So, I suggest you read your chemistry properly and especially the chemical reactions which I am going to present to you for about 20 parameters for pollution monitoring that is where we are going to concentrate in the next four classes.

Thank you very much.