Trace and ultra trace analysis of metals Using atomic absorption spectrometry

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Lecture – 20

Instrumentation in AAS VI: Optics

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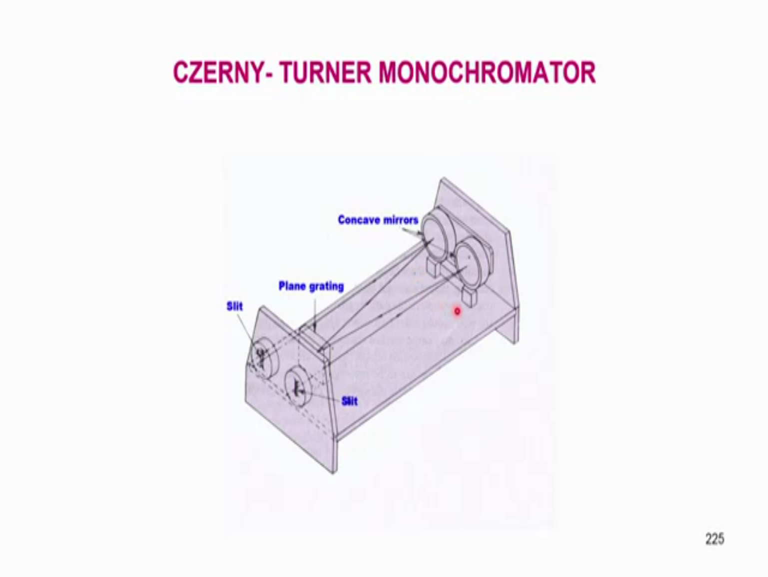

CZERNY- TURNER MONOCHROMATOR

Czerny turner Monochromator I have shown you this figure there is there are two slits one is for incoming and then this is a plate grating, there is a concave mirror, plain grating is fixed at the focal length of this concave mirror, and then the radiation after selection of the resonance line reaches another Monochromator and comes out through another slit.

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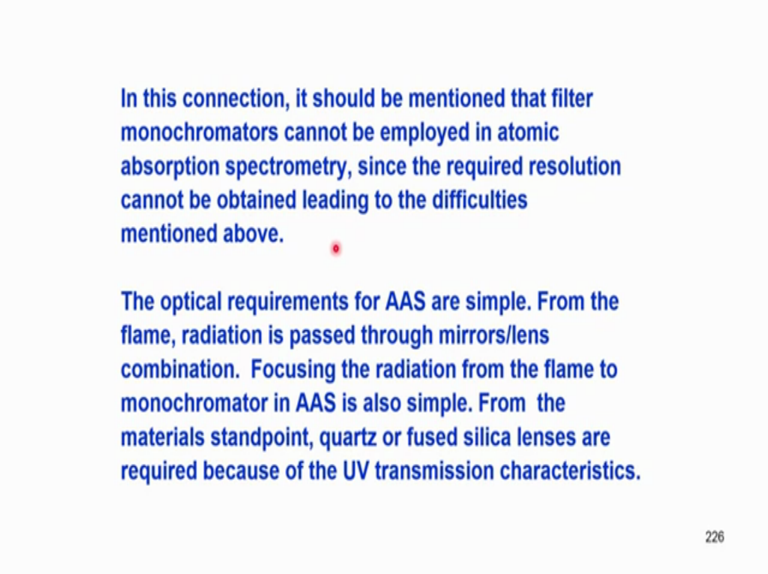

In this connection, it should be mentioned that filter monochromators cannot be employed in atomic absorption spectrometry, since the required resolution cannot be obtained leading to the difficulties mentioned above.

The optical requirements for AAS are simple. From the flame, radiation is passed through mirrors/lens combination. Focusing the radiation from the flame to monochromator in AAS is also simple. From the materials standpoint, quartz or fused silica lenses are required because of the UV transmission characteristics.

So, in this connection we have to mention here that filter monochromators cannot be employed in atomic absorption spectrometry, because the required resolution cannot be obtained if we if you remember our earlier discussion filter photometers and colori metric filters etcetera I have a got a band pass width of about 20 to 30 nanometers. So obviously, such things cannot be used the only thing we can use in atomic absorption spectrometry are the prisms and gratings.

So, the optical components for atomic absorptions are basically very simple, from the flame radiation is passed through the mirrors or lenses combination mirrors or lens and lens combination, focusing the radiation from the flame to monochromator is also simple from the material standpoint quartz or fused silica lenses are required because many of the elements in the periodic table have resonance line in UV ultraviolet range and very few are having in the visible range.

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SPECTRAL BAND SELECTION

The term monochromator is in reality, a misnomer. Monochromatic radiation is the radiation with only one wavelength. All spectral band selection devices pass a band of wavelengths that may be larger or smaller according to the quality of the device.

The basic requirement for a wavelength selector is the ability to separate the desired resonance line from other lines emitted by the sharp-line source. If any background radiation is emitted by the source, a curved calibration graph will be obtained, but curvature can be minimized by using a narrow-pass monochromator to reduce the propagation of unabsorbed light.

So, we need to select these spectral band. So, the term monochromator is in reality a misnomer, I think I have we have discussed this above also earlier what it means is we are getting a radiation with only one length which is not correct, we always get a combination a small group of frequencies whenever we employ any monochromator. So, all spectral band selection devices pass a band of wavelength that may be larger or smaller according to the quality of the device. So, the basic requirement for a wavelength selector is the ability to separate the resonance line, from other lines emitted by the sharp line source; that is hollow cathode lamp radiation must be separated that is the job of the monochromator.

So, if any background radiation is emitted by the source a curved calibration curve graph will be obtained. What we need is a linear calibration graph, but curvature can be minimized using a narrow pass monochromator to reduce the propagation of the unabsorbed light. So, how do we get a narrow pass chromo monochromator is by using a diffraction unit.

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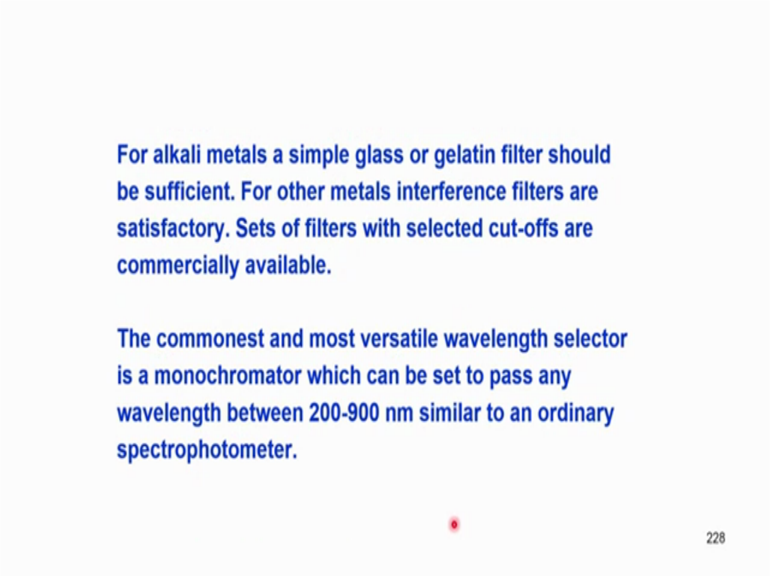

For alkali metals a simple glass or gelatin filter should be sufficient. For other metals interference filters are satisfactory. Sets of filters with selected cut-offs are commercially available.

The commonest and most versatile wavelength selector is a monochromator which can be set to pass any wavelength between 200-900 nm similar to an ordinary spectrophotometer.

So, for alkali metals what happens? If I want to determine sodium potassium straw cesium etcetera, I can use a simple glass or gelatin filter because most of them have a emission wavelength in the visible range even atomic absorption resonance lines are in the visible range. But for other elements like chromium, potassium, vanadium, tungsten all those iron cobalt nickel and many of these things have got UV lines only.

So, for alkali metals it is visible range. So, for other metals interference filters are satisfactory, but sets of filters which selected cut offs are commercially available. That means, if I have to remove flame resonance line then I can use a filter, but if I have to choose a resonance line then I need a grating. If I have to remove anything from the flame I need I can use filter, but if I have to choose the resonance line I need a grating. So, that is the bottom line. So, the commonest and most versatile wavelength selector is a monochromator, which can be set to pass any wavelength between 200 and 900 nanometers, this is what is being used in almost all atomic absorption spectrometers.

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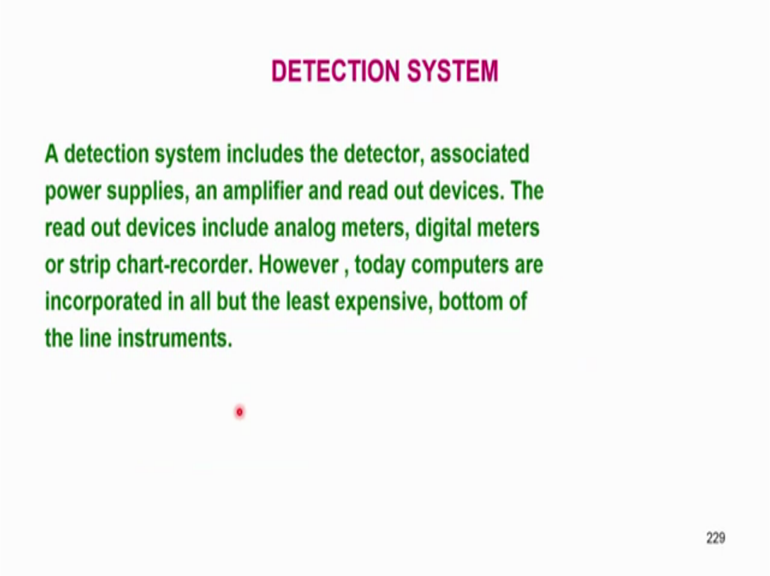

DETECTION SYSTEM

A detection system includes the detector, associated power supplies, an amplifier and read out devices. The read out devices include analog meters, digital meters or strip chart-recorder. However , today computers are incorporated in all but the least expensive, bottom of the line instruments.

So, now we move on to other aspect of atomic absorption system and that is detector. So, what is a detector? The job of the detector is to collect the radiation and we have discussed the detectors earlier during the introduction to atomic absorption after the atomic structure. So, it detection system includes the detectors associated power supplies and amplifier and readout devices all of them can be combined into one, and then nowadays computers are used for controlling all these operations, that is power supplies and then amplifier and read out device whatever is the data required.

So, the read out devices what actually they include are analog meters earlier they used to be analog meters nowadays lot of digital meters are available, and if you want to record you can have it on a strip chart recorder, but again strip chart recorders have become out of fashion since last 20 30 years everything is recorded in the computer, and from the computer screen you can take a printout or whatever you feel comfortable. However, today computers are incorporated in all, but the least expensive bottom line bottom of the line instruments.

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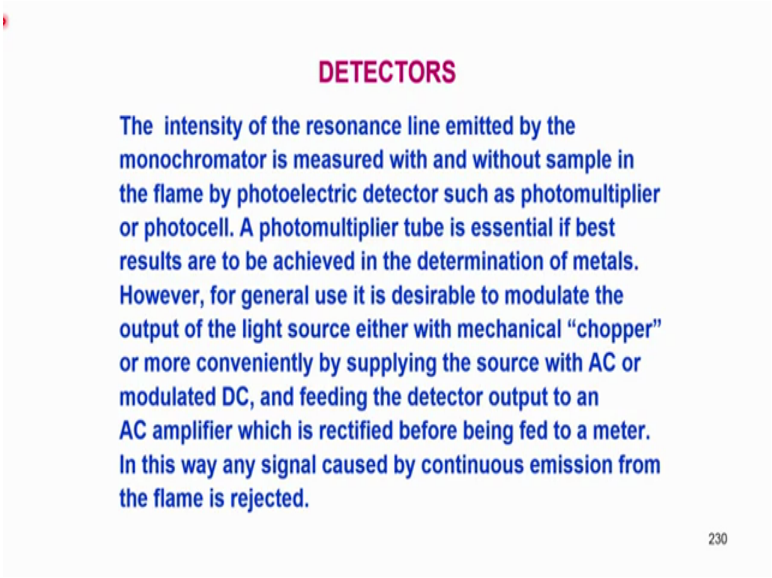

DETECTORS

The intensity of the resonance line emitted by the monochromator is measured with and without sample in the flame by photoelectric detector such as photomultiplier or photocell. A photomultiplier tube is essential if best results are to be achieved in the determination of metals. However, for general use it is desirable to modulate the output of the light source either with mechanical "chopper" or more conveniently by supplying the source with AC or modulated DC, and feeding the detector output to an AC amplifier which is rectified before being fed to a meter. In this way any signal caused by continuous emission from the flame is rejected.

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Most of the atomic absorption nowadays include the computers, without computers and micro devices controller it is sort of a little unimaginable nowadays something like you know first version mobiles or first version computers they were costly and not efficient, but nowadays you see that most of the atomic absorptions in spectrometers have a computer controlled operation, in most of the requirements except for sample preparation and sample handling dilation etcetera. So, human interference is very less in atomic absorption except during the preparation of the samples.

So, coming back to the detectors the intensity of the resonance line emitted by the monochromator is measured with and without the sample in the flame by the photoelectric detector. So, we have already discussed the photoelectric detector earlier we had discussed about photomultiplier cells, photo cells and in my other course I have discussed other course is on spectrophotometry molecular spectrophotometry there I have discussed about photocell barrier layer cell, and many LED cells etcetera, but nowadays what we are looking at is mostly photomultiplier cells or a photocell. So, a photomultiplier tube is essential if best results are to be achieved in the determination of metals nowadays people use diode array metals diode array detectors also. So, what happens is if you wish to continue to use several anal analyze several metals simultaneously, a diode array may tube is diode array detector is much better and faster and simpler also.

So, the choice of detector is only between multiple photomultiplier tube or diode array detector in the current instruments. For general use its desirable to modulate the output of the light source by putting a chopping mirror with mechanical chopper or more conveniently by supplying the source with AC, this also we had discussed earlier or we can use even a modulated d c and feeding the detector output to an AC amplifier which is rectified before being fed to a meter. In this way any signal caused by continuous emission from the flame would be rejected that is the whole idea of using a detector and chopper.

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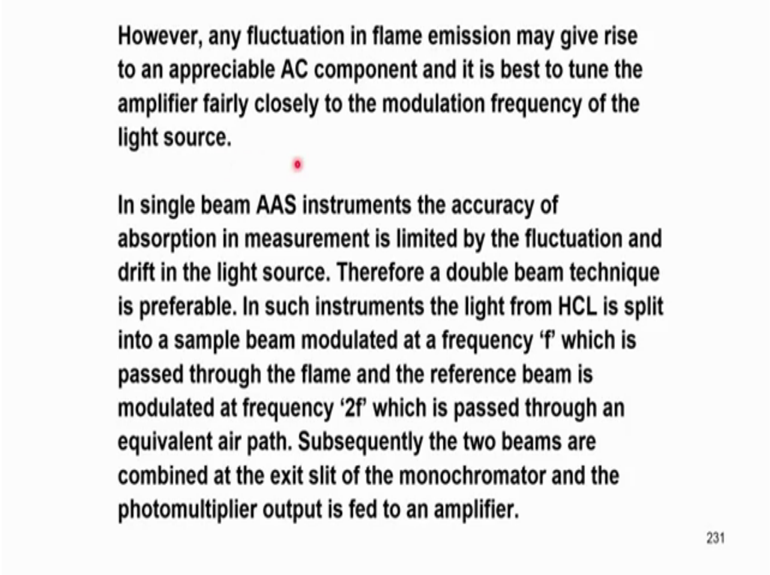

However, any fluctuation in flame emission may give rise to an appreciable AC component and it is best to tune the amplifier fairly closely to the modulation frequency of the light source.

In single beam AAS instruments the accuracy of absorption in measurement is limited by the fluctuation and drift in the light source. Therefore a double beam technique is preferable. In such instruments the light from HCL is split into a sample beam modulated at a frequency ‘f’ which is passed through the flame and the reference beam is modulated at frequency ‘2f’ which is passed through an equivalent air path. Subsequently the two beams are combined at the exit slit of the monochromator and the photomultiplier output is fed to an amplifier.

So, any fluctuation in the flame emission may give rise to appreciable AC component. So, we are discussing about the signal quality now, in the signal quality what we want is we do not want any fluctuation in the quality of the radiation coming from the hollow cathode lamp through the flame. So, if the flame itself is fluctuating then it may give rise to appreciable AC component. So, it is best to tune the amplifier fairly closely to the modulation frequency. So, the moment it changes here it automatically re reflects in the light source.

So, we all we have to do is now we have to lock it with in the amplifier, these lock-ing mechanisms and other things are all electronics related subjects and for our purpose to for that is chemical engineers and chemists it will be suffice to say that the fluctuation in the flame is locked amplifier locked to the modulation frequency, to reduce the unwanted signal.

So, in single beam instruments the accuracy of absorption is limited by the fluctuation obviously, and there is a drift in the light source in single beam. So, because there is a time gap between the measurement, because in single beam first we put a sample and then take out the first we put a water sample without any analyte and then see what is the blank reading reference reading and then we take it out put (Refer Time: 12:34) sample aspirate it wait for standard a wait for equilibrium and then take the measurement in between the flame might have changed, its characteristics or the hollow cathode lamp might have undergone some changes about the intensity of the lamp etcetera. So, all these things are not reflected in a single beam instrument measurement therefore, 99 percent of the atomic absorption spectrometers are nowadays double beam instruments ok.

So, sometimes what happens is even single beam instruments, the information is stored in the computer and once it is stored in the computer the you can choose the other radiations, but still other analysis you can perform and compare it to the standard values stored in the computer memory. But still to account for momentary changes it is always preferable to use a double beam instrument. So, whenever you are buying an atomic absorption spectrophotometer for your work in your laboratory, in your university, in your company etcetera always go for a double beam spectrophotometer atomic absorption. So, in such instruments light from HCL itself you split into two beams one passes through the flame one passes without the flame both of them are combined, and the ratio is taken care off. So, the sample beam is modulated at a frequency f which is passed through the flame and the reference beam is modulated at a frequency of 2f twice the wave length twice the frequency which is passed through an equivalent air path.

So, subsequently the two beams are combined to give the at the exit slit of the monochromator and photomultiplier output is fed to an amplifier.

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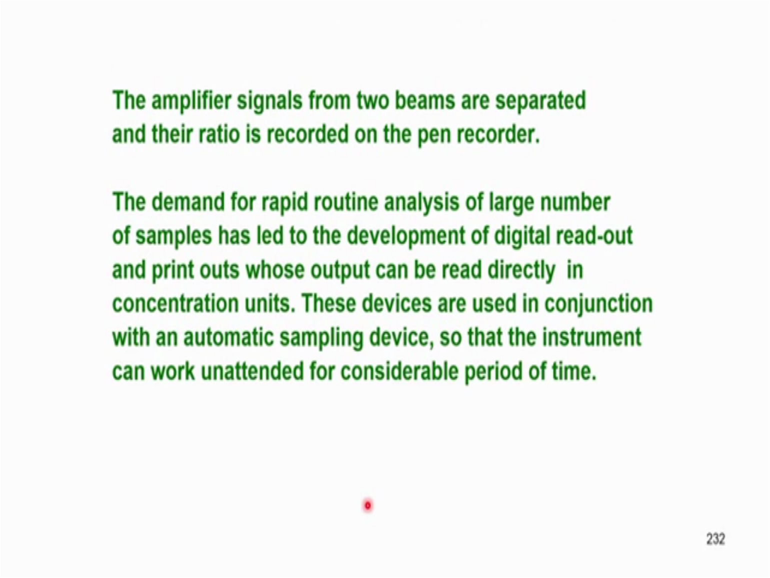

The amplifier signals from two beams are separated and their ratio is recorded on the pen recorder.

The demand for rapid routine analysis of large number of samples has led to the development of digital read-out and print outs whose output can be read directly in concentration units. These devices are used in conjunction with an automatic sampling device, so that the instrument can work unattended for considerable period of time.

So, the amplifier signals from the two beams are separated again, and their ratio is recorded on the pen recorder or on the computer depending upon the requirement. So, the demand for rapid routine analysis of large number of samples has led to the development of digital readout meters and printouts, whose output can be read directly in concentration units. Nowadays you know you do not have to make a calibration curve put your sample plot and then from the plot you would calculate what is the concentration of the of the analyte all those things are taken care of by the computer itself. So, once you feed the computer it will store the data, you can make a calibration curve store in the computer and then make the analysis, make 2 3 analysis and then it cans compare the results compute the standard deviation, absorbance deviation and all those things and then it can give you co several inform much more information at the push of the button, but in the end it is the sample and the chemist that has to make a sense out of the all the information that is available.

Therefore what I suggest is whenever you do the atomic absorption spectrophotometer determinations using atomic absorption spectrophotometers, the operator should understand the working of the computer and working of the machine rather than blindly go by the result that is produced by the atomic absorption spectrometer. So, this aspect is very important in almost all analytical instruments and analytical measurements, and the devices are used in conjunction with automatic sampling also nowadays.

Suppose you want to determine two hundred samples of an ore continuous analysis from morning to evening, then what you will do you cannot be sitting in front of the comp atomic absorption spectrometer making calibration curve every time. So, it makes lot of sense to have a calibration curve in the computer and then compute the concentrations directly from the computer so that the instrument can work unattended also. So, we what we do normally is there are several samples which need to be prepared and put in a carousel and then. So, that the atomic absorption instrument the capillary will dip into one and then insert into the flame and then once the reading is taken it can come back for multiple determinations or the carousel will move, and again the sample will be picked up and put into the flame.

So, this kind of arrangements automatic sampling devices are available nowadays, and many of them permit you to do the work unattended for considerable period of time you just have to come back and check whether the light is on flame is the on and things like that and you can do lot of determinations.

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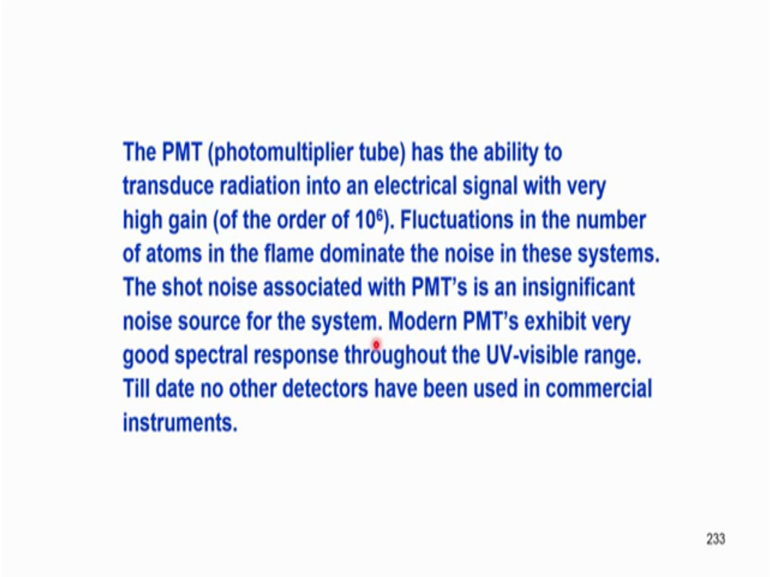

The PMT (photomultiplier tube) has the ability to transduce radiation into an electrical signal with very high gain (of the order of 10^6). Fluctuations in the number of atoms in the flame dominate the noise in these systems. The shot noise associated with PMT's is an insignificant noise source for the system. Modern PMT's exhibit very good spectral response throughout the UV-visible range. Till date no other detectors have been used in commercial instruments.

So, the photo multiplier tube has the ability to transduce radiation into an electrical signal that is done with high gain of the order of about 10 raised to 6. So, what happens to the fluctuations? Fluctuations in the number of free atoms in the flame they dominate the noise in such systems its understood if the if there is a steady state exact number of atoms will be produced and there will not be any fluctuation and your output reading of the absorbance will be steady; but if there is fluctuation absorbance also will vary you will think that computer has done something wrong, but it may be in the system also.

So, the short noise associated with photomultiplier tube is basically insignificant noise source of the system that is a little bit of noise comes from the photomultiplier tube itself that is known as short noise. I have again discussed all these things in in my earlier course on spectrophotometry. So, modern photomultiplier tubes exhibit very good spectral response throughout the UV and visible range. Till date no other detectors have been used in commercial instruments, but this is only a statement to be taken with a pinch of salt because apart from photomultiplier tubes nowadays we have cathode array detectors, array detectors have been used they are there in atomic absorption almost many instruments in the market the use array detectors.

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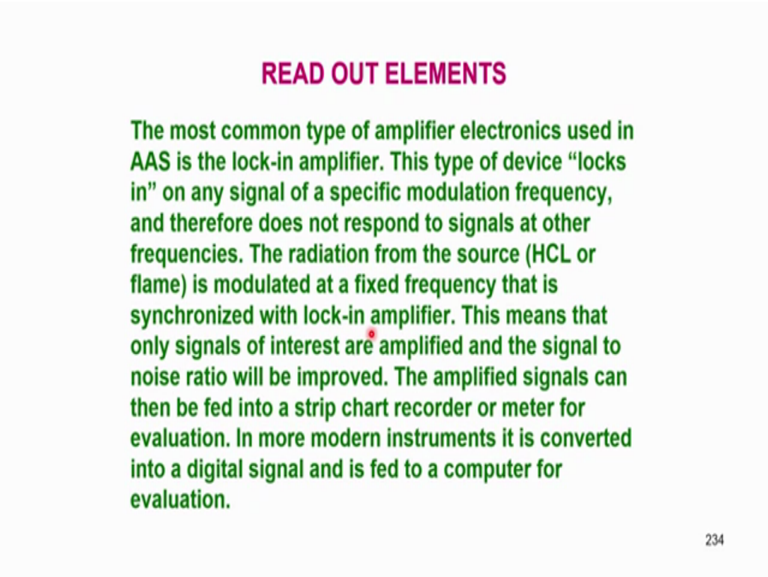

READ OUT ELEMENTS

The most common type of amplifier electronics used in AAS is the lock-in amplifier. This type of device "locks in" on any signal of a specific modulation frequency, and therefore does not respond to signals at other frequencies. The radiation from the source (HCL or flame) is modulated at a fixed frequency that is synchronized with lock-in amplifier. This means that only signals of interest are amplified and the signal to noise ratio will be improved. The amplified signals can then be fed into a strip chart recorder or meter for evaluation. In more modern instruments it is converted into a digital signal and is fed to a computer for evaluation.

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So, now we will not we will discuss about the readout elements, it is not much to discuss except that what the computer screen tells you. The computer screen tells you that the most common type of amplifier electronics is used is lock-in amplifier this we have already discussed, this type of device locks in on any signal or a specific modulation frequency. So, you can choose the wavelength and fix it and it does the job. So, it does not respond to signals at other frequencies; this is very important because we do not want signals from other frequencies in atomic absorption we want signal only at the resonance wavelength. So, the radiation from the source is modulated at a fixed frequency that is synchronized with the lock-in amplifier this means that only signals of interest are amplified and the signal to noise ratio will be improved. The amplified signals can then be fed into a strip chart recorder or meter or computer or anything. So, in modern instruments it is converted into a digital signal and fed to a computer for evaluation.

So, these are the readout elements earlier there is to be your a meter analog meter which will show you the absorbance which is on the log scale, but nowadays all these things have been taken care of and the computer will do the job for you. So, it is computer really act as some sort of a helper to the analyst rather than taking over the job; because the interpretation of accuracy sensitivity and all those things are still left to the analyst. So, most of the commercial instruments are being marketed today have a dedicated computer.

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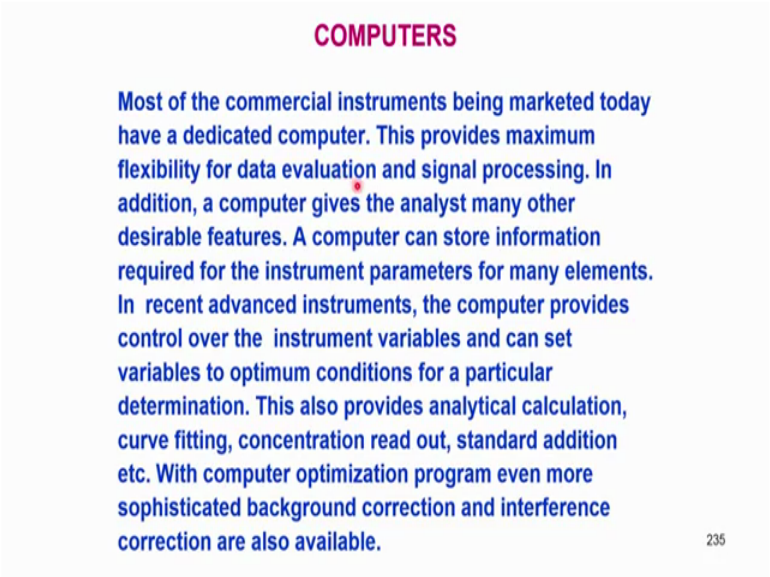

COMPUTERS

Most of the commercial instruments being marketed today have a dedicated computer. This provides maximum flexibility for data evaluation and signal processing. In addition, a computer gives the analyst many other desirable features. A computer can store information required for the instrument parameters for many elements. In recent advanced instruments, the computer provides control over the instrument variables and can set variables to optimum conditions for a particular determination. This also provides analytical calculation, curve fitting, concentration read out, standard addition etc. With computer optimization program even more sophisticated background correction and interference correction are also available.

So, a dedicated computer what does it do? Normally we want the computer to fix the ratio of the fuel gas and the other gas that is oxidizer. So, it can if there are any variations in the flow of the gas computer can adjust it with a looping mechanism, and if there is variation it will automatically adjust and try to give you a steady flame, that is known as gas mixing it is known as gas box in the atomic absorption spectrometers. So, gas box control is one aspect where atomic where computer can help, and then flame lighting maintenance and other things computer can help, and then I can increase the slit width mechanically mechanical increase that also I can do by servo controlled computer and then the flexibility data evaluation flexibility for data will signal processing that also can be done, statistical evaluation can be done.

So, a computer gives the analyst several other desirable features and when you want to buy a spectrophotometer at or atomic absorption spectrometer a you should check what are the capabilities of the computer that are built in to the system. So, it helps for example, gas box control may not be included in the software. So, then you will have to do it mechanically yourself for example, the change of the nebulizer suppose you want to change from air acetylene to acetylene nitrous oxide, the burner head should move from one end to another end and the nitrogen's burner should come there in that place such movements can be controlled by the computer and sample introduction carousel that also can be co controlled by the computer. So, a computer can also store information required for the instruments parameters for example, I want you to for every element you want to determines you need a hollow cathode lamp. So, what is the resonance line of the hollow cathode lamp how many lines are there which one to be chosen?

So, the whole periodic table wherever all the elements in the periodic table which have hollow cathode lamp, all that information can be stored in the computer and you can whenever you hit come copper the screen will show you all the important parameters of hollow cathode lamp, and what are the slit widths you should employ, what is the resonance line etcetera all that information what is the temperature method temperature of the flame should you use a air acetylene or nitrous oxide acetylene like that almost all those parameters can be stored in the atomic absorption spectrometer computer of course.

So, the computer provides control over the instrument variables and it can set variables to optimize conditions also for a particular determination, the whole procedure can be stored. So, this provides analytical calculation curve fitting concentration readout standard edition and all these things can be controlled by the computer. So, with computer optimization program even more sophisticated background correction and interference corrections are available.

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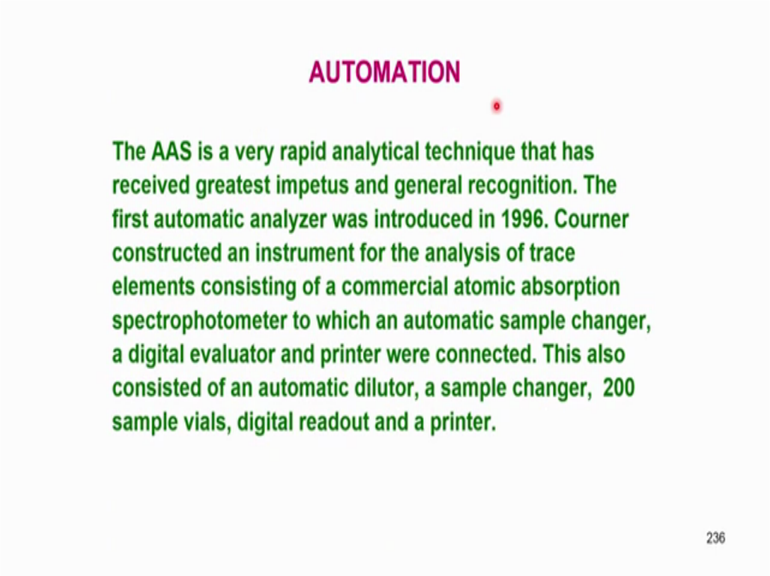

AUTOMATION

The AAS is a very rapid analytical technique that has received greatest impetus and general recognition. The first automatic analyzer was introduced in 1996. Courner constructed an instrument for the analysis of trace elements consisting of a commercial atomic absorption spectrophotometer to which an automatic sample changer, a digital evaluator and printer were connected. This also consisted of an automatic dilutor, a sample changer, 200 sample vials, digital readout and a printer.

So, automation as I have already been telling you since last 5 minutes, atomic absorption is a very rapid analytical technique that has received greatest impetus and general recognition. The first automatic nebulizer was introduced in 1996 nowadays many instruments are there. So, the Courner constructed an instrument for the analysis of trace elements consisting of commercial atomic absorption spectrometer, to which an automatic sample changer digital evaluator and printer were connected nowadays all these things have become standard features of atomic absorption spectrometer. So, it the Courner's AAS consisted of an automatic diluter also a sample changer, sample vials digital readout and a printer fantastic improvement in the automation.

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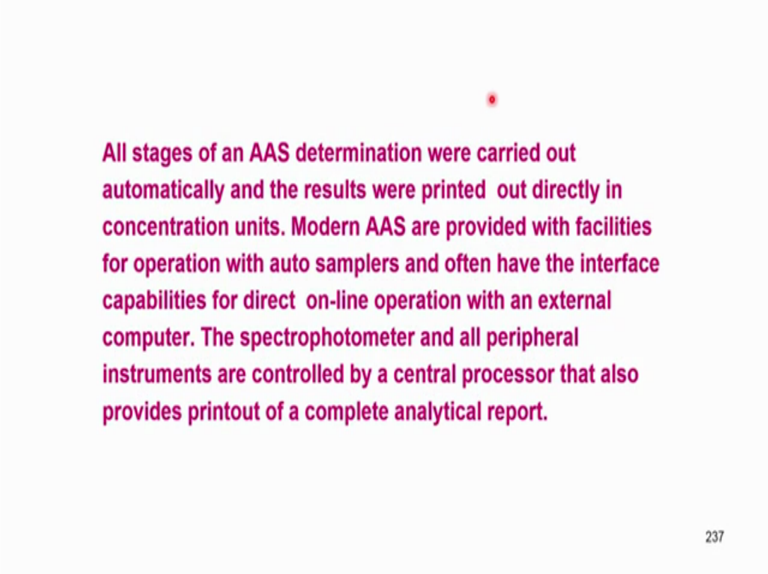

All stages of an AAS determination were carried out automatically and the results were printed out directly in concentration units. Modern AAS are provided with facilities for operation with auto samplers and often have the interface capabilities for direct on-line operation with an external computer. The spectrophotometer and all peripheral instruments are controlled by a central processor that also provides printout of a complete analytical report.

So, all stages of atomic absorption spectra determinations are carried out automatically and the results or printed out directly in concentration units. Modern AAS are provided with facilities for operation with auto samplers and often have the interface capabilities for direct online operation with an external computer also. Earlier they used to put the microchips inside the comp inside the AAS and if the chip goes you just have to import.

Nowadays an external computer can access the software and then control the operations that helps. So, the spectrophotometer and all peripheral instruments can be controlled by a central processor that also provides printout etcetera of a complete analytical report. So, automation per say does not bring any substantial improvement in the savings of time are also improved, nor does it improve a method the method control is still the operators responsibility.

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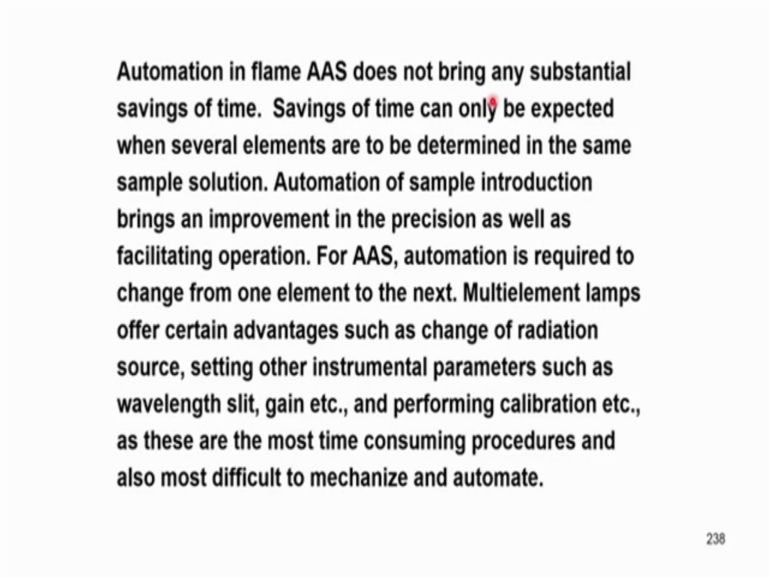

Automation in flame AAS does not bring any substantial savings of time. Savings of time can only be expected when several elements are to be determined in the same sample solution. Automation of sample introduction brings an improvement in the precision as well as facilitating operation. For AAS, automation is required to change from one element to the next. Multielement lamps offer certain advantages such as change of radiation source, setting other instrumental parameters such as wavelength slit, gain etc., and performing calibration etc., as these are the most time consuming procedures and also most difficult to mechanize and automate.

So, saving of time can be only be expected when several elements are to be determined in the same sample. So, automation of sample introduction brings an improvement in the precision as well as facilitating operation. For atomic absorption automation is required to change from one element to another again in most of the modern instruments what they do is they fix 4, 4 or 5 6 hollow cathode lamps. So, that if you want to determine the different elements in the same sample you just have to change the hollow cathode lamp fixed in the turret.

So, the hollow cathode lamp has to move and another hollow cathode lamp will come and it will be fixed to it will be automatically adjusted to the slit width and optics. So, multi element lamps again are available if you we have already discussed it. So, setting of other instrumental parameters can be done by computer wavelength, etcetera etcetera and performing calibration this is done and these things save the timing times for the operator.

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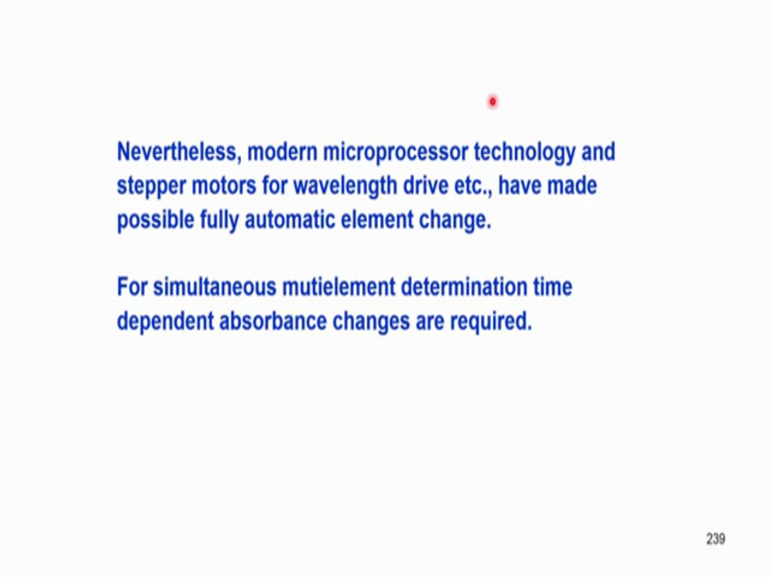

Nevertheless, modern microprocessor technology and stepper motors for wavelength drive etc., have made possible fully automatic element change.

For simultaneous mutielement determination time dependent absorbance changes are required.

So, modern microprocessor technology and stepper motors have made possible fully automatic element change. So, for simultaneous multielement determination time dependent absorption charge changers changes are required.

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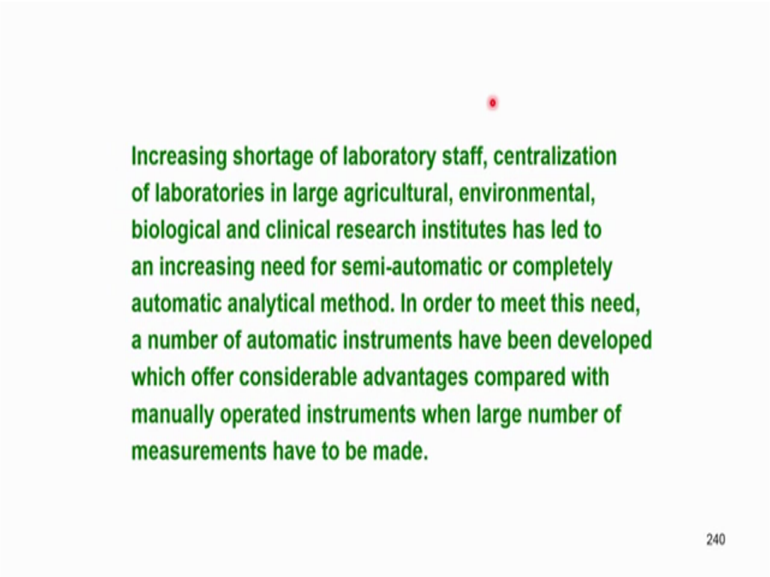

Increasing shortage of laboratory staff, centralization of laboratories in large agricultural, environmental, biological and clinical research institutes has led to an increasing need for semi-automatic or completely automatic analytical method. In order to meet this need, a number of automatic instruments have been developed which offer considerable advantages compared with manually operated instruments when large number of measurements have to be made.

So, with the use of all these things atomic absorption has become a very important aspect of any laboratory. So, increasing shortage of laboratory staff a centralization of laboratories you may have to send the result to Delhi if you are in Bangalore, simultaneously the data can be transmitted. So, applications in agriculture environmental biological research and clinical research all these things have led to an increasing need for automatic or at least semi-automatic analytical methods. So, in order to meet this need a number of automatic dedicated instruments have also been developed, which offer considerable advantage compared with manually operated instruments.

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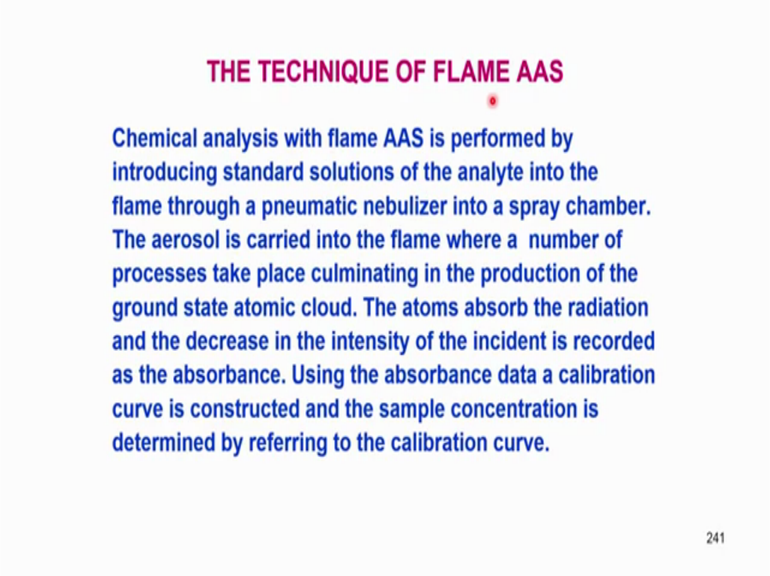

THE TECHNIQUE OF FLAME AAS

Chemical analysis with flame AAS is performed by introducing standard solutions of the analyte into the flame through a pneumatic nebulizer into a spray chamber. The aerosol is carried into the flame where a number of processes take place culminating in the production of the ground state atomic cloud. The atoms absorb the radiation and the decrease in the intensity of the incident is recorded as the absorbance. Using the absorbance data a calibration curve is constructed and the sample concentration is determined by referring to the calibration curve.

So, this aspect if you remember we will assume that we have discussed most of the aspects of atomic instrumental aspects of atomic absorption, and then now what we can what we can do is we will discuss about other aspects of atomic absorption that is what are the techniques, how do I go about preparing a sample like that we can discuss other things. Now in the next class we will discuss about flame atomic absorption technique: how to go about analyzing a given sample using flame technique, like that we will discuss other aspects.

Thank you very much we will continue our discussion in the next class.