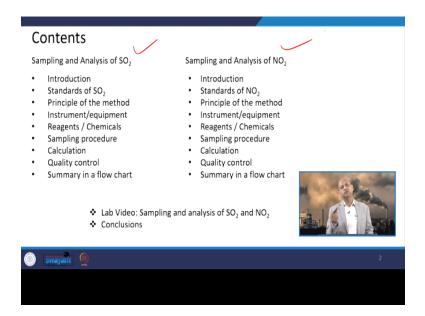
Air Pollution and Control Professor Bhola Ram Gurjar Department of Civil Engineering Indian Institute of Technology, Roorkee Lecture 57

Sampling and Analysis of SO2 and NO2 in Ambient Air

Hello friends, so these days we are discussing about experimental aspects or practical aspects of air quality monitoring. So, we have discussed about how to monitor pm 10 or $PM_{2.5}$. Today we will look into the sampling and analysis of sulphur dioxide or nitrogen dioxide in ambient air. So, kind of monitoring gaseous components or gaseous compounds in the ambient air.

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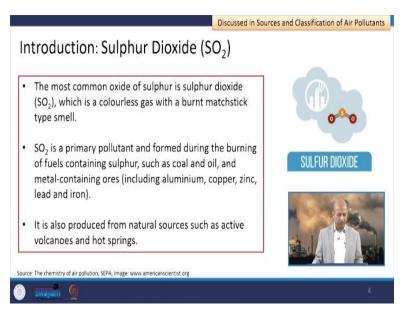
So, this is the content list of this particular presentation, we have two parts basically the sampling and analysis of sulphur dioxide and the second is sampling analysis of nitrogen dioxide and both have similar content like introduction, then what are the standards of SO_2 or NO_2 , then principle of the method, that sampling method I mean what are the instruments and equipments which are used for sampling purpose.

Then the reagents and chemicals which are used in analysis procedure and how to calculate and ultimately the sampling procedure in terms of the flow chart which will give you at one place the step by step procedure of the sampling and later on we will have a short video which will give kind of feeling how to handle this equipment basically for a particular purpose of sampling or monitoring of SO₂ or NO₂ and then we will conclude.

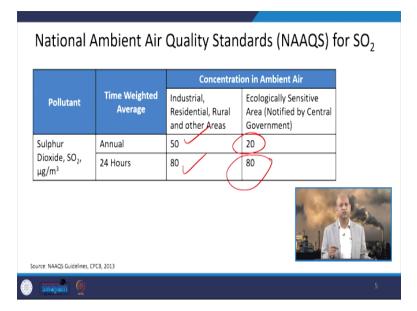
(Refer Slide Time: 1:50) Sampling and Analysis of SO₂ in Ambient Air (Improved West and Gaeke Method) Improved West and Gaeke Method

So, first let us look into sampling and analysis of sulphur dioxide which is present in ambient air. As you know sources of SO_2 are many like coal burning or even diesel based vehicular emissions and it is this sampling and analysis method is basically known as Improved West and Gaeke Method for SO_2 monitoring.

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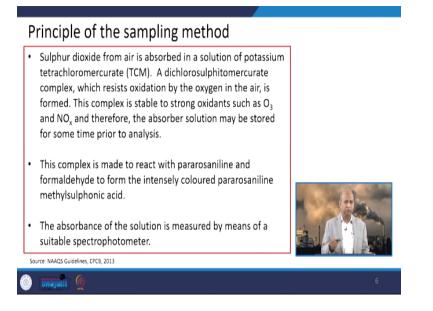
Well in this you can see like there are many sources and SO_2 is known for several kind of effects not only the health but environmental effects because it can get converted into secondary aerosols or it can also acidify certain environmental components.



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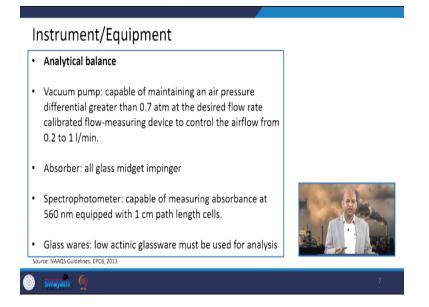
If we look into what are the prescribed standards, so like industrial, residential or rural areas they are known for annual standard 50 microgram per cubic meter and 24 hours 80 but if we go for ecologically sensitive then the annual average is only 20 very stringent and 24 hours it is same 80 microgram per cubic meter.

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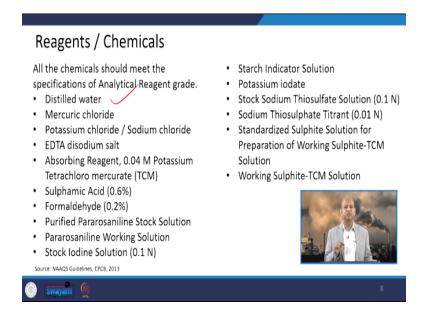
The principle which is used for this particular monitoring or sampling of SO_2 , so basically it is based on absorption in a particular solution of this potassium tetrachloromercurate (TCM) in brief we call it, so the TCM solution is used and this is the, why this is used because it is also a particular chemical which resists the oxidation because of other compounds like ozone or NO_x , so those kind of interference it can be removed, it can remove easily, so that way this is a good procedure and it is made of certain chemicals like formaldehyde and others, then at certain places or at certain steps we use different kind of reagents and chemicals.

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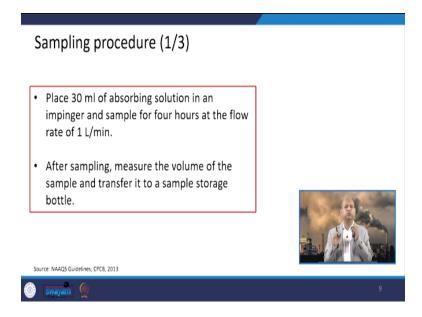
And we will look into these analytical like balance, then vacuum pump is used for extraction of the gases, then it is passed through that chemical which is in impinger and so it is absorbed there basically, then ultimately spectrophotometer is used for measuring this absorbance in terms of color matrix kind of procedure and there are need of glass wears also because we need to form solutions etc.

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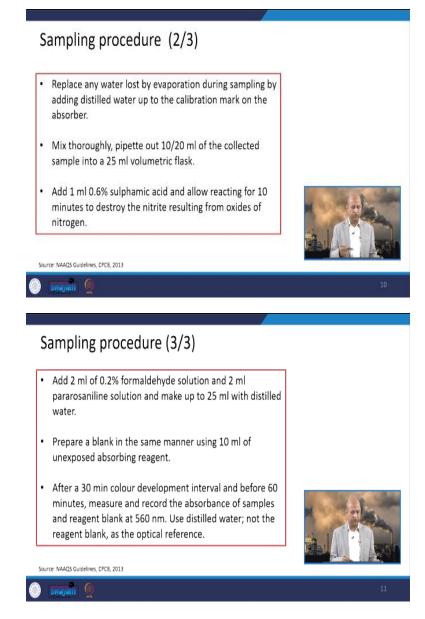
So, you can see different kind of reagents and chemicals which are used for this particular analysis in laboratory, distilled water then mercury chloride, potassium chloride. So, all these chemicals, reagents we need in our laboratory for this particular purpose.

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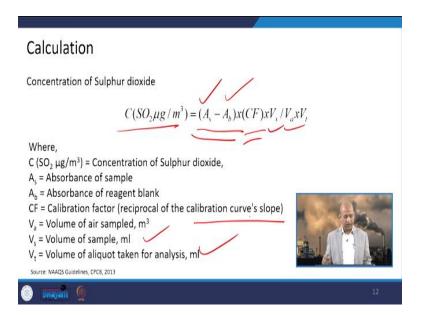
Then if you go for sampling procedure, then first of all we have to have 30 milliliter of this absorbing solution which is needed in the impinger, so that when gas, this air passes through this impinger in this solution so SO_2 get absorbed basically.

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And we do certain procedure we will look into just later on in steps by step.

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I come to this calculation, this is again like how much concentration of sulphur dioxide is there. So, basically first of all absorbance of sample is needed, so difference of the blank sample and the which is exposed and then this calibration factor CF is needed which is again we can derive from different kind of solutions, this curve is based on the slope so concentration can be calculated when we know a particular kind of concentration of this absorbance.

$$C(SO_2 \,\mu g/m^3) = (A_s - A_b) \times CF \times \frac{V_s}{V_a} \times V_t$$

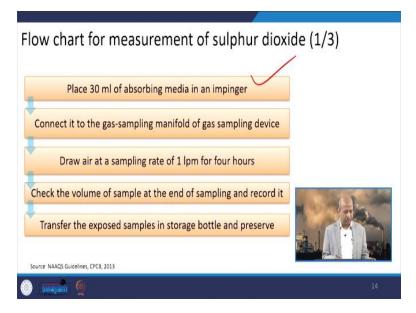
Then there is this volume of the air sampled, how much air has been passed through that solution and volume of the sample we have taken, so Va and Vs and then Vt that is volume of aliquot taken for analysis, means in the pipette how much we are taking for particular analysis.

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| Quality Control | |
|--|----|
| Quality Control (QC) is ensured by using certain techniques that fulfill requirements for quality. | |
| The QC procedures for the air sampling and monitoring sections of this protocol include ✓ preventative maintenance of equipment, ✓ calibration of equipment, ✓ analysis of field blanks and lab blanks. | |
| Source: NAAQS Guidelines, CPC8, 2013 | |
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Quality control, it is the same we have done in PM_{10} and $PM_{2.5}$ similarly, we have to follow certain protocols so that there is no error in the monitoring or sampling.

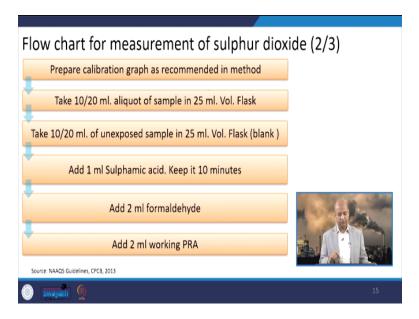
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So, this is the flow chart which gives different steps for the measurement of sulphur dioxide like as I said, first of all we have to place 30 milliliter of absorbing media in the impinger because this will absorb the SO₂, then we have to connect it in the gas sampling manifold of gas sampling device there is a particular frame where it has to connect.

Then we have to draw air at a sampling rate of around 1 liter per minute for 4 hours or it can be 8 hours depending upon how much do we need to sample it, then we have to check the volume of the sample at the end of the sampling and record it because it will get reduced then we have to fill some distilled water, I will tell you later on, so transfer this exposed samples in a storage bottle and we have to preserve it properly.

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Then we need to prepare calibration graph as recommended so that we can get the concentration after using this particular graph then we need to take 10 or 20 milliliter of this aliquot of sample in 25 milliliter volume of the flask and this unexposed sample is also taken as the blank, then we need to add 1 milliliter of this Sulphamic acid and we keep it for 10 minutes, after that we add 2 milliliter of formaldehyde and then we add 2 milliliter of working PRA.

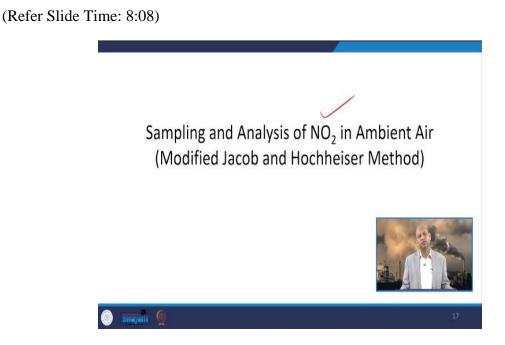
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| Flow chart for measurement of sulphur diox | ide (3/3) |
|---|-----------|
| Make up to mark (25 ml.) with distilled water | |
| Keep it 30 minutes for reaction | |
| Set Zero of spectrophotometer with Distilled water | |
| Measure absorbance at 560 nm | |
| Calculate concentration using calibration graph | 13.95 |
| Calculate concentration of Sulphur dioxide in µg/m ³ | |
| Source: NAAQS Guidelines, CPCB, 2013 | |
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| | |
| Calculation | |
| Concentration of Sulphur dioxide | |
| $C(SO_2\mu g / m^3) = (A_s - A_b)x(CF)xV_s / V_b$ | / v// |
| $C(5O_2\mu g/m) = (A_s - A_b)A(CT)AT_s/V$ | aAri |
| Where, | |
| C (SO ₂ μ g/m ³) = Concentration of Sulphur dioxide, | |
| A _s = Absorbance of sample A _h = Absorbance of reagent blank | 67 |
| CF = Calibration factor (reciprocal of the calibration curve's slope) | A |
| V _a = Volume of air sampled, m ³ | |
| V _s = Volume of sample, ml | |
| V_t = Volume of aliquot taken for analysis, ml | |
| Source: NAAQS Guidelines, CPCB, 2013 | |
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Then make it up to 25 milliliter because certain volume reduction is there, so we mix with distilled water, then we keep it for 30 minutes for the reaction and we set the Zero of spectrophotometer with the distilled water because we have to compare with the distilled water not with the blank, blank with distilled water and the exposed solution also with the distilled water we have to compare.

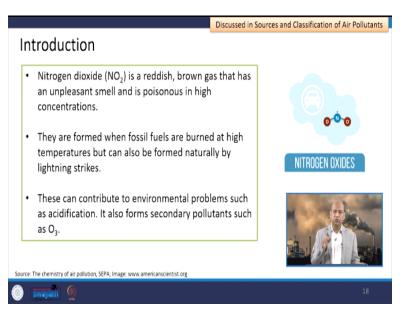
So, measure the absorbance at the 560 nanometer and calculate the concentration using calibration graph, we have already prepared so that graph will be used, then we calculate

the concentration of sulphur dioxide using that particular equation which I just discussed, this one.



So, this is the way we calculate concentration of SO_2 which is present in ambient air, similarly the sampling and analysis is done for NO_2 nitrogen dioxide in ambient air and the method which is used is known as modified Jacob and Hochheiser method.

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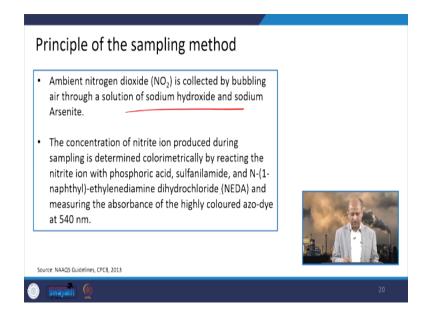
And again it has its own characteristics and NO_2 is also known for like creating acid rain related problem or it can have respiratory issues, health effects also, it also contribute into haze formation, smoke formation, also precursor for formation of the ozone, so that way it is a problematic gaseous component in the air basically.

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| National / | | | dards (NAAQS) f | |
|----------------------------|--------------------------|--|--|--|
| Pollutant | Time Weighted Average | Industrial, Residential, Rural and other Areas | Ecologically Sensitive Area (Notified by Central Gevernment) | |
| Nitrogen | Annual | 40 | 30 | |
| Dioxide, NO₂, µg/m³ | 24 Hours | 80 | 80 | |
| aurce: NAAQS Guidelines, (| :PCB, 2013 | | | |

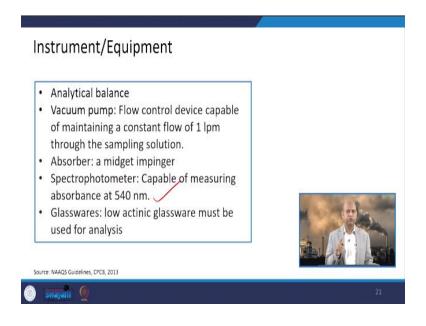
If we look into the air quality standards, National Ambient Air quality standards of NO₂ then we can see like 40 and 80 for industrial, residential and rural areas, 40 for annual average, 24 hours average is 80 micro gram per cubic meter, it should not exceed whatever we are observing it should not exceed with these given values otherwise it is a problem. And for ecologically sensitive areas it is 30 to 80, so that means for annual average value is less, it is stringent because whole year if you are inhaling polluted air then it will create problems in the system, our body.

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The principle of sampling method, so again this is collected by bubbling air through a solution of sodium hydroxide and sodium arsenite, so bubbles are there and then it will get absorbed basically. The concentration of nitrite ion produced during the sampling is determined again by colorimetric method and by reacting the nitrite ion with phosphoric acid and all other chemicals which are listed here.

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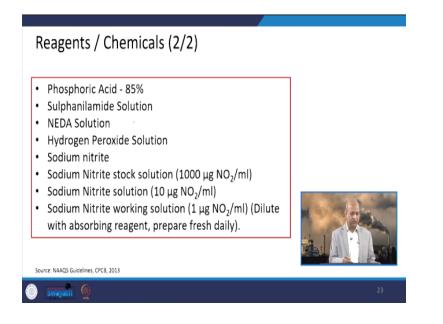
Well, so instruments as we know analytical balance is needed, vacuum pump is needed and absorber in the impinger, then capable of measuring the absorbance at 540 nanometer, a spectrophotometer of that capability is needed, glass wears are of course needed.

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| Reagents / Chemicals (1/2) | |
|---|----|
| All the chemicals should meet the specifications of Analytical Reagent grade. | |
| Distilled water Sodium hydroxide Sodium Arsenite Absorbing solution (Dissolve 4.0 g of sodium hydroxide in distilled water, add 1.0 g of sodium Arsenite, and dilute to 1,000 ml with distilled water). Sulphanilamide N-(1-Naphthyl)-ethylenediamine Di-hydrochloride (NEDA) Hydrogen Peroxide - 30% | |
| Source: NAAQS Guidelines, CPCB, 2013 | |
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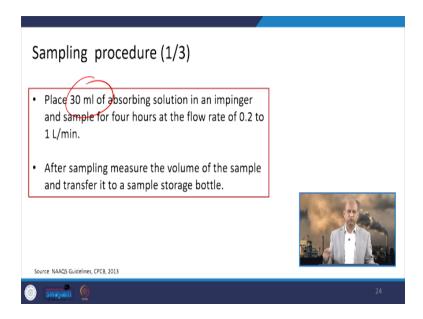
Then other reagents and chemicals are listed here like distilled water, sodium hydroxide and sodium arsenite and other absorbing solutions.

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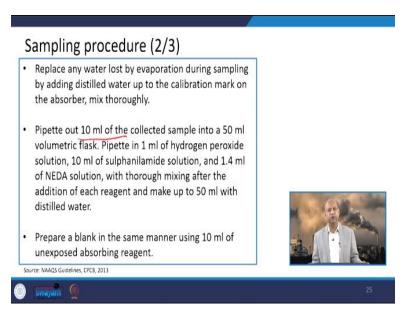
Then these are additional reagents and chemicals.

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Procedure is as I said earlier also like first of all place this 30 ml of absorbing solution in the impinger and impinger is placed in the instrument where this air will pass, basically we do it in the same instrument where we are taking observation or sampling of PM_{10} or $PM_{2.5}$ we can this particular assembly we can use with that instrument also taking air at a particular flow.

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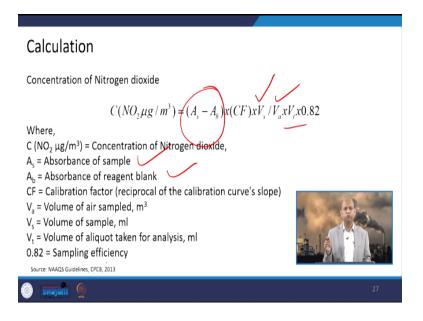
So, we replace any water lost by evaporation during sampling by adding the distilled water to make the same volume which we took, then we prepared 10 milliliter of the collected sample into 50 millimeter volumetric flask.

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| Sampling procedure (3/3) | |
|---|----|
| After a 10 min colour development interval, measure and record the absorbance of samples and reagent blank at 540 nm. | |
| Use distilled water; not the reagent blank, as the optical reference. | |
| Samples with absorbance greater than 1.0 must be reanalyzed after diluting an aliquot of the collected samples with an equal quantity of unexposed absorbing reagent. | |
| A randomly selected 5-10% of the samples should be re- analyzed as a part of an internal quality assurance program. | |
| Source: NAAQS Guidelines, CPCB, 2013 | |
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And do some those laboratory based analysis.

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And then calculation is done as earlier as I said this As absorbance of the sample which has been exposed, absorbance of the reagent blank, and then CF is calibration factor which we derived from the graph curve and then volume of air sampled and volume of the sample, volume of aliquot which we have taken and then we multiply with sampling efficiency around 0.82 depending upon the sampling rate.

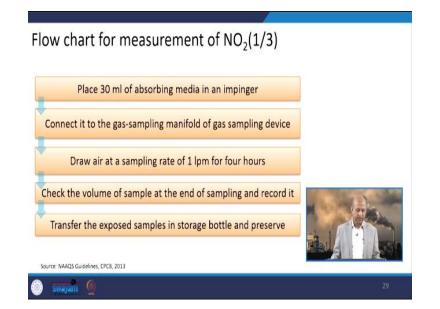
$$C(NO_2 \,\mu g/m^3) = (A_s - A_b) \times CF \times \frac{V_s}{V_a} \times V_t \times 0.82$$

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| | ality Control (QC) is the techniques that used to fulfill requirements for quality. | |
|---------|--|--|
| mo ✓ | QC procedures for the air sampling and nitoring sections of this protocol include preventative maintenance of equipment, calibration of equipment, analysis of field blanks and lab blanks. | |

Then quality control is the same, we have to follow the protocol so that there is no error in monitoring and analysis at the laboratory.

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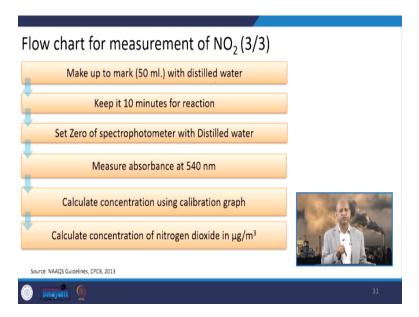
So, this is the flow chart which will give you in nutshell what is the procedure which we follow. So, place 30 ml absorbing media in the impinger, connect it to the gas sampling manifold that device particularly, we do the gas sampling device, draw air sampling at the rate of 1 liter per meter for 4 hours or 8 hours or whatever you need to do as per the requirement, then we check the volume of the sample at the end of the sampling and record it because it will reduce, then transfer the exposed sample in storage bottle and preserve it, so that we can take it without disturbing to the laboratory.

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| Flow chart for measurement of $NO_2(2/3)$ | |
|---|--|
| Prepare calibration graph as recommended in the method | |
| Take 10 ml. aliquot of sample in 50 ml. Vol. Flask | |
| Take 10 ml. of unexposed sample in 50 ml. Vol. Flask (blank) | |
| Add 1 ml hydrogen peroxide | |
| Add 10 ml sulphanilamide | |
| Add 1.4 ml NEDA | |
| Source: NAAQS Guidelines, CPCB, 2013 | |
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We prepare calibration graph as recommended earlier, then we take 10 milliliter of this aliquot through the pipette and put in 50 milliliter of the volume flask, then we take 10 milliliter of unexposed sample as a blank in 50 milliliter volume flask, add 1 milliliter of hydrogen peroxide, 10 milliliter of sulphanilamide and 1.4 milliliter of NEDA, all these chemicals are taken.

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Then we make up to the mark of 50 milliliter with distilled water, then we keep it up to 10 minutes for reaction purpose set Zero spectrophotometer with distilled water and we measure the absorbance of both blank as well as the exposed solution, so we calculate the concentration using calibration graph and then we calculate the concentration with that particular equation.

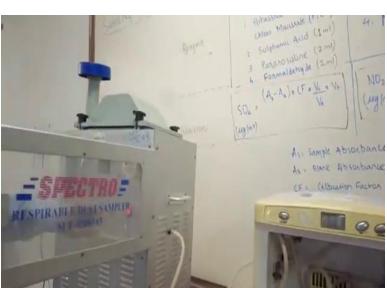
So, here we present a short video which will illustrate you the sampling of both sulphur dioxide and NO_2 nitrogen dioxide and this video has been prepared in air pollution lab of civil engineering department, so enjoy the video.

(Video Being Played)

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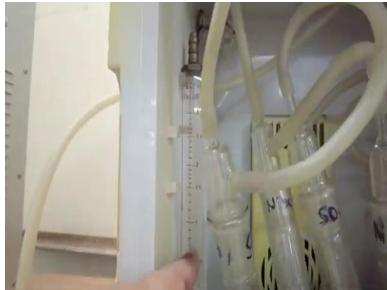




















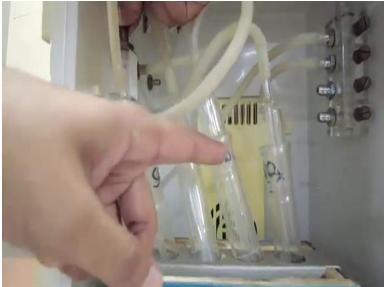






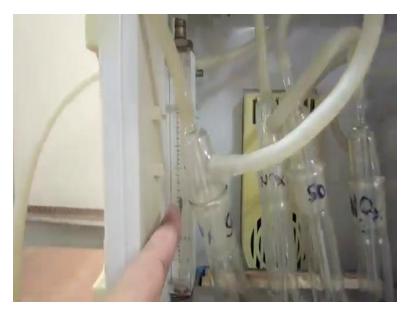






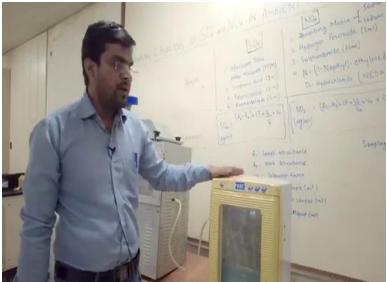














Good morning friends, I welcome you all in the experiment part of our subject air pollution and control and here I am coming with another experiment and this experiment is for measurement of SOx and NOx in the ambient air. So, in our one of the previous experiment I have explained how to measure the pm 10 in the ambient air and for that we use the high volume sampler and in that I have already explained you how the sampling of PM_{10} is carried out through the high volume sampler, like the ambient air is sucked through this inlet, then it passed through the filter assembly and then it exists from here.

Now, using this instrument along with another accessory we can also measure the SOx and NOx in the ambient air. Now, in order to measure it how we do that I will explain in today's

experiment. So, basically what happens like when we start our device, so it sucks the air and then it exits from here. So, now what happens like here we added one attach one tube that is connected with this box that is called as an impinger box, okay, so what is its functioning that I will tell you.

So, we connect this tube through this imbinger box, so what happens like whatever the air which is coming out through the high volume sampler that will be allowed to go into this impinger box, now what are the different component of the impingr box is that we have the impinger tray and impinger tubes and we have a rotameter to maintain the flow rate.

So, basically what we do for measurement of SOx and NOx we do measure it through the colorimetric analysis and in order to do this we prepare some absorbent in the lab like for measurement of SOx we do prepare the potassium tetrachloromercurite and for the measurement of NOx we do prepare the absorbent of which is prepared by the sodium hydroxide and sodium arsenite.

So, after preparing these two absorbent we place in these four tubes, actually here we have two tubes for NOx, we have already mentioned so that while sampling we will be able to know like which impinger tube is for which absorbent. So, these two tubes where we have mentioned the NOx here we add the absorbance of NOx and for measurement of SOx we add the absorbance for SOx in this tube and this tube, so we have kept here four tubes.

Now, how the constant flow rate of 1 liter per minute is maintained in this impinger box, so in order to do this we have a rotameter here through which we are able to regulate our flow rate, so that only 1 liter per minute of air flow can pass through these four tubes. So, how do we do it that I will explain now.

So, I will just start this device, so you can see we have these four loops are connected with these two, so the air is coming from here then it is going there and then this tube is connected to this tube and this tube is connected to this tube, now if you want to maintain the flow rate of 1 liter per minute we connect this tube here and you can see that flow rate is around 1 liter per minute, if it is not 1 liter per minute then through the adjustment screw

here we can change or we can open up or close it down, so that flow rate will be maintained to 1 liter per minute.

So, now these two tubes are having flow rate of 1 liter per minute of air that is passing through this, similarly for another tube this one and this one we have this another opening, so we just place here and we check that whether the flow rate is 1 liter per minute or not, so here it is little round, so we can just adjust this flow rate by opening and closing this screw, you can see this marker is moving and here we have adjusted at 1 liter per minute. So, now the flow rate is set at the 1 liter per minute, then we take out these tubes and so that like this is the procedure for keeping the flow rate of 1 liter per minute of the air which is passing through these four impinger tubes.

So, then after what we do, as I said like we place the absorbent media in these four tubes like for NOx we add in this first and third tube and for SOx in the second and fourth tube and after that we close the door of the impinger box and another thing is like we have to maintain a constant temperature inside the box, so it has a fan inside the box, so that like what if it is heating more it has a thermostat inside so it will accordingly adjust the temperature.

So, that right now we are having let us say temperature of 28 degree centigrade inside, so we can just use this up and down buttons to maintain the temperature and at the same time let us say more sampling is going on and we want to see whether everything is okay inside, we just switch on this light button, so we can check inside whether everything is fine or not.

So, this is how the ambient air is passed or allowed to pass through this absorbent media which is present in these four impinger tubes. So, generally sampling is carried out say 4 hours in the ambient air when we are doing sampling for pm 10 so along with that we can attach this impinger box and we can also measure the SOx and NOx in the ambient air. So, after finishing our sampling we take out the sample from these impinger tubes and we go for the colorimetric analysis in the laboratory.

So, here in this calculation I have explained you or I have presented here the SOx and NOx what are the different chemicals which has to be added, let us say for the SOx this is our PTCM which is the absorbent we have placed inside this tube and after doing the sampling we come back to the lab and then we take out 10 ml of the sample and to this we add 1 ml sulphanic acid or 2 ml of pararosaniline and 2 ml of formaldehyde and then we make up it to the 50 ml and after that we take the absorbance of this sample through the spectrophotometer.

Similarly, we have the blank sample in the lab which is not sampled or we say that unsampled, so for that also we measure the absorbance, so the difference of these two is represented here is As minus Ab and then here we have the calibration factor that is taken from the calibration curve with the standard which we prepare in the lab so that we will be able to calculate the SO_2 concentration.

$$C(SO_2 \,\mu g/m^3) = (A_s - A_b) \times CF \times \frac{V_s}{V_a} \times V_t$$

And Vs and Va is your volume of sample and Va is the volume of air sample, so volume of air sample we can obtain from this high volume sampler which I have already explained in our previous experiment and then Vd is the volume of aliquot, so using this formula we are able to calculate the SO₂ in the ambient air in terms of microgram per meter cube.

Similarly, if we go to the measurement for NOx as I said like we use the absorbing media as sodium hydroxide and sodium arsenite, so when the NOx passes through this then it fixes in the form of nitrate and then we come back to the lab and we take the sample like for SO_2 we have taken so we take the 10 ml of sample and then we make up it by adding 1 ml of hydrogen peroxide and then 10 ml of sulfanilamide and NEDA of 1.4 ml, so after adding this we make up the sample up to 50 ml and then we take the absorbance, so after taking the absorbance we use this formula for the NO₂ concentration.

$$C(NO_2 \,\mu g/m^3) = (A_s - A_b) \times CF \times \frac{V_s}{V_a} \times V_t \times 0.82$$

Here again the Ab stands for the blank absorbance which is unsampled absorbing media, so the difference of these two is presented here and then CF is standing for the calibration

factor, Vs is the volume of sample and Va is the volume of air and Vd is the volume of aliquot which we have taken let us say 10 ml and then 0.82 is the sampling efficiency, so using this formula we are able to calculate the NO_2 into the ambient air. So, this is how we do measure the SOx and NOx in the ambient air using the impinger box, thank you very much.

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Conclusions

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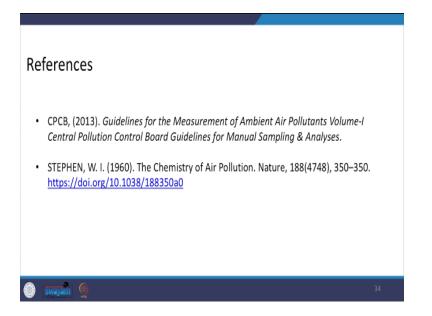
- Both SO₂ and NO₂ are major pollutants in the atmosphere, as their greater concentrations have a variety of effects on vegetation, buildings, and human health.
- Sampling of these gaseous pollutants is essential for calculating mass concentrations, which provides useful information for lowering SO₂ and NO₂ levels.
- The sampling of these gaseous pollutants also contributes to the co-benefits of reducing the responsible sources in the ambient air and understanding how they are removed from the environment.
- The observed values are compared with NAAQS values of these gaseous pollutants to learn whether their ambient air concentrations are within the limits or not.



We can conclude that both sulfur dioxide and NO_2 are major pollutants in the atmosphere that is why we do sampling and this vegetation and buildings and human health can be affected by these pollutants that is why measurement and to compare them with the prescribed standards are needed and sampling is done as we have described in this particular lecture and short video presentation has been there.

So, we compare all these concentration with NAAQS, we can look into the problem if there is a problem, if it is not exceeding the prescribed standard then it is fine but the monitoring is needed so that we can know whether the sulphur dioxide and now this NO_2 are within the limits or not.

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So, this is all for today and this is the reference list which you can go through at leisure, so thank you very much for your kind attention, see you in the next lecture.