Advance Analytical Course

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Lecture No # 21

Taking into account the analytical aspect of the air pollutants, today's lecture is dedicated to the various types of measurements that are required, followed by the effects of air pollutants. One by one, we will go through it and we will see that how air pollutants are measured, are sampled, and then measured, and then, how this data is made, interpreted by means of various numbers. And, there are governmental rules for air pollution. And therefore, if the values are being raised, from those stringent values, then it is an alarming effect.

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Air quality measurement – what is air quality? Yesterday, we did mention about it and we did learn about it. Complicated by a lack of knowledge as to what is clean and what does it mean by quality. When we say air quality, how do we try to interpret? Air should be very pure when we are breathing. That means it should not have any of these toxic pollutants. Main reason for air pollution control program is to protect public and define the air quality based on its effects on people and the environment. So, it is very simple

that why do we need an air pollution control? Because, mainly, it is for the health of the people and to protect the public health, air quality should be very good. The effects of air pollution are that they are very chronic and they do not show an immediate and obvious effect. It is a slow pollutant and it does make a lot of difference by inhalation over a long period of time, and that is what the effectivity of air pollutants is.

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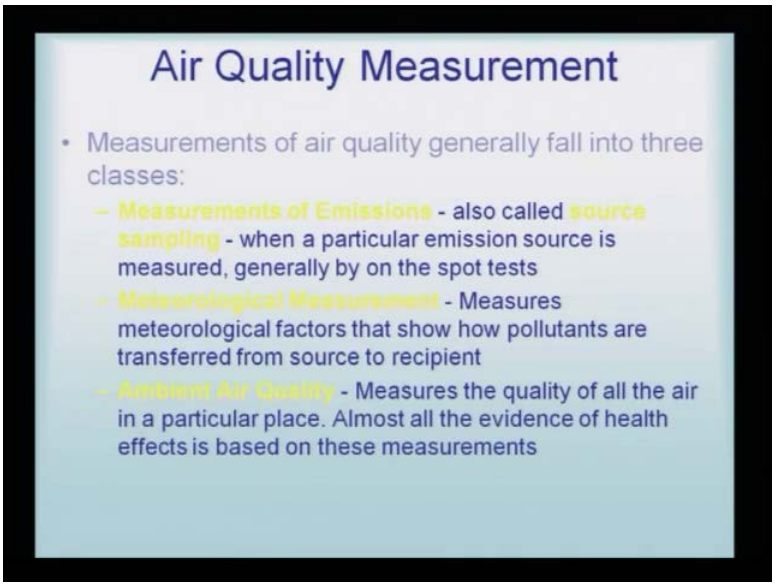

Measurements of air quality generally fall into three classes. Measurements of emissions are called source sampling – when a particular emission source is measured generally on the spot tests. Second is the meteorological measurement – measurements done by meteorological factors that show how pollutants are transferred from source to recipient. And, the third is the ambient air quality – the quality that I was mentioning that in every place in big centers of the big cities, there are these air quality values displayed for public to see whether the air quality is good or bad – measures the quality of all the air in a particular place. Almost all the evidence of health effect is based on these measurements. So, if we say that a place has an ambient air quality, we definitely understand that there is nothing going to be harmful if large number of people are inhaling this particular air quality.

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Air measurements – also now have the industrial hygiene sampling for testing the air quality inside the factories and places of work. You must have seen that some factories have very dirty and very smoky atmosphere. Now, how good or bad it is for their workers is of at most important, because the workers are working there for eight hours, and eight hours of continuous inhalation of these pollutants can definitely cause a serious health problem.

Similarly, residential indoor sampling – to evaluate the air quality within the living space. Yesterday, I showed you some slides, where I showed that even inside the house, the air is not very pure, because there are gadgets that give out some kind of gases and these gases do not have enough space to be evacuated, or there are not many exhausts, which can remove these gases. And therefore, the air quality within the house or the residential indoor air quality also falls.

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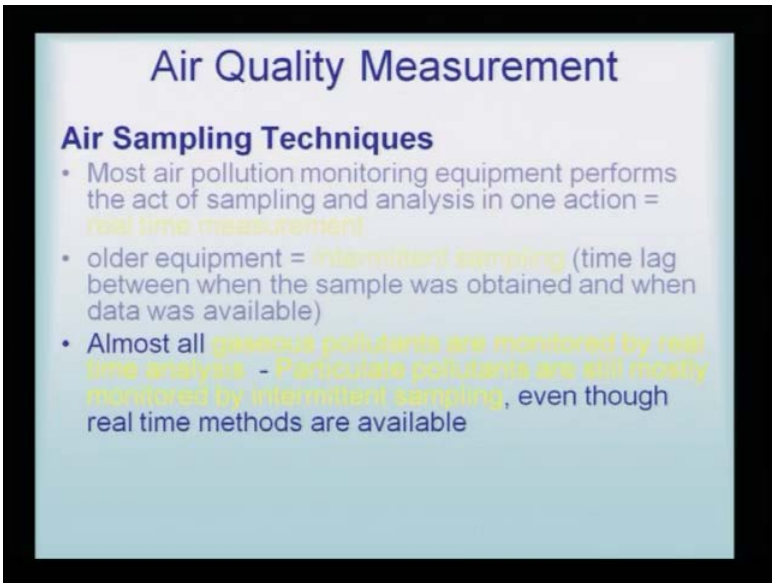

Air quality therefore, needs to be measured. So, there has to be air sampling techniques. Most air pollution monitoring equipment performs the act of sampling and analysis in one action. That means it is a real time measurement that they will trap the sample as well as analyze at the same time. Older equipments, however, had intermittent sampling. That means the samples were first collected. There was a time lag and then they were taken to the laboratory, where they were analyzed. So, there was a time lag between the sample and when the data was available after the analysis. However, almost all gaseous pollutants are monitored by real time analysis. Particulate pollutants are still mostly monitored by intermittent sampling. So, by enlarge, the carbon monoxide, the NOX, the SOX and the ozone layer are all analyzed by the real time analysis. That means, on the spot it is selected and on the spot it is analyzed. However, the particulate matter needs to be analyzed by an intermittent method, even though real time methods are also available.

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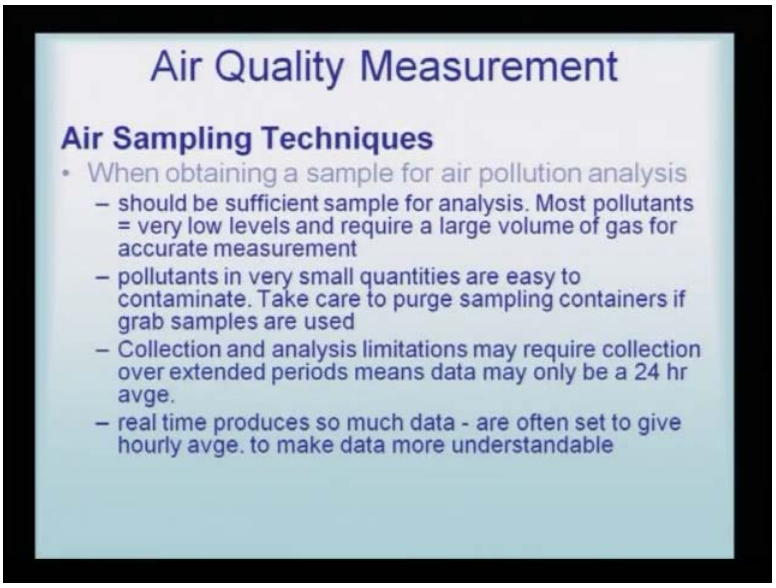

Air sampling technique – therefore, how does it go about? When obtaining a sample for air pollution analysis, one should keep in mind that there should be sufficient sample for analysis. If not, it just takes a very small pinch of air and you think that you can analyze. That is not enough. Most pollutants – very low levels, require a large volume of gas for accurate measurement. So, large canisters are designed, so that good amount of volume of air can be trapped and therefore, the analysis can be carried out properly.

Pollutants in very small quantities are easy to contaminate. Take care to purge sampling containers if grab samples are used. So, it is important that the transfer from the canister to the analytical machine must be further not contaminated. If there are small contaminants, they should be properly transferred from the canister, that is, the sampling device to the analytical device.

Collection and analysis limitations may require collection over extended period; mean data may only be a 24 hour average. What does this mean? That means between the conduction time and the analytical time, sometimes, it may take 24 hours for the entire process to get covered. Real time produces so much data – are often set to give hourly average to make data more understandable. But, real time or on the spot analysis are much faster and almost in one hour, they will generate the results and the data.

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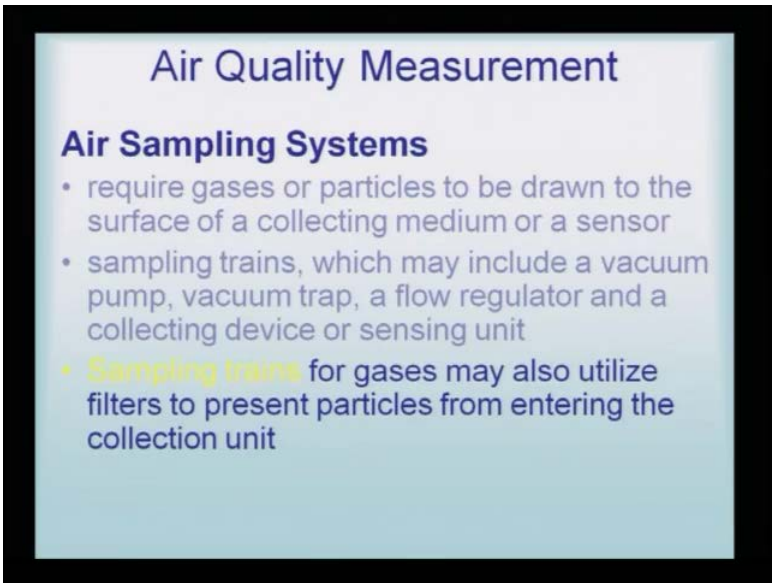

Air sampling requires gases or particles to be drawn to the surface of a collecting medium or a sensor. Obviously, because it is a gaseous sample, the particles or the gases must be collected on to the surface of the medium. Sampling trains, which may include a vacuum pump, a vacuum trap, a flow regulator and a collecting device or sensing unit; so, these are the different types of traps for collecting the gases. And, along with the air, it brings in the air pollutants also. Sampling trains for gases may also utilize filters to present particles from entering the collecting unit. So, it also uses some kind of filtration device, so that it is once trapped will remain trapped.

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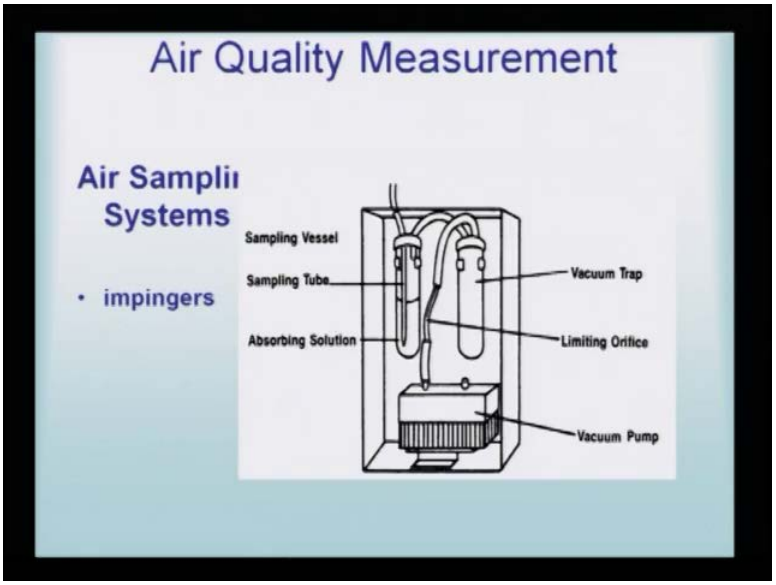

This is the kind of air quality measuring device. You see, there is a sample vessel, there is sample tube, and then there is an absorbing solution. So, all that is trapped is absorbed. And, this is sucked by the vacuum trap, and there is a limiting RFS and a big vacuum pump to generate this vacuum trap. So, this kind of vessel or this kind of device is used for just the air sampling. So, as I told you, from different sample to different sample, the sampling procedure, the analytical procedure has to be different, so that it actually suffices the need of that particular type of sample. And here, we are talking about air quality measurements. So, we have air quality measurement devices. So, there is an impinger and that is what the normal procedure of using an air quality measuring device is.

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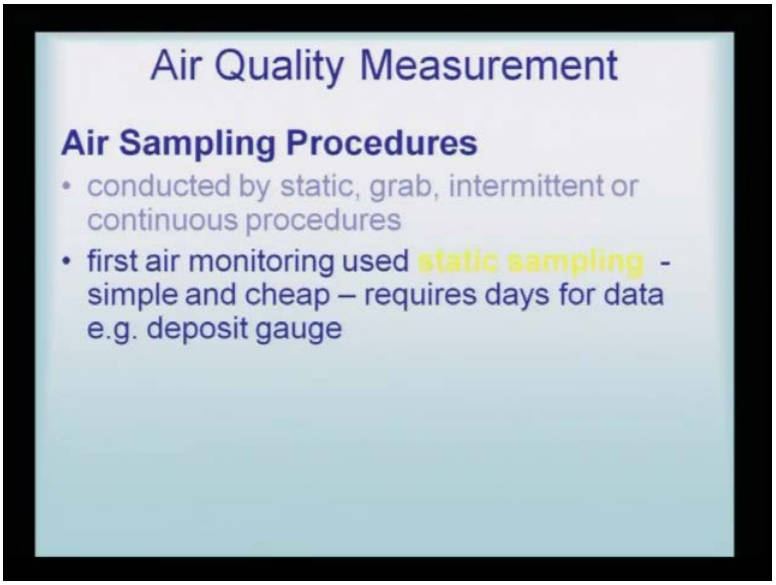

Air sampling procedures – conducted by static, grab, intermittent or continuous processes. So, air sampling can be done by any of these four methods. It could be a static method; it could be a grabbing method; it could be an intermittent; that means, after a time gap, some gas is collected; after another time gap, another sample is collected or it can be a continuous trapping device. First air monitoring used static sampling – simple and cheap requires days for data, deposit gauge. So, that is a long drawn process, because it is a slow process. Static sampling was one of the first air monitoring sampling procedure and it was not a very foolproof method. The grab sampling – not commonly used to monitor ambient air quality; uses bladders of syringes. So, they were just collecting some sample in a bladder of syringes and then trying to analyze.

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Site selection – general requirement for site selection – how do we choose, where to collect the air sample? I told you that in most of the busy places, where the vehicular population is very high or in factory areas, where these possibility of the carbon monoxide, and the NOX, and the SOX, to be very high. These are certain generalized areas of selection of site. Purpose of monitoring; number and type of instruments that may be required; duration of measurements; best available general guide comes from AS2922. That means, there are some very standard air quality measurement protocols, and one of them is AS2922, which needs to be followed in order to have a guide line for general site selection. And, why it should be monitored, how many times it should be monitored, what is the kind of instrument that should be used? are all given there; should be easy and accessible. It should not be that if we want to take a sample from a chimney top, how to reach that chimney? The place or the site should be accessible to the analyzer or to the analyst.

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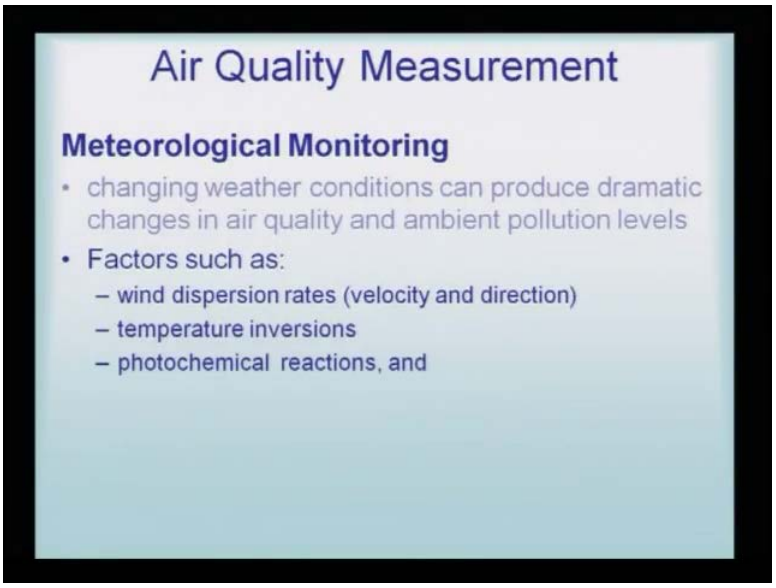

Meteorological monitoring – changing weather conditions can produce dramatic changes in the air quality and ambient pollution levels. You must have seen that in winters, there is a lot of smoke. Now, this smog has actually come, because these gases could not raise up and the temperature at the earth surface was fairly low, and so, it was keeping it condense towards the surface of the earth. But, the same air or the same smog in summer weathers, can raise up, because the earth surface is very heated. So, it goes up. So, these are certain meteorological conditions of the weather conditions, which can produce various types of smog quality and smog positioning, and which subsequently reflex on the air quality.

Factors such as wind dispersion rates; that is, which way the wind is blowing – whether it is the westerly winds, or the easterly winds, will also decide the air quality. Then, its velocity – whether it is fast, it is medium or it is low, will also decide the air quality. Temperature inversions – I just gave you an example how in a cold weather, the smog is quite near the earth surface; whereas, in summer, weathers the smog raises up. So, that is affected by the temperature inversion. Photochemical reactions – there are a lot of these free radicals that are generated, because of these particulate matters and the sun light, and so on and so forth. Rains also can make a lot difference on this monitoring.

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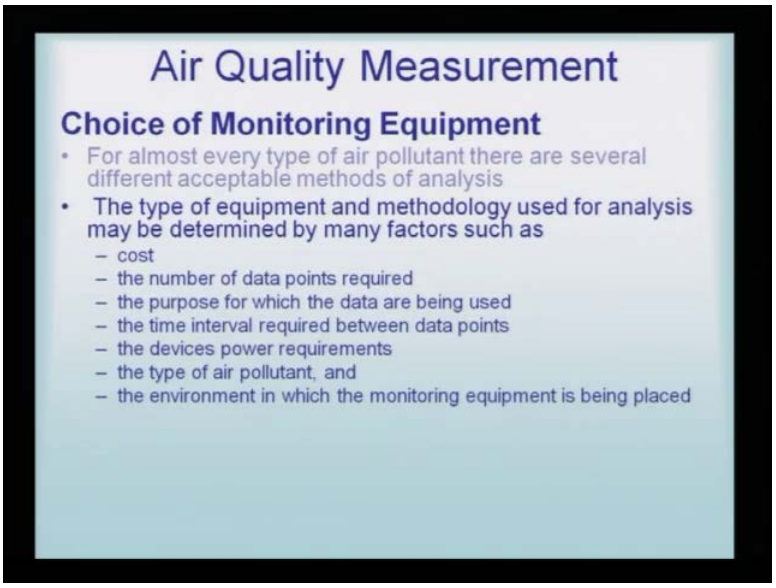

Choice of monitoring equipment – for almost every type of air pollutant, there are several different acceptable methods of analysis. The type of equipment and methodology used for analysis may be determined by many factors, such as cost, the number of data points required, the purpose for which the data are being used, the time interval required between data points, the devices power requirement, the type of air pollutant, and the environment in which the monitoring equipment is being placed. So, when we are using an air quality measurement device, what are the different types of monitoring devices or equipment? And, when we are making a choice between a, b, c, d? What are the factors that must be kept in mind?

Firstly, the machine should be cheap. That means there is a factor of cost. The number of data points – now, if the analytical machine gives too large a number or two few a number, the data cannot be interpreted in the proper manner. The purpose for which the data are being used and what is that we have to analyze on the particular machine, should be very clear. The time interval required between the data points. I told you that in real time, it gives hourly data; whereas, in the intermittent time, it takes as long as 24 hours. So, that choice we have to make – whether we are trying to look at a very polluted site or a reasonably polluted site. And, that would be the limiting factor or the deciding factor – which device to use?

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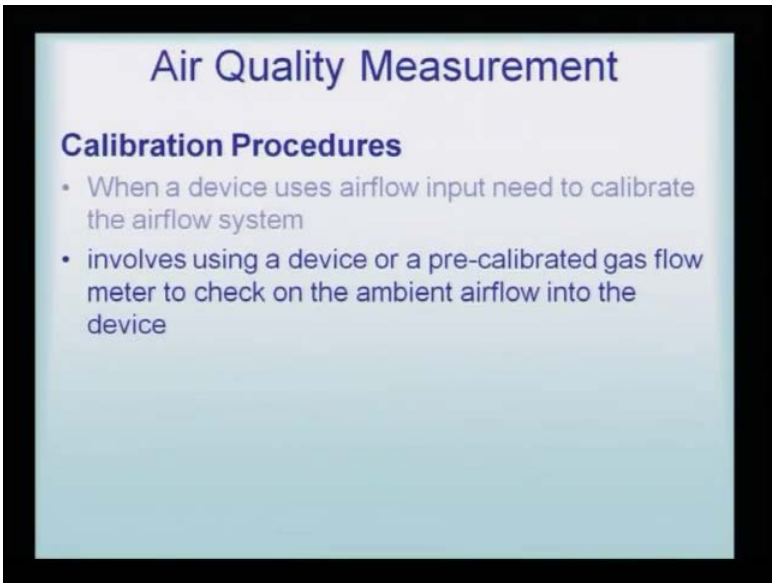

Calibration procedures – any methodology, which is based on comparison, is actually based on calibration. When a device uses airflow input, need to calibrate the air flow system. Obviously, if we do not have something to compare, how would we say that the air quality is good or bad. So, for being able to discriminate the good and the bad, there has to be a comparative or a calibration procedure. Involves using a device or a pre-calibrated gas flow meter to check on the ambient airflow into the device; therefore, there is a necessity to even check whether the flow of the gas is properly coming into the collecting device. And, that is called a pre-calibration gas flow meter. That should be connected to the device – collecting device.

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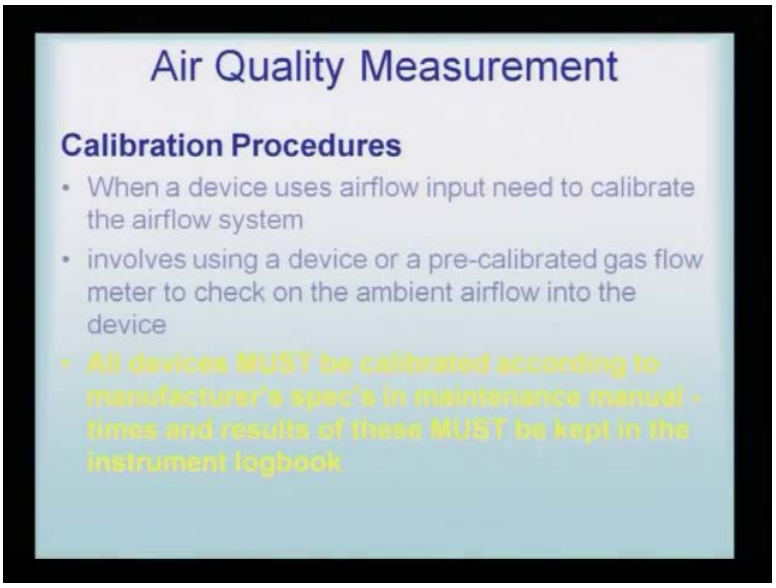

All devices must be calibrated according to manufactures specification in maintenance manual. Times and results of these must be kept in the instrument logbook. It is important to have an instrument logbook to be able to see when was the machine validated, whether it is working in the proper condition or not, because any machine can go wrong anywhere. And, it is important that these are kept up to date with all the regular checking of the machine, so that the operation of the machine can be taken that it is working in a normal and precise manner.

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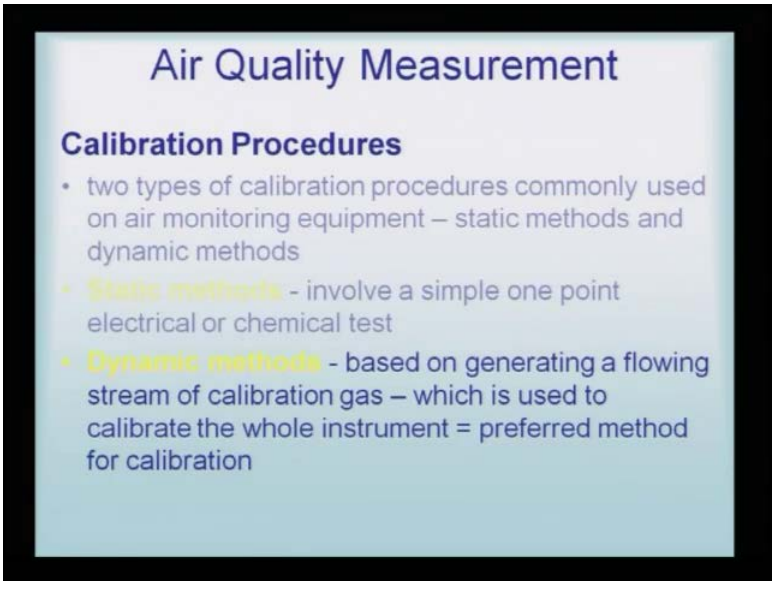

Calibration processes again have two more important things to be told. Two types of calibration procedures mainly used on air monitoring equipment are the static methods and the dynamic methods. The static method involves a simple one point electrical or chemical test. As the name suggests, you know into the air sample, some reagent may be added and just on the spot, it is kind of tested.

The next method is the dynamic method – based on generating a flowing stream of calibration gas, which is used to calibrate the whole instrument. And, that is equal to preferred method for calibration. So, a dynamic method is definitely having an edge over the static method. A static method – we can always say, it is more qualitative. But, dynamic method is quantitative in its data.

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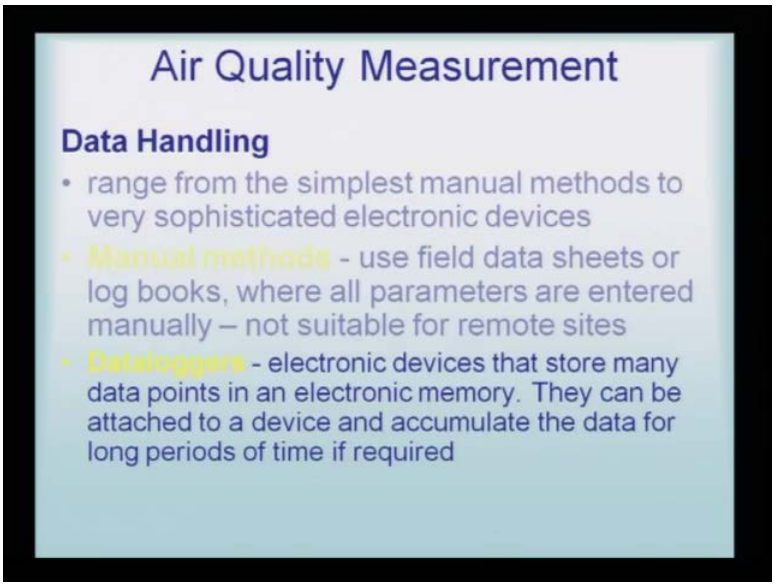

Data handling – once we have the data in hand, how do we make an interpretation, how do we make sense out of the data? Range from the simplest manual methods to very sophisticated electronic devices. So, the data handling can be on a simple manual method that this is the value and at this time of the day, the value was x number; after 6 hours, the value was y; and, after 10 hours, the value was z. That is a very simple method of the manual method. But, there are very sophisticated devices, which continuously provide the data on-line.

Manual methods – use field data sheets or log books, where all parameters are entered manually – not suitable for remote sites. Now, when there are very remote site, this is not

a very good method for such a situation. However, data loggers, that is, electronic devices that store many data points in an electronic memory, is what the latest trend of the data handling devices is. They can be attached to a device and accumulate the data for long periods of time if required. So, if we want to compare, say what was the air quality on June 30th 1990, and then 2010, and then 2020? Now, these kinds of data can be collected, because in the computers, this can be stored as a memory.

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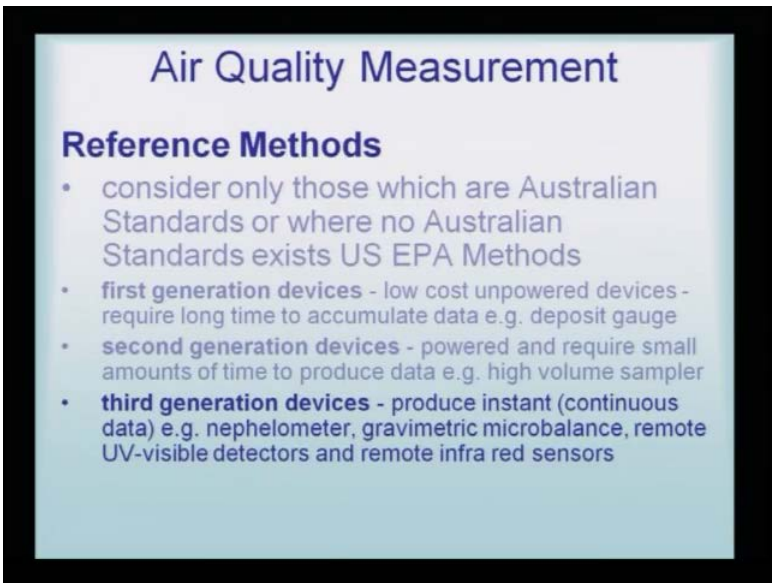

Reference method – consider only those which are Australian Standards or where no Australian Standards exists US EPA methods. It is not necessary that one should only follow the Australian methods; one can follow any countries – like for our country, we can follow the BIS method, which is again taken from the US EPA method. So, you can understand that US EPA method is the ultimate standard and all other countries have taken norms, and accordingly, adjusted them according to their own air quality conditions.

First generation devices – what were the first types of air quality measuring devices? Low cost unpowered devices require long time to accumulate data, and therefore, it is now, almost obsolete. Second generation devices – they are now powered. That means, they work on electricity and require small amount of time to produce data, and therefore, high volume of samples can be analyzed on them. Third generation devices are still more advanced. They produce constant continuous data. Nephelometer, gravimetric

microbalance, remote UV-visible detectors and remote infrared sensors are the third generation devices, which are the latest devices of today's air sampling measurement devices. Now, you see that some of them – the names are nephelometer, gravimetric microbalance, remote UV-visible detector and remote infrared sensors are some of the latest devices.

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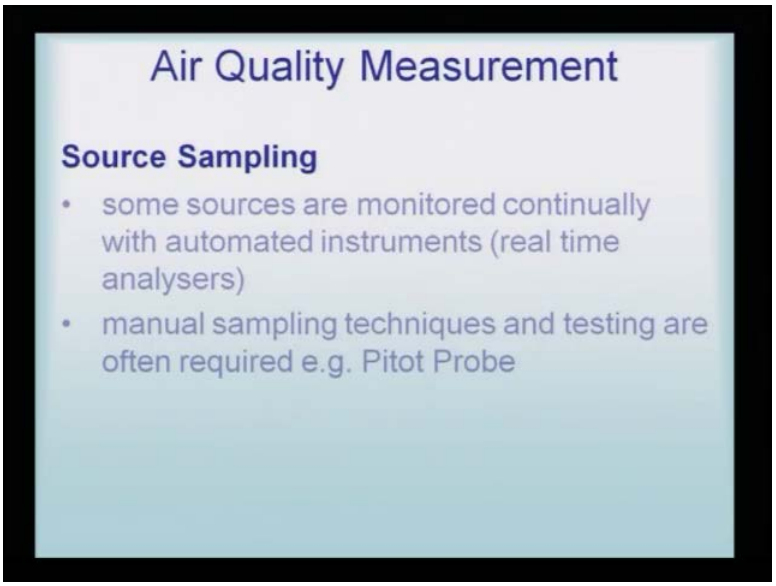

Source sampling – some sources are monitored continuously with automated instrument, that is, the real time analyzers; manual sampling technique and testing are often required; for that, Pitot Probe is used.

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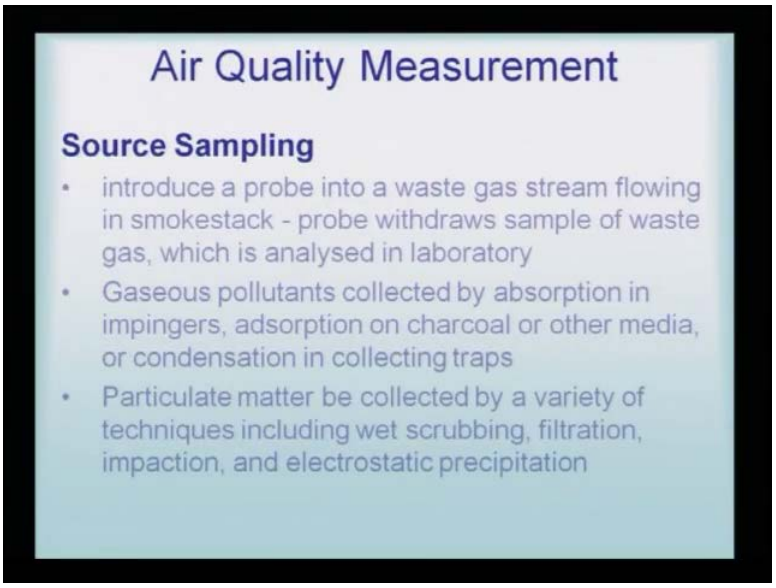

Source sampling – how does it take place? Introduce a probe into a waste gas stream flowing in smokestack – probe withdraws sample of waste gas, which is analyzed in laboratory. So, how does this take place? Introduce a probe into a waste gas stream flowing in smokestack, and then, try to probe. The probe then, withdraws the sample from the waste gas.

Gaseous pollutants collected by absorption in impingers, adsorption on charcoal or other media, or condensation in collecting traps. So, other types of gaseous pollutants can be simply absorbed on impingers, or the adsorption on charcoal can also take place, or they can be made to condense on collecting traps. Particulate matter be collected by a variety of techniques including wet scrubber, filtration, impaction, and electrostatic precipitation. So, for particularly, particulate matter… See the other gaseous pollutants. that is, the carbon monoxide, carbon dioxide, NOX and SOX – it is mainly by absorption or adsorption or condensation, but for particularly, particulate matter – it is wet scrubbing, filtration, impaction or electrostatic precipitation.

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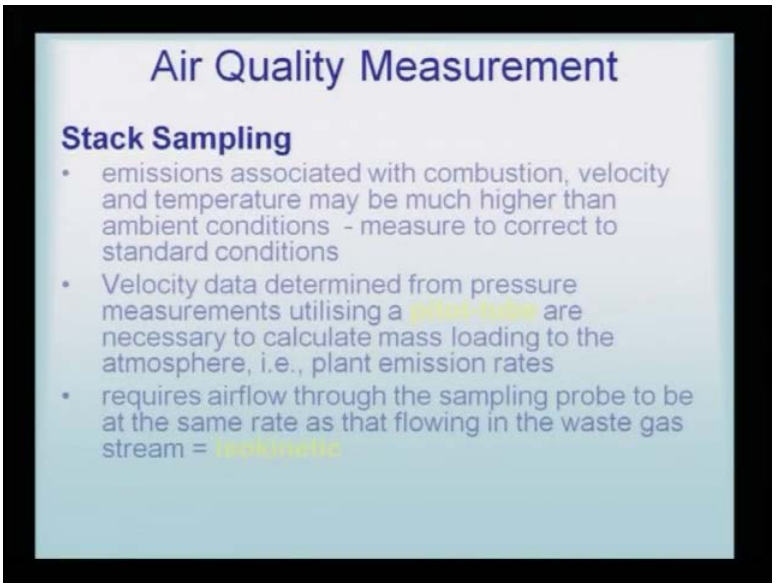

Stack sampling – emissions associated with combustion, velocity and temperature may be much higher than ambient conditions – measure to correct to the standard conditions. Now, what happens in factories? One needs to put a check on what are the emissions rates; sometimes, the combustion – if it has not taken place properly in the furnace, it will emit all kinds of bad gases and the notorious pollutants, and that needs to be checked.

Velocity data determined from pressure measurements utilizing a pilot tube are necessary to calculate mass loading to the atmosphere. That means, plant emission rate. If a steel plant or if in from the blast furnace, there are emissions, then, there should be a flow-rate, and the velocity data should be determined very perfectly. Required airflow through the sampling probe to be at the same rate as that flowing in the waste gas stream; so, it should be isokinetic. The airflow in the sampling probe should have the same flow or same rate of the waste gas stream also. If the speeds are different, then it would be that something should go unanalyzed.

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Real time analysis – several methods provide real time analysis, the most popular is the remote UV detection for sulfur dioxide. As I told you time and again, I have been telling you, that every pollutant, every chemical, needs to be treated as a special identity, and the method of determination of these are very typical and specific.

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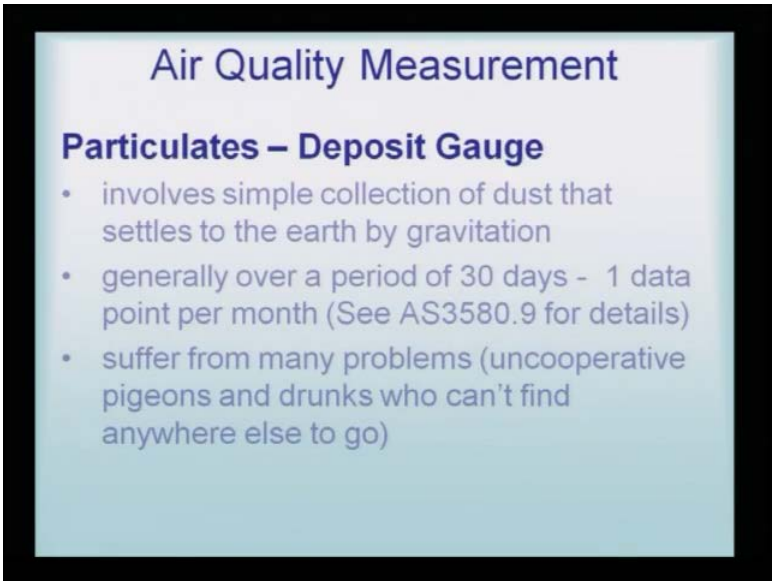

Particulates are actually measured on deposit gauge – involves simple collection of dust that settles on earth by gravitation. Generally, over a period of 30 days – a data point per month, that is, if you refer to the AS3580.9, more details can be obtained. Suffers from

many problems – it is uncooperative pigeons and drunks, who cannot find anywhere else to go. So, there are many problems that can arise in this kind of particulate deposit gauge.

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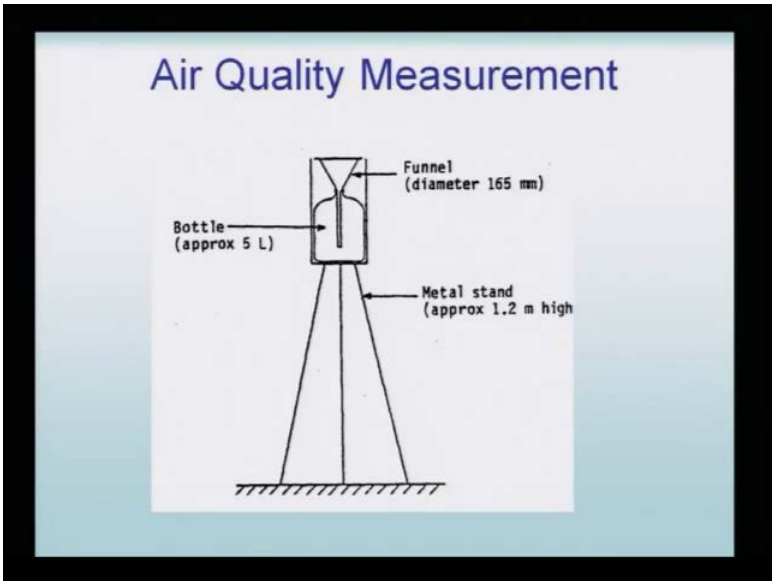

Now, this is how it looks like – there is a bottle, there is a fennel, and there is a metal stand. So, in the bottle, it is trapped and there is a gauge at the point of entry. Particulates high volume sampler – this is called a particulate high volume sampler.

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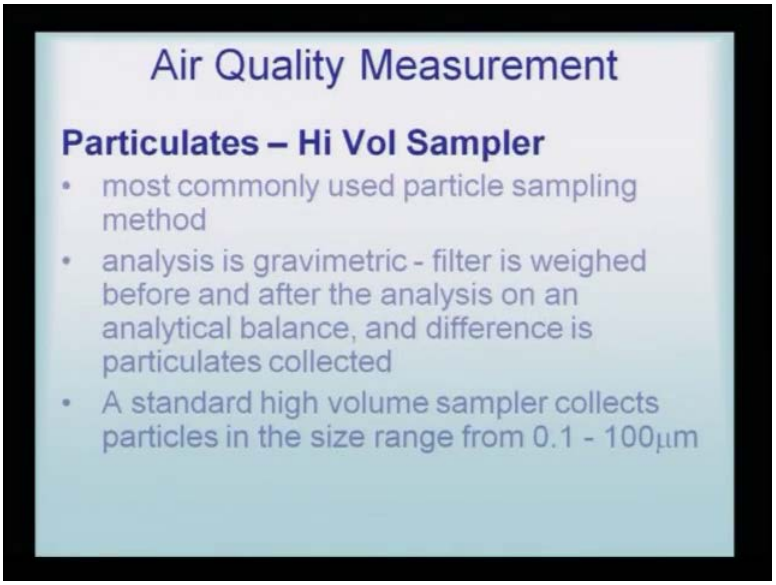

Most commonly used for particle sampling method, because these are now, most prevalent for the collection of the particulate matter; the PM 2.5 and the PM 10 are collected by high volume samplers. Analysis is gravimetric – it is a filter; filter is weighed before and after the analysis on an analytical balance, and the difference gives the particulates that are settled on the filter papers. It is a very simple method, but the microbalance should be up to four places of decimal. Then only, even the trace quantities or microgram quantities can be analyzed. A standard high volume sampler collects particles in the size range of 0.1 to 100 micrometer.

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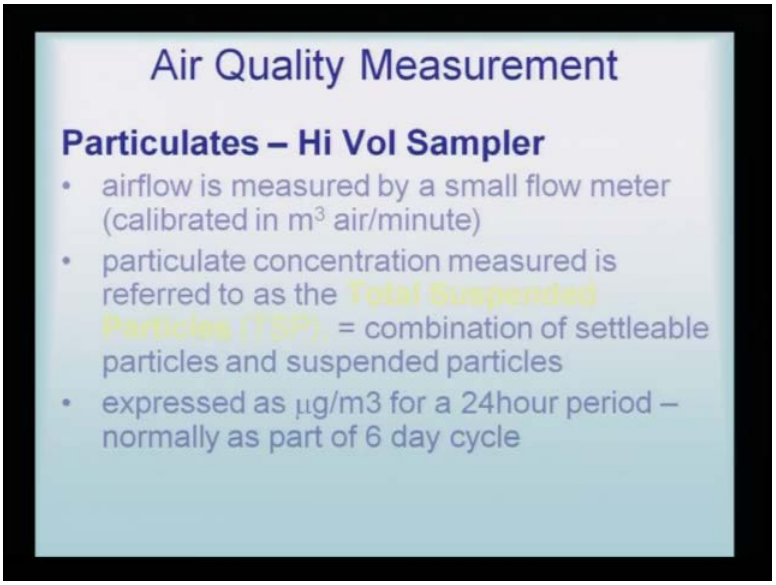

Particulates high volume samplers – airflow is measured by small flow meter, calibrated in meter cube air per minute. Particulate concentration measured is referred to as total suspended particle, that is, the TSP – combination of settleable particles and suspended particles. So, it is total combination of what settles and what is suspended. Expressed in microgram per cubic meter for a 24 hour period – normally, as part of 6 day cycle, every day after 24 hours, the particulate matter is analyzed. So, that is what it means. And, it only goes up to from Monday to Saturday; Sunday is a holiday for such an analysis.

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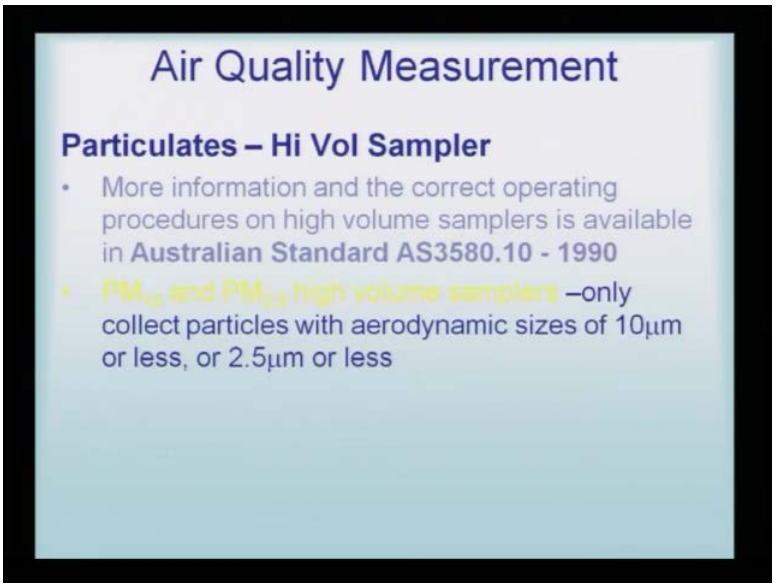

Particulate high volume sampler – more information and correct operating conditions can also been learnt from another standard, Australian standard, AS3580.10, which was released in 1990. Here, the PM 10 and the PM 2.5 high volume samplers only collect particles with aerodynamic sizes of 10 micron or less or 2.5 microns or less; recognized by PM 10 head, which looks like a cross between a flying saucer and an overgrown wok.

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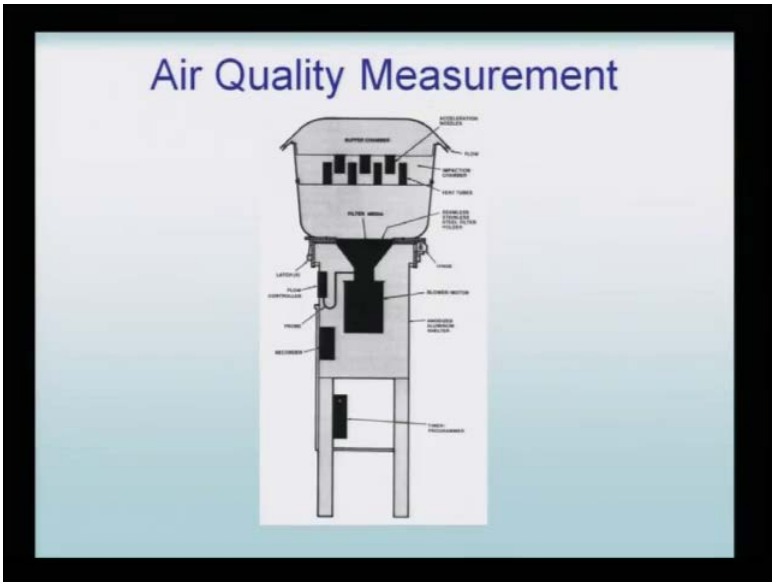

So, this is what it looks like – it is a little complicated device, but the nevertheless, it has all the ingredients to be able to collect, and at the same time, there is a fitted balance,

which then measures the increase in weight, because of the deposition of these particulate matter.

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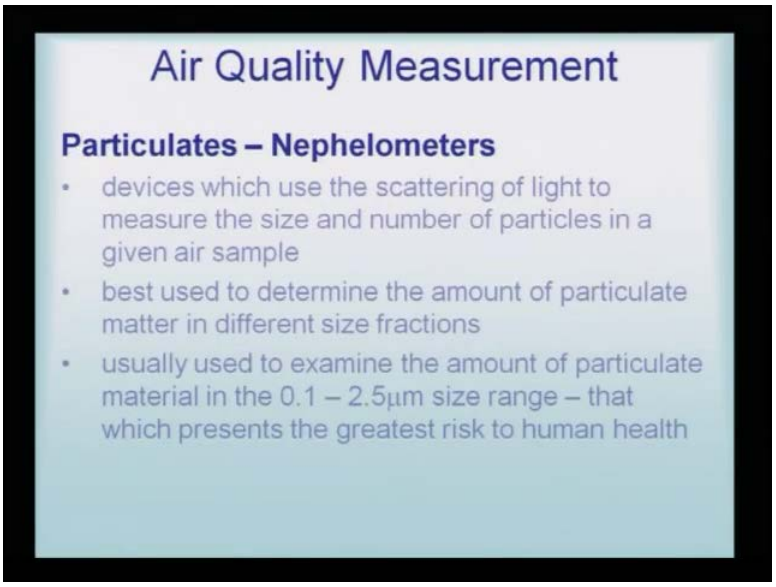

Particulates can also be measured by nephelometers and devices, which use the scattering of light to measure the size and number of particles in a given air sample; best used to determine the amount of particulate matter in different size fractions. So, there, I have the combination and the capability that this is based on using scattering of light to be able to measure the different sizes and the number of particles in the air sample. Also, they can determine the amount of particulate matter of different sizes also by fractionation. And, it is usually used to examine the amount of particulate material in the 0.1 to 2.5 micrometer size range as well – that which represents the greatest risk to human health. So, smaller and even smaller particulate matter can also be analyzed through these nephelometers.

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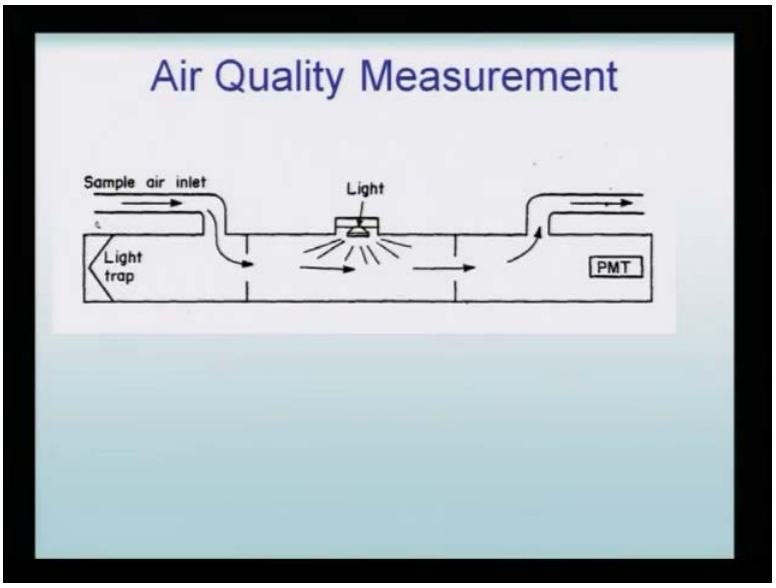

And, this is how it looks like – there is a source of light; there is a sample, an air inlet and it has a flowing path, and during the path, it is trapped and analyzed by the detector.

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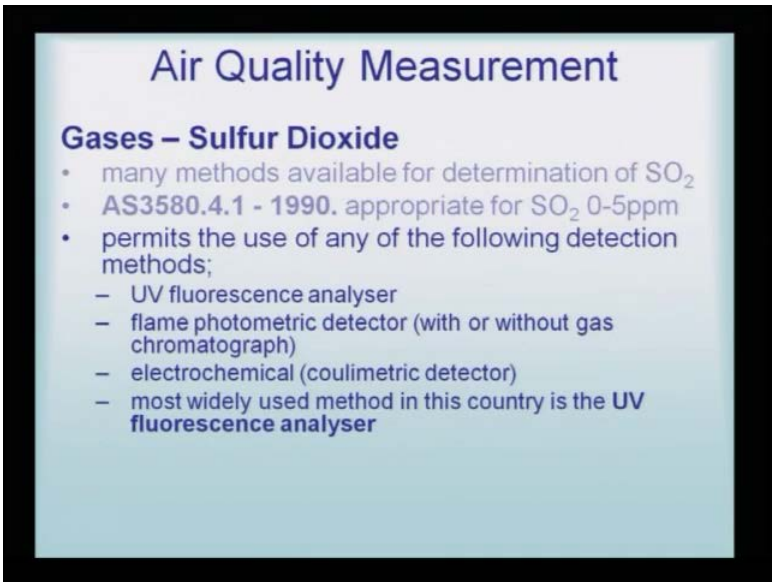

Then, comes the gaseous sampling and analysis of various other pollutants – the first one being sulfur dioxide – many methods are available for determination of sulfur dioxide; one of the method of course, is the AS3580.4.1, which was released 1990, which is most appropriate for sulfur dioxide to be analyzed between the range of 0-5 parts per million or ppm; permits the use of any of the flowing detection methods. That means, one can

detect it by UV fluorescence analyzer, flame photometric detector with or without gas chromatograph, electrochemical or calorimetric detector, most widely used method in this country is the UV fluorescence analyzer. So, because of the ease of usability, the UV fluorescence analyzer is the best and ideally suited for sulfur dioxide contaminants to be analyzed.

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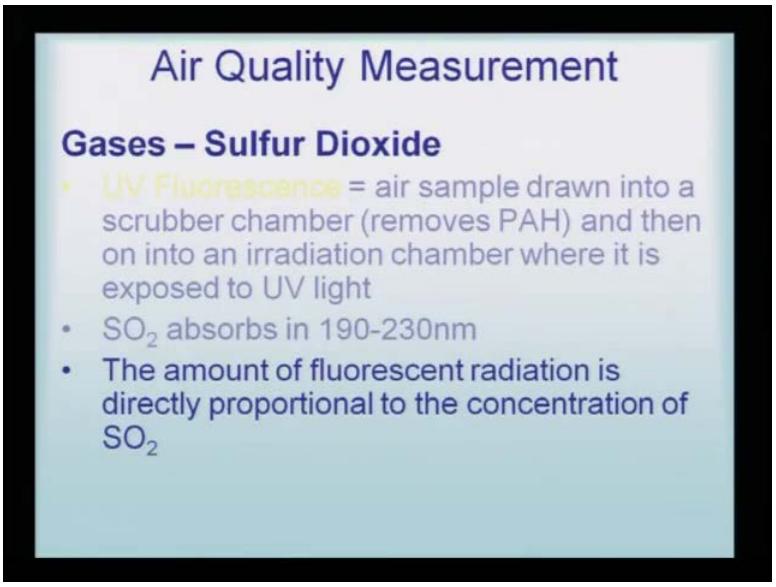

Now, there are these various methods. A little bit of detailing I would give for the UV fluorescence – air sample drawn into a scrubber chamber after the removal of poly aerometric hydrocarbon, and then, on into an irradiation chamber, where it is exposed to UV light. So, there, the sulfur dioxide combines with this and it is able to get excited and it is analyzed. Sulfur dioxide particularly has an UV absorption between 190 to 230 nanometers, and the machine of the UV fluorescence actually ranges from 190. So, it is well-suited for the analysis. The amount of fluorescent radiation is directly proportional to the concentration of the sulfur dioxide, because only that much will be absorbed as what sulfur dioxide moieties are present.

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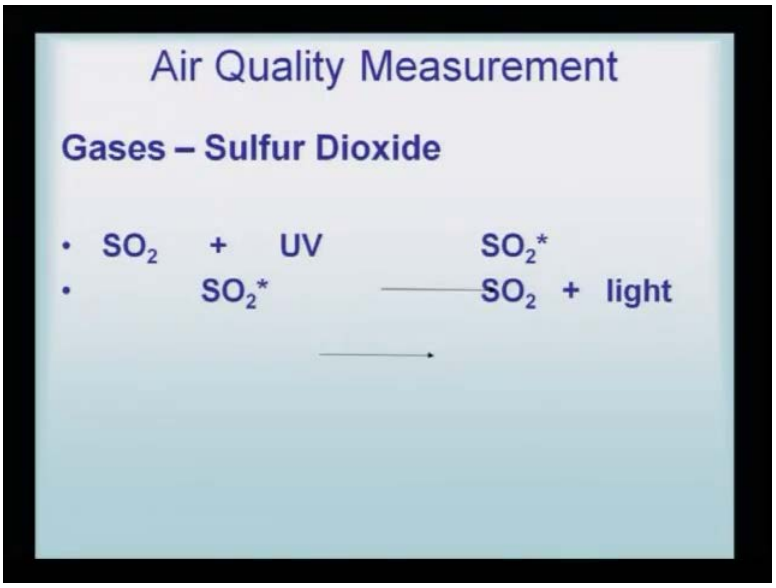

Earlier also I said, in UV radiation and absorption, the concentration is always proportional to the absorption unless and until there is some other kind of chemical reactivity that is taking place. So, this is how sulfur dioxide when it reacts with UV light, it produces SO 2 star, and this SO 2 star then emits light and becomes SO 2. And, this is the procedure that takes place.

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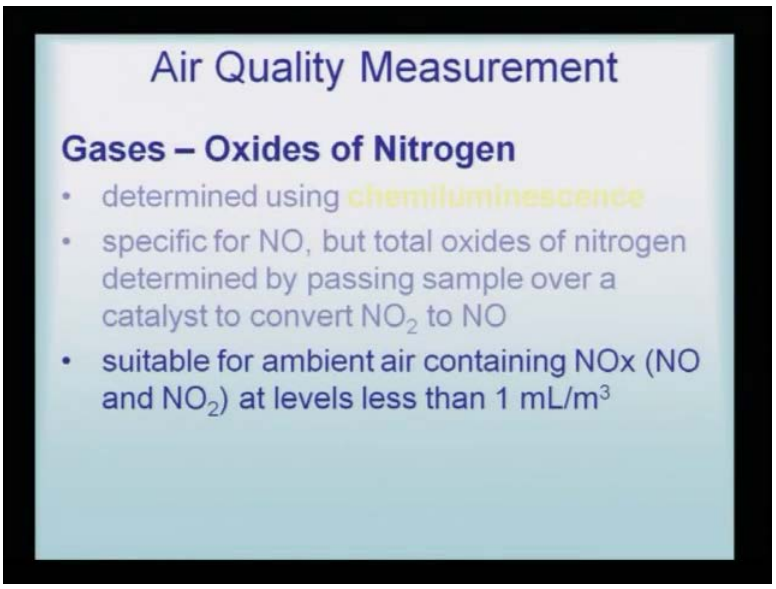

Then, gases of nitrogen, because I have been referring to this as NOX; it should be kept clearly in mind that this is more than one type of nitrogen oxide that needs to be referred.

And, it is determined using chemiluminescence. Specific for the NOs, that is, nitrogen oxide, but total oxides of nitrogen determined by passing sample over a catalyst to convert NO 2 to NO. So, it is only analyzing one particular species and that is NO. And, all the nitrogen dioxide is first converted into NO, and then analyzed. Suitable for ambient air containing NOX, that is, wok NO and NO2 at levels less than 1 milliliter per cubic meter.

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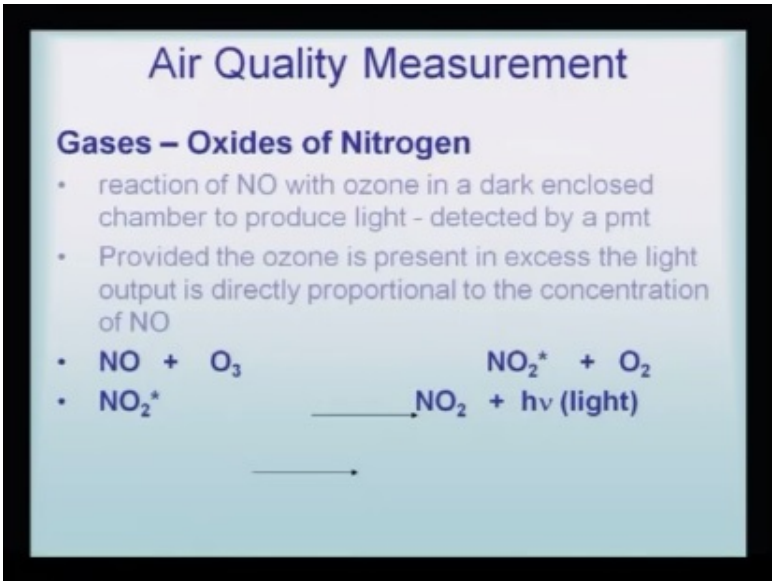

Gaseous samples of nitrogen – reaction of NO with ozone in a dark closed chamber to produce light and that is detected by a pmt. Provided the ozone is present in excess, the light output is directly proportional to the concentration of the NO. So, this is how the reaction takes place; NO and ozone react and the NO 2 star is generated. And, it then, forms NO and then, it emits light. So, this is how the NOX are analyzed.

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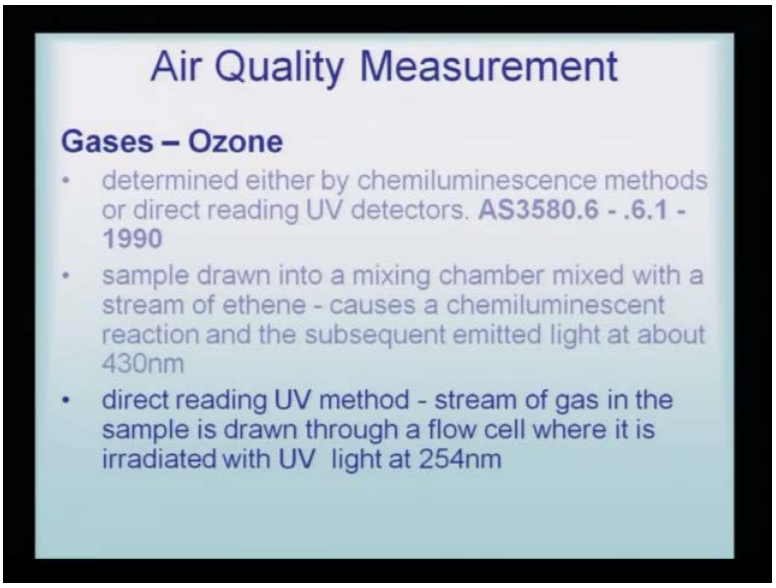

Ozone – determined either by chemiluminescence methods or direct reading by UV detectors. Sample drawn into a mixing chamber mixed with a stream of ethane – causes a chemiluminescence reaction and the subsequent emitted light at about 430 nanometer. Direct reading of UV method – stream of gas in the sample is drawn through a flow cell, where it is irradiated with UV light at 254 nanometers. So, it is a very simple UV method of analysis and it is a foolproof method of analyzing ozone.