Modern Instrumental Methods of Analysis

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Lecture No. # 30

Inductively Coupled Plasma Atomic Emission Spectrometry-3

Comparison of ICP & AAS

Last class, we were discussing about the activation calibration procedures using internal standard. And then, I had also referred to some of the interferences that are expected in inductively coupled plasma atomic emissions spectrometry. What I had told you in the last class was, chemical and matrix interferences are significantly lower with plasma sources, compared to other atomizers. However, at low analyte concentrations, the background emission due to recombination of argon ions with electrons would become significant; because, the concentrations of the analyte atoms are very small. So, for both single channel and double channel instruments, some amount of correction is necessary and it is made by taking an average of the background readings on either side of the emission peak.

Nowadays, instrument software accomplishes this task automatically or at the discretion of the operator; that means, you also have some sort of a freedom to choose where a peak starts and where a peak ends, so that, the total number of counts in that peak area, in which you have chosen, can be used for calibration curve purposes. So, spectral interferences, if we want to talk about spectral interferences, they are always possible in ICP analysis, because, emission spectra of many elements are rich in lines.

Every element will have number of emissions spectra, and because we are operating around 6000 to 8000 degree kelvin, most of the elements will emit emission lines. So, apart from the analyte, you are always getting lot of emission lines with respect to concomitant metal ions present in the sample. So, you have to be very careful in choosing an analytical line, where the emission lines of other elements do not overlap, the emission line what you have chosen for ICP; that is, for the analyte, the emission line should be chosen in such a way that, it becomes specific for the analyte.

So, therefore, it is preferable to have a knowledge of other matrix element in the sample and their emission lines also you should know. And then, you have to choose an emission line which has no interference from other matrix elements. The software for ICP instruments, in general, has number of powerful routines for wavelength selection, calibration, spectral analysis and deconvolution of the overlapping lines to some extent, not always; deconvolution is not possible.

So, additionally, integrated databases of spectral lines of other elements, make spotting and correcting for interferences, an integral part of the analytical procedures. So, what happens is, the analytical lines, the moment you want to do an analysis in ICP, the ICP operator will ask you, what are the other elements present in the sample?

So, you should know what other elements are there in the sample, so that, their emission lines should be checked, with the whether they overlap with the analytical emission lines, what you are trying to determine. So, for this, software helps; because, these are, many of these emission lines are already put in the software, so, if it shows you, if you choose a particular emission line, it will show you a list of other elements, which have got same analytical line emissions to some extent or completely overlapping.

So, if they are completely overlapping, what you should do is, you have to remove, you have to choose some other line. If it overlaps partially, then software can take care of the interference; because, finally, the interference, as I have been already, as I have been repeatedly telling you, interference is only some sort of Interpretation, because you are only counting the number of hits on the photon, photon hits. So, the number of counts is what you are always looking for.

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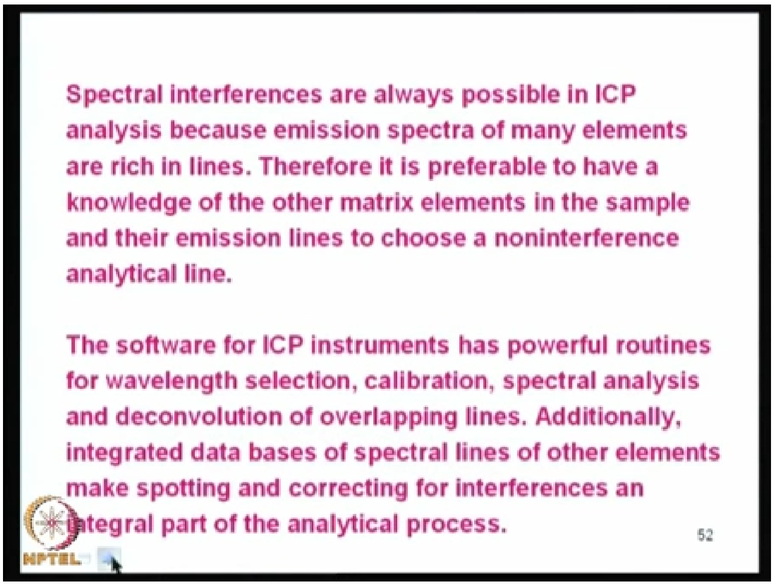

Spectral interferences are always possible in ICP analysis because emission spectra of many elements are rich in lines. Therefore it is preferable to have a knowledge of the other matrix elements in the sample and their emission lines to choose a noninterference analytical line.

The software for ICP instruments has powerful routines for wavelength selection, calibration, spectral analysis and deconvolution of overlapping lines. Additionally, integrated data bases of spectral lines of other elements make spotting and correcting for interferences an integral part of the analytical process.

So, what I would like to do is this; that you should know the elements present in the sample to choose a proper line.

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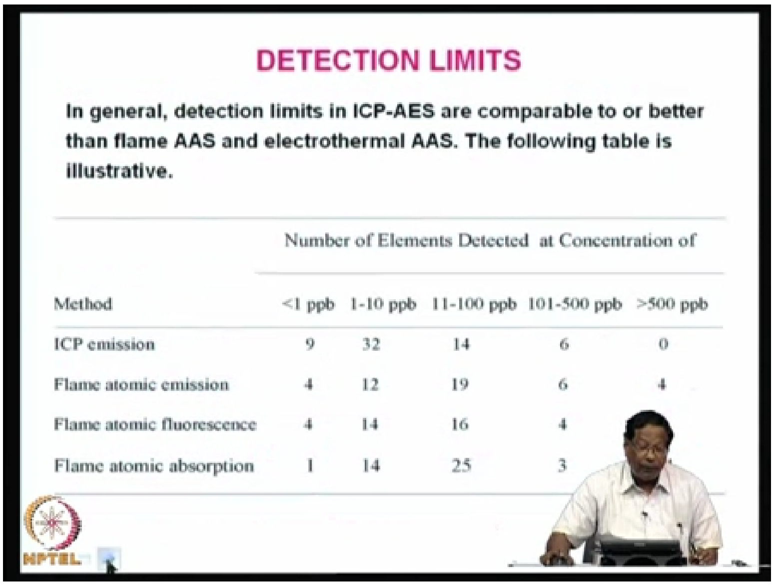

DETECTION LIMITS

In general, detection limits in ICP-AES are comparable to or better than flame AAS and electrothermal AAS. The following table is illustrative.

	Number of Elements Detected at Concentration of				
Method	<1 ppb	1-10 ppb	11-100 ppb	101-500 ppb	>500 ppb
ICP emission	9	32	14	6	0
Flame atomic emission	4	12	19	6	4
Flame atomic fluorescence	4	14	16	4	[illegible]
Flame atomic absorption	1	14	25	3	[illegible]

So, some of the detection limits; we will not go too much into the interference, but the detection limits, I have put in this table; and you can see that, in general, detection limits in ICP-AES are either comparable to or better than flame AAS and more comparable to electro thermal AAS.

The following table is very, very... this table is very, very illustrative. For example, here, I have put the method on the left side, that is, ICP emission, Flame atomic emission, Flame atomic emission, and then Flame atomic fluorescence, and then Flame atomic absorption. And here, you can see that the detection limits are less than number of 1 ppb, parts per billion; ICP emission, you can determine approximately 9 elements in quantities less than 1 parts per billion. And, between 1 and 10, you have about 32 elements; and between 11 and 100 ppb, there are about 14 elements; and 101 to 500 ppb, there are 6, and there are no elements in the range above 500 ppb. So, similarly, if you take a comparison of the detection limits using Flame atomic emission, that is what we have discussed earlier, the Numbers, you can see that there are only 4 less than 1 ppb, 12 in the range of 1 to 10, 19 in 11 to 100, and there are 4 elements which are detectable in flame emission above 500 hundred ppb.

Similarly, Flame atomic fluorescence, if you measure, again the number is very small compared this compared to 9 and 4, and 32 and 14, 14 and 16, and 6 and 4, and more than 500, it is only three elements. In a Flame atomic absorption, there is only one element or maximum two; if you count the hydride generation and mercury etcetera; and then 1 to 10 is 14, 11 to 100 is 25, and 100 to 100, 500 is 3, and above 500 is 14. So, you can see that ICP emission spectrometry is quite good in this range - 9 to less than 1 ppb to 100 ppb, quite good. So, it becomes a method of choice for the elements you want to determine, the elements in parts per billion levels.

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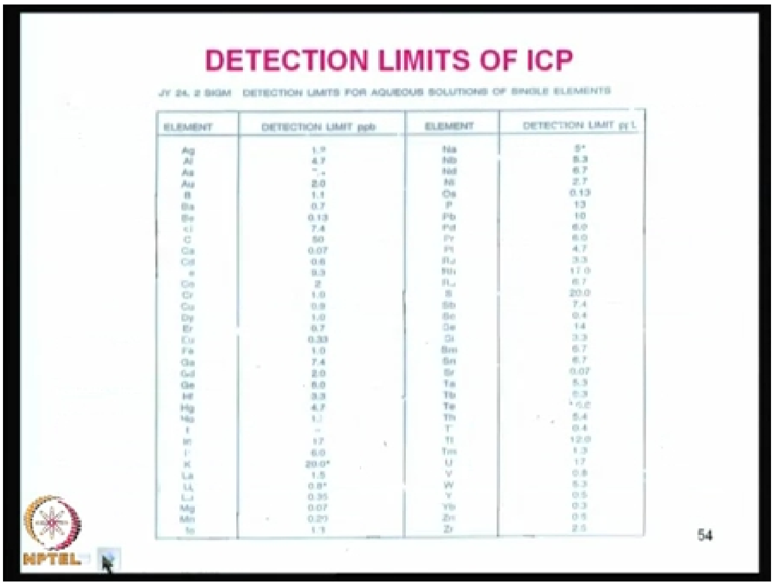

DETECTION LIMITS OF ICP

JY 24, 2 SIGM DETECTION LIMITS FOR AQUEOUS SOLUTIONS OF SINGLE ELEMENTS

ELEMENT	DETECTION LIMIT ppb	ELEMENT	DETECTION LIMIT μg L
Ag	1.7	Na	5*
Al	4.7	Nb	5.3
As	[illegible]	Nd	6.7
Au	2.0	Ni	2.7
B	1.1	Os	0.13
Ba	0.7	P	13
Be	0.13	Pb	10
Bi	7.4	Pd	6.0
C	50	Pr	6.0
Ca	0.07	Pt	4.7
Cd	0.6	Re	3.3
Ce	9.3	Rh	17.0
Co	2	Ru	6.7
Cr	1.0	S	20.0
Cu	0.9	Sb	7.4
Dy	1.0	Sc	0.4
Er	0.7	Se	14
Eu	0.33	Si	3.3
Fe	1.0	Sm	6.7
Ga	7.4	Sn	6.7
Gd	2.0	Sr	0.07
Ge	8.0	Ta	5.3
Hf	3.3	Tb	5.3
Hg	4.7	Te	[illegible]
Ho	1.1	Th	5.4
I	–	Ti	0.4
In	17	Tl	12.0
Ir	6.0	Tm	1.3
K	20.0*	U	17
La	1.5	V	0.8
Li	0.8*	W	5.3
Lu	0.35	Y	0.5
Mg	0.07	Yb	0.3
Mn	0.21	Zn	0.5
Mo	1.1	Zr	2.5

Here, I have the detection limits of ICP. The table is not very, it contains lot of data. So, the detection limits, I have put it, in this case, because this is for JY 24, 2 Sigma Detection Limits for Aqueous Solutions of Single Elements.

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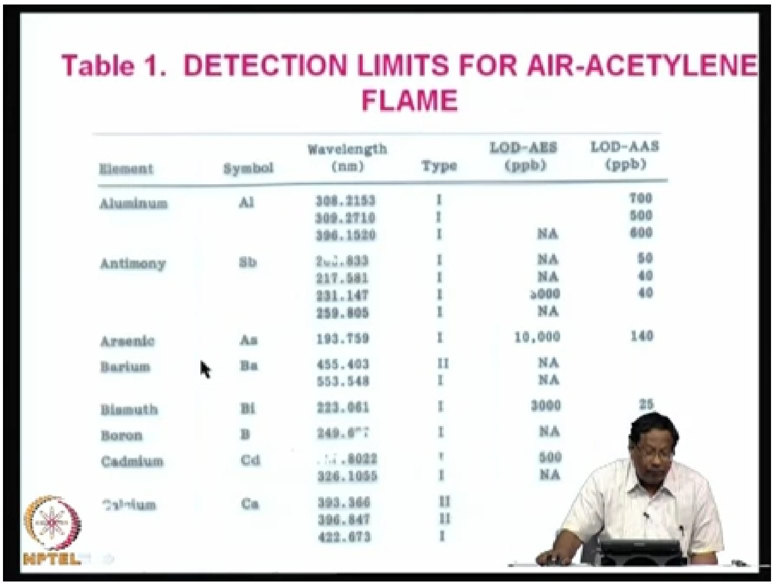

Table 1. DETECTION LIMITS FOR AIR-ACETYLENE FLAME

Element	Symbol	Wavelength (nm)	Type	LOD-AES (ppb)	LOD-AAS (ppb)
Aluminum	Al	308.2153	I		700
		309.2710	I		500
		396.1520	I	NA	600
Antimony	Sb	[illegible]	I	NA	50
		217.581	I	NA	40
		231.147	I	[illegible]	40
		259.805	I	NA	
Arsenic	As	193.759	I	10,000	140
Barium	Ba	455.403	II	NA	
		553.548	I	NA	
Bismuth	Bi	223.061	I	3000	25
Boron	B	[illegible]	I	NA	
Cadmium	Cd	[illegible]	[illegible]	500	
		326.1055	I	NA	
Calcium	Ca	393.366	II		
		396.847	II		
		422.673	I		

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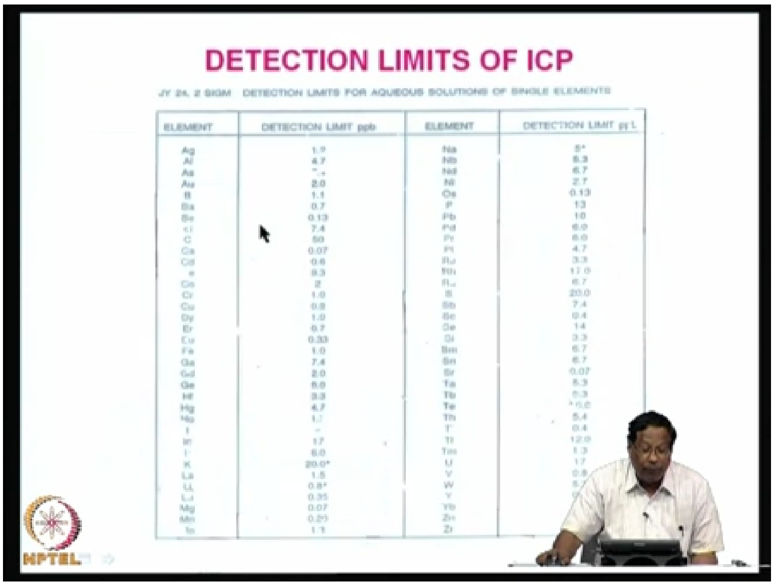

DETECTION LIMITS OF ICP

JY 24, 2 SIGM DETECTION LIMITS FOR AQUEOUS SOLUTIONS OF SINGLE ELEMENTS

So, here I have listed from silver to iodine and silver to molybdenum, and you can see that the detection limits are, up to molybdenum is 1.3, and up to zirconium it is about 2.5, that is, with the ICP. Now, you can also see that the detection limits for air-acetylene, they are all listed here.

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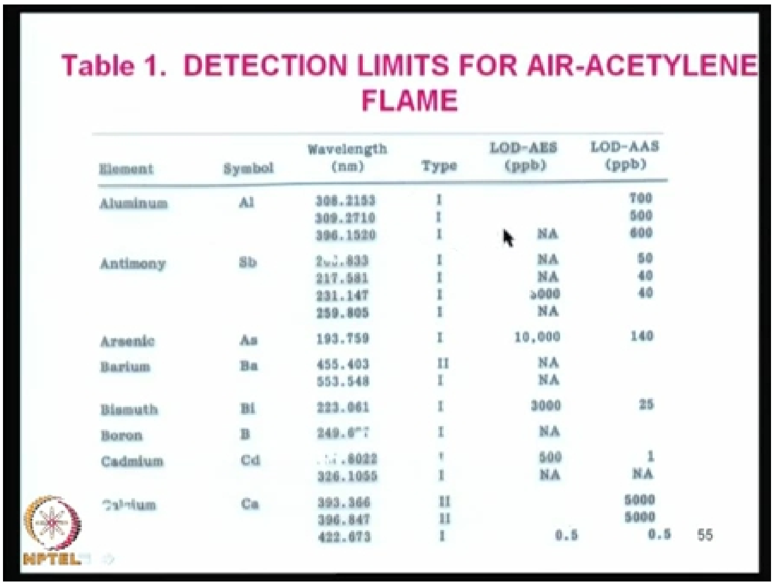

Table 1. DETECTION LIMITS FOR AIR-ACETYLENE FLAME

Element	Symbol	Wavelength (nm)	Type	LOD-AES (ppb)	LOD-AAS (ppb)
Aluminum	Al	308.2153	I		700
		309.2710	I		500
		396.1520	I	NA	600
Antimony	Sb	[illegible].833	I	NA	50
		217.581	I	NA	40
		231.147	I	[illegible]000	40
		259.805	I	NA	
Arsenic	As	193.759	I	10,000	140
Barium	Ba	455.403	II	NA	
		553.548	I	NA	
Bismuth	Bi	223.061	I	3000	25
Boron	B	249.6[illegible]	I	NA	
Cadmium	Cd	[illegible].8022	[illegible]	500	1
		326.1055	I	NA	NA
Calcium	Ca	393.366	II		5000
		396.847	II		5000
		422.673	I	0.5	0.5

For example, for aluminum, if you choose 308.2153 wavelength lines, the limit of detection in AES is not possible, that is flame; but in AAS, it is about 700 ppm. Like that, I have given you a list of these elements, which can be determined in different ranges.

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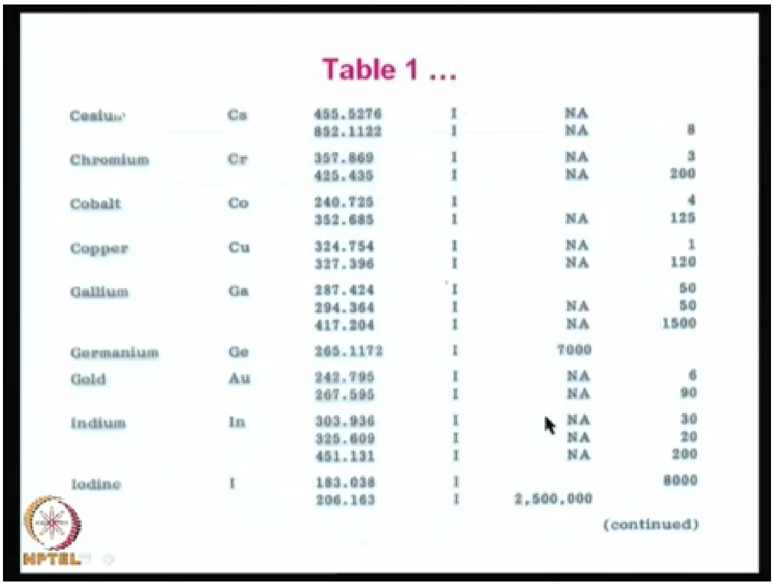

Table 1 ...

Cesium	Cs	455.5276	I	NA	
		852.1122	I	NA	8
Chromium	Cr	357.869	I	NA	3
		425.435	I	NA	200
Cobalt	Co	240.725	I		4
		352.685	I	NA	125
Copper	Cu	324.754	I	NA	1
		327.396	I	NA	120
Gallium	Ga	287.424	I		50
		294.364	I	NA	50
		417.204	I	NA	1500
Germanium	Ge	265.1172	I	7000	
Gold	Au	242.795	I	NA	6
		267.595	I	NA	90
Indium	In	303.936	I	NA	30
		325.609	I	NA	20
		451.131	I	NA	200
Iodine	I	183.038	I		8000
		206.163	I	2,500,000	

(continued)

So, this thing, I am putting it on the NPTEL course, so that, you can have a quick reference for the elements you want to determine. These are all continuing up to zirconium; from aluminum to zirconium, almost all the metals and some of the nonmetals, you can continue, you can have the data at your fingertips.

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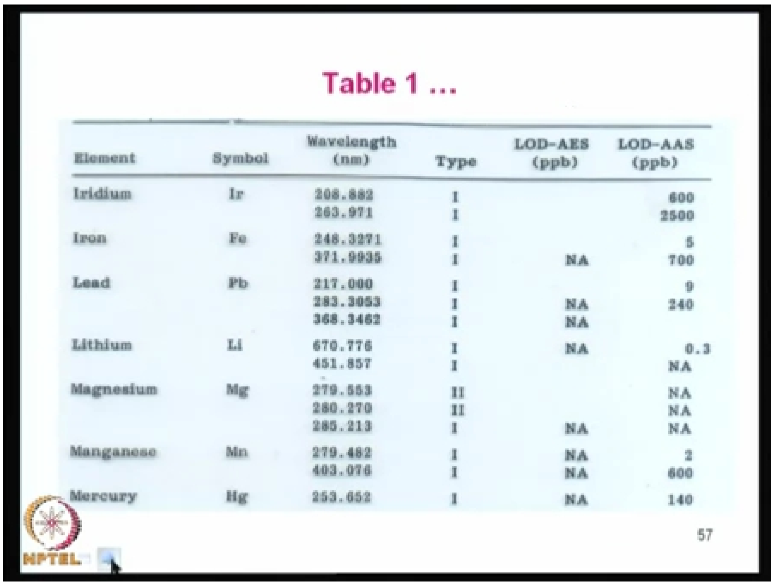

Table 1 …

Element	Symbol	Wavelength (nm)	Type	LOD-AES (ppb)	LOD-AAS (ppb)
Iridium	Ir	208.882	I		600
		263.971	I		2500
Iron	Fe	248.3271	I		5
		371.9935	I	NA	700
Lead	Pb	217.000	I		9
		283.3053	I	NA	240
		368.3462	I	NA	
Lithium	Li	670.776	I	NA	0.3
		451.857	I		NA
Magnesium	Mg	279.553	II		NA
		280.270	II		NA
		285.213	I	NA	NA
Manganese	Mn	279.482	I	NA	2
		403.076	I	NA	600
Mercury	Hg	253.652	I	NA	140

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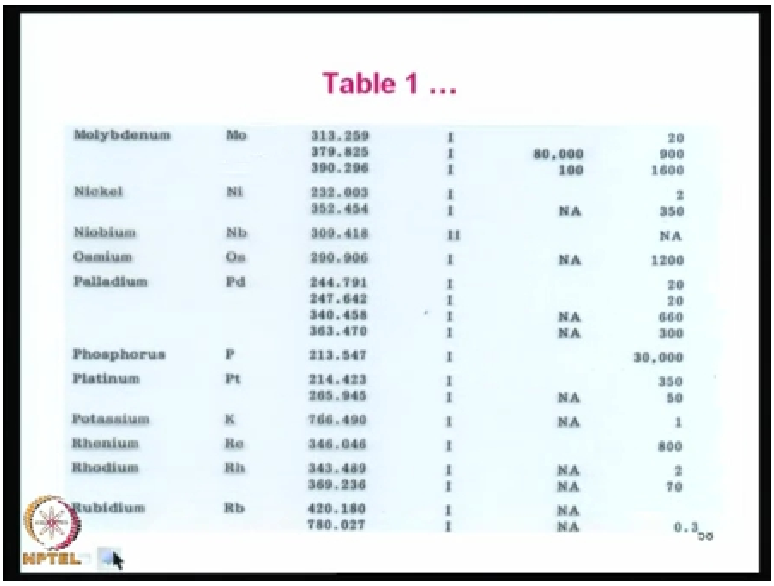

Table 1 …

Molybdenum	Mo	313.259	I		20
		379.825	I	80,000	900
		390.296	I	100	1600
Nickel	Ni	232.003	I		2
		352.454	I	NA	350
Niobium	Nb	309.418	II		NA
Osmium	Os	290.906	I	NA	1200
Palladium	Pd	244.791	I		20
		247.642	I		20
		340.458	I	NA	660
		363.470	I	NA	300
Phosphorus	P	213.547	I		30,000
Platinum	Pt	214.423	I		350
		265.945	I	NA	50
Potassium	K	766.490	I	NA	1
Rhenium	Re	346.046	I		800
Rhodium	Rh	343.489	I	NA	2
		369.236	I	NA	70
Rubidium	Rb	420.180	I	NA	
		780.027	I	NA	0.3

So, you can see that molybdenum, rudenium, molybdenum etcetera, they are all up to 20, and that is the highest resonance line. And, suppose, you go to 390, that is another, third resonance line, it is around 600.

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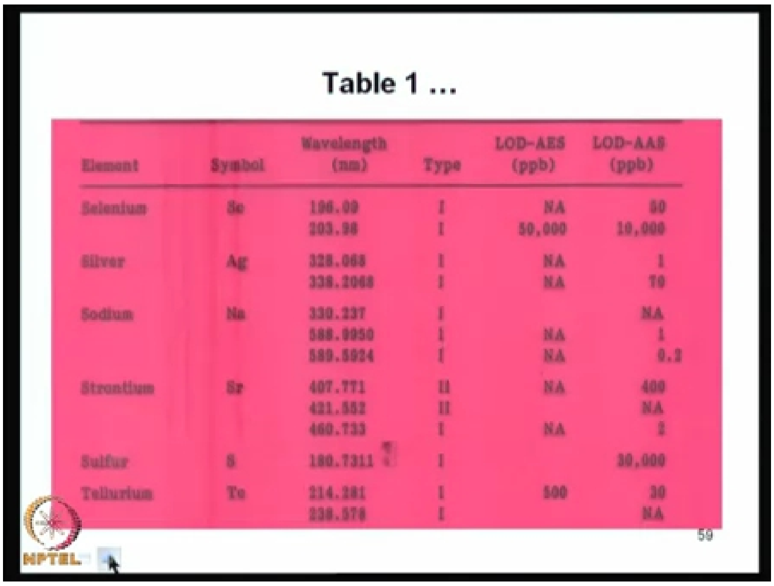

Table 1 ...

Element	Symbol	Wavelength (nm)	Type	LOD-AES (ppb)	LOD-AAS (ppb)
Selenium	Se	196.09	I	NA	50
		203.98	I	50,000	10,000
Silver	Ag	328.068	I	NA	1
		338.2068	I	NA	70
Sodium	Na	330.237	I		NA
		588.9950	I	NA	1
		589.5924	I	NA	0.2
Strontium	Sr	407.771	II	NA	400
		421.552	II		NA
		460.733	I	NA	2
Sulfur	S	180.7311	I		30,000
Tellurium	Te	214.281	I	500	30
		238.578	I		NA

Similarly, you can have all these data for comparison. And, this is AES, AAS, atomic emission and atomic absorption. You can see that, for selenium, there is no detection limit is possible; detection is not possible, but, in limit of detection in AAS is about 50. But, if you go to 203.98 line, detection limit becomes 10000 here, compared to atomic emission of 50000. Similarly, you can take a look at most of the atomic absorption detection limit and atomic emission detection limit. This will help you in choosing different detection different techniques for the chemical analysis of different elements.

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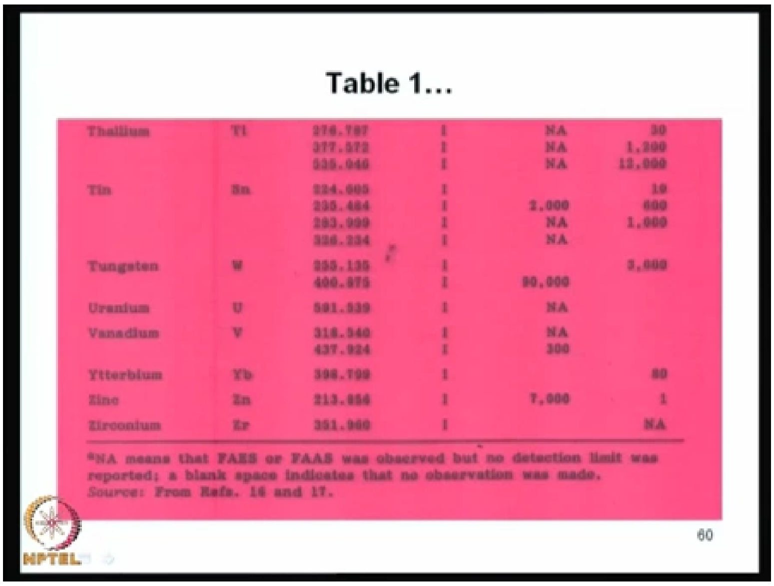

Table 1...

Thallium	Tl	276.787	I	NA	30
		377.572	I	NA	1,200
		535.046	I	NA	12,000
Tin	Sn	224.605	I		10
		235.484	I	2,000	600
		283.999	I	NA	1,000
		326.234	I	NA	
Tungsten	W	255.135	I		3,000
		400.875	I	90,000	
Uranium	U	591.539	I	NA	
Vanadium	V	318.540	I	NA	
		437.924	I	300	
Ytterbium	Yb	398.799	I		80
Zinc	Zn	213.856	I	7,000	1
Zirconium	Zr	351.960	I		NA

[a] NA means that FAES or FAAS was observed but no detection limit was reported; a blank space indicates that no observation was made.
Source: From Refs. 16 and 17.

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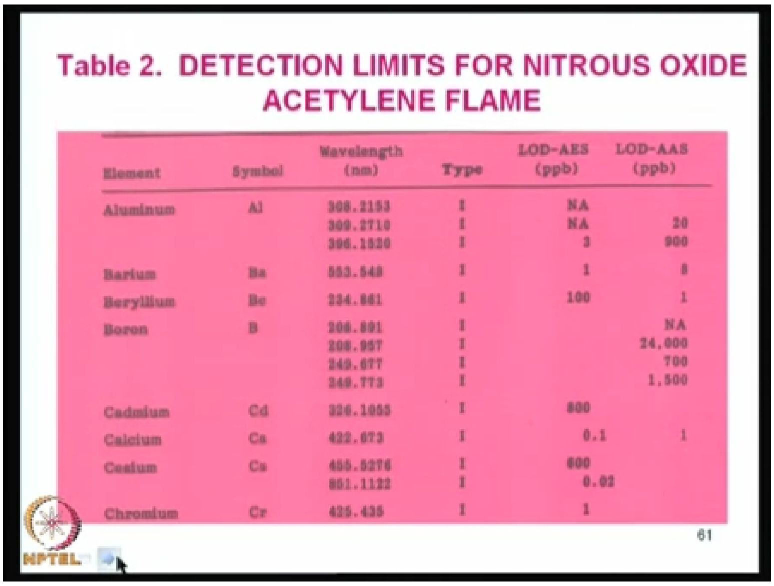

Table 2. DETECTION LIMITS FOR NITROUS OXIDE ACETYLENE FLAME

Element	Symbol	Wavelength (nm)	Type	LOD-AES (ppb)	LOD-AAS (ppb)
Aluminum	Al	308.2153	I	NA	
		309.2710	I	NA	20
		396.1520	I	3	900
Barium	Ba	553.548	I	1	8
Beryllium	Be	234.861	I	100	1
Boron	B	208.891	I		NA
		208.957	I		24,000
		249.677	I		700
		249.773	I		1,500
Cadmium	Cd	326.1055	I	800	
Calcium	Ca	422.673	I	0.1	1
Cesium	Cs	455.5276	I	600	
		851.1122	I	0.02	
Chromium	Cr	425.435	I	1	

Now, you can study this table in leisure, but I have, I am continuing to show these detection limits because it will give you a ready reference. Now, this table shows you for nitrous oxide-acetylene flame. Again, you can see that aluminum can be determined up to 20 ppb using nitrous oxide-acetylene flame, but if you choose, that is, at 309. But, 396, if you choose, the detection limit increases to 900 ppb, that is, the nitrous oxide-acetylene flame; that is, I am comparing the detection limits in atomic absorption as well as in atomic emission. Whereas, it is 900 here, it is 3 here, this number. Similarly, for barium, beryllium etcetera, I have put all the almost all the numbers and you can take a look at your leisure.

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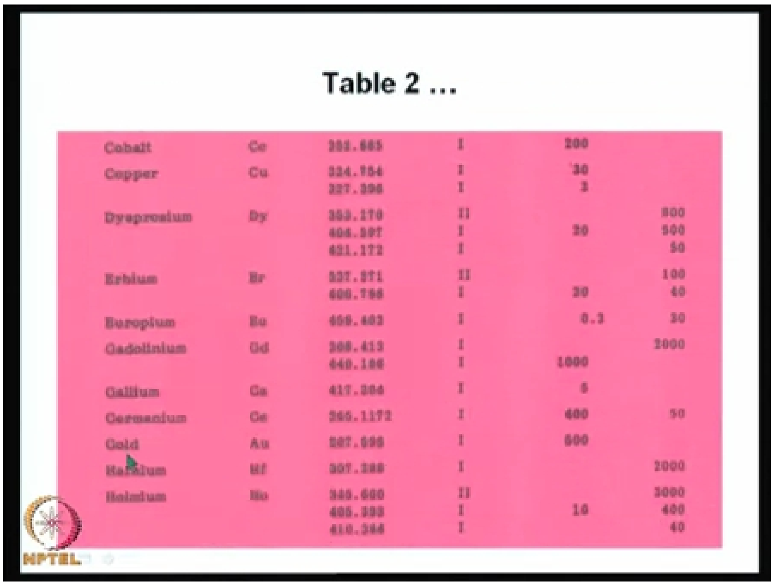

Table 2 ...

Cobalt	Co	252.665	I	200	
Copper	Cu	324.754	I	30	
		327.396	I	3	
Dysprosium	Dy	353.170	II		800
		404.597	I	20	500
		421.172	I		50
Erbium	Er	337.271	II		100
		400.796	I	20	40
Europium	Eu	459.403	I	0.2	20
Gadolinium	Gd	368.413	I		2000
		440.186	I	1000	
Gallium	Ga	417.204	I	5	
Germanium	Ge	265.1172	I	400	50
Gold	Au	267.595	I	500	
Hafnium	Hf	307.288	I		2000
Holmium	Ho	345.600	II		3000
		405.393	I	10	400
		410.384	I		40

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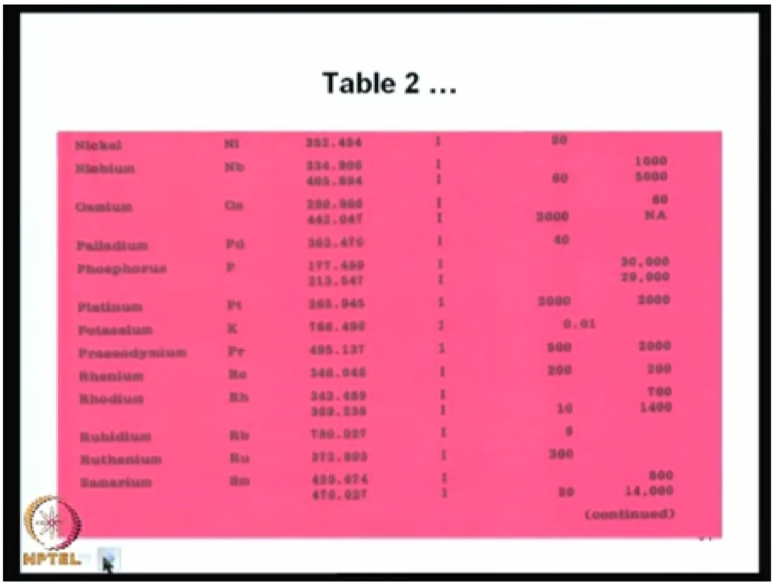

Table 2 ...

Nickel	Ni	352.454	I	20	
Niobium	Nb	334.906	I		1000
		405.894	I	60	5000
Osmium	Os	290.906	I		80
		442.047	I	2000	N.A
Palladium	Pd	363.470	I	40	
Phosphorus	P	177.499	I		30,000
		213.547	I		29,000
Platinum	Pt	265.945	I	2000	2000
Potassium	K	766.490	I	0.01	
Praseodymium	Pr	495.137	I	500	2000
Rhenium	Re	346.046	I	200	200
Rhodium	Rh	343.489	I		700
		369.236	I	10	1400
Rubidium	Rb	780.027	I	9	
Ruthenium	Ru	372.803	I	300	
Samarium	Sm	429.674	I		800
		476.027	I	20	14,000

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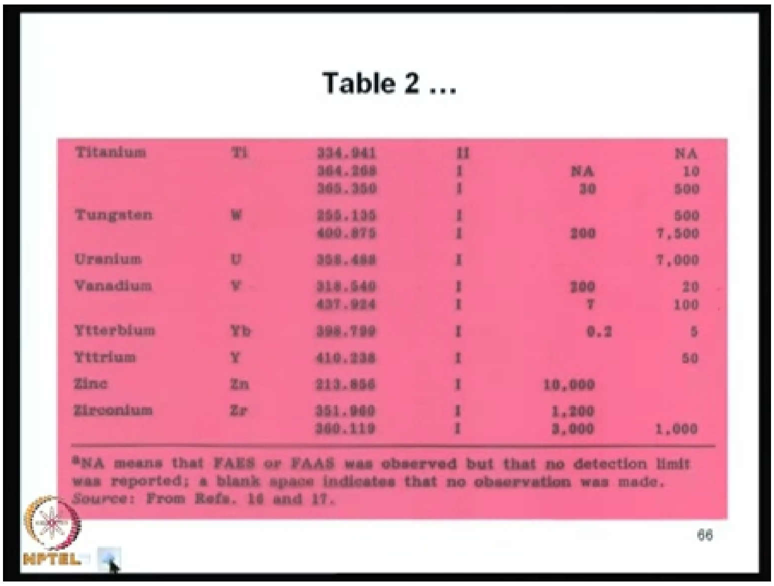

Table 2 ...

Titanium	Ti	334.941	II		NA
		364.268	I	NA	10
		365.350	I	30	500
Tungsten	W	255.135	I		500
		400.875	I	200	7,500
Uranium	U	358.488	I		7,000
Vanadium	V	318.540	I	200	20
		437.924	I	7	100
Ytterbium	Yb	398.799	I	0.2	5
Yttrium	Y	410.238	I		50
Zinc	Zn	213.856	I	10,000	
Zirconium	Zr	351.960	I	1,200	
		360.119	I	3,000	1,000

[a]NA means that FAES or FAAS was observed but that no detection limit was reported; a blank space indicates that no observation was made.
Source: From Refs. 16 and 17.

Some of the figures, you would be interested to know, that zirconium can be determined up to 1000 ppb; this is one of the most difficult elements and not easy to determine zirconium by atomic emission and nitrous even in not nitrous oxide flame.

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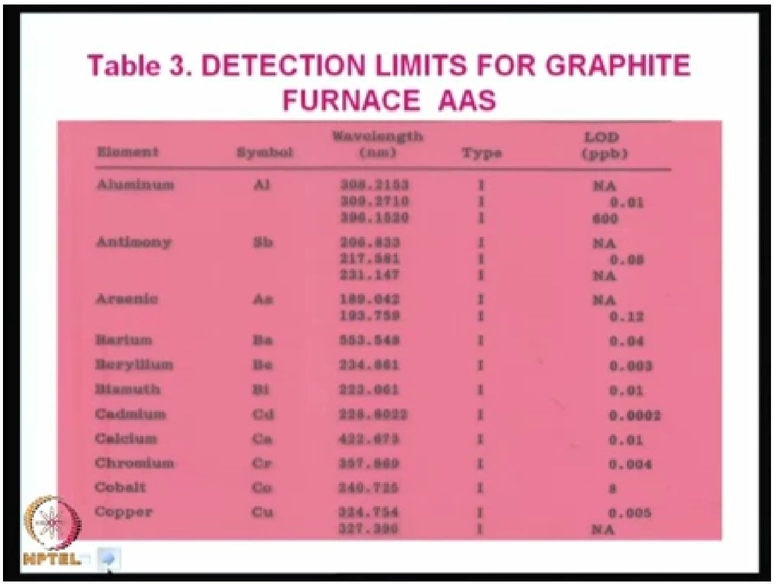

Table 3. DETECTION LIMITS FOR GRAPHITE FURNACE AAS

Element	Symbol	Wavelength (nm)	Type	LOD (ppb)
Aluminum	Al	308.2153	I	NA
		309.2710	I	0.01
		396.1520	I	600
Antimony	Sb	206.833	I	NA
		217.581	I	0.08
		231.147	I	NA
Arsenic	As	189.042	I	NA
		193.759	I	0.12
Barium	Ba	553.548	I	0.04
Beryllium	Be	234.861	I	0.003
Bismuth	Bi	223.061	I	0.01
Cadmium	Cd	228.8022	I	0.0002
Calcium	Ca	422.673	I	0.01
Chromium	Cr	357.869	I	0.004
Cobalt	Co	240.725	I	8
Copper	Cu	324.754	I	0.005
		327.396	I	NA

But, if you compare the detection limits for graphite furnace, you can see that aluminum, it is not possible using 308 line; but 309 line, you can determine up to 0.01 ppb, using graphite furnace; that is, eletro-thermal graphite; and if you choose 396, it is 600.

Like that, you can go down the list, antimony, arsenic, barium, beryllium, bismuth, cadmium etcetera; and, you can see the cadmium, for example, detection limit is 0.0002 ppb; that means, almost up to 2.22 femto grams, that is, 10 raised 2 raised 10 raised to minus 15; it is possible. Same thing goes, same thing is true for chromium, copper etcetera, they are all 0.005 detection limit.

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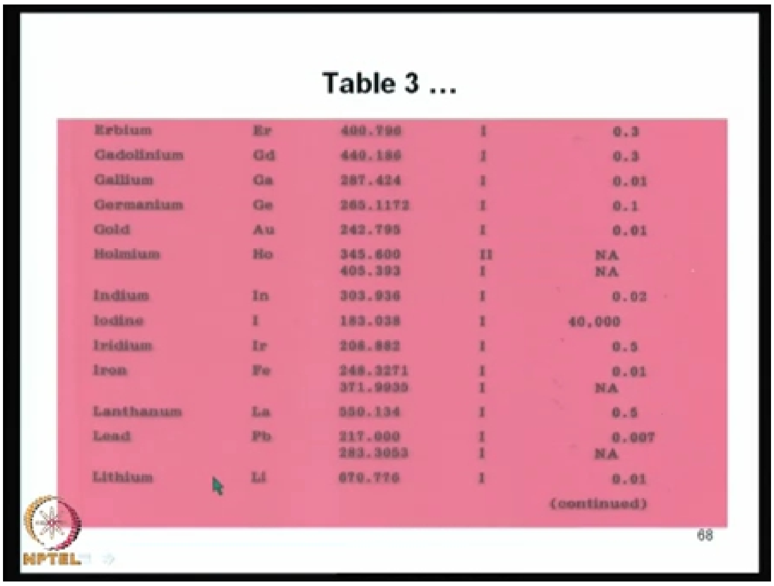

Table 3 ...

Erbium	Er	400.796	I	0.3
Gadolinium	Gd	440.186	I	0.3
Gallium	Ga	287.424	I	0.01
Germanium	Ge	265.1172	I	0.1
Gold	Au	242.795	I	0.01
Holmium	Ho	345.600 405.393	II I	NA NA
Indium	In	303.936	I	0.02
Iodine	I	183.038	I	40,000
Iridium	Ir	208.882	I	0.5
Iron	Fe	248.3271 371.9930	I I	0.01 NA
Lanthanum	La	550.134	I	0.5
Lead	Pb	217.000 283.3053	I I	0.007 NA
Lithium	Li	670.776	I	0.01

(continued)

You have to remember here, that the detection limits are 2 sigma or 3 sigma; that means, the standard deviation multiplied by 2 or 3 So, the quantitative determination is possible even at these concentrations.

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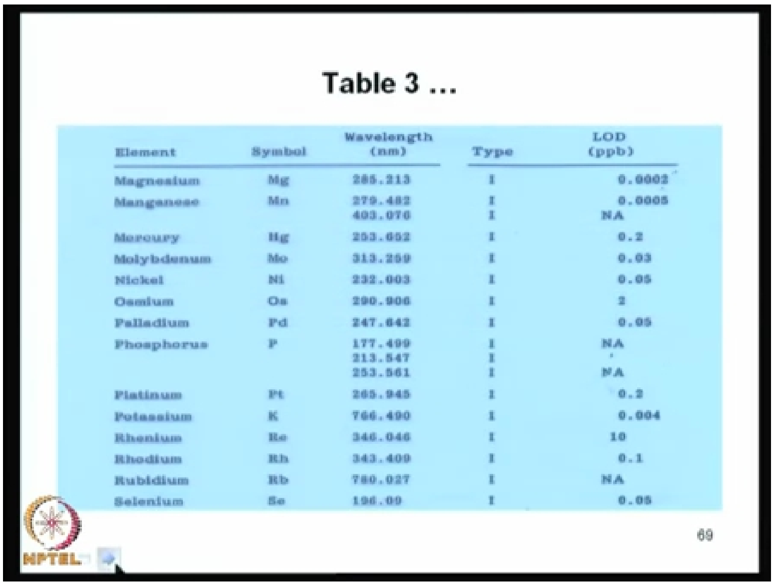

Table 3 ...

Element	Symbol	Wavelength (nm)	Type	LOD (ppb)
Magnesium	Mg	285.213	I	0.0002
Manganese	Mn	279.482 403.076	I I	0.0005 NA
Mercury	Hg	253.652	I	0.2
Molybdenum	Mo	313.259	I	0.03
Nickel	Ni	232.003	I	0.05
Osmium	Os	290.906	I	2
Palladium	Pd	247.642	I	0.05
Phosphorus	P	177.499 213.547 253.561	I I I	NA NA
Platinum	Pt	265.945	I	0.2
Potassium	K	766.490	I	0.004
Rhenium	Re	346.046	I	10
Rhodium	Rh	343.409	I	0.1
Rubidium	Rb	780.027	I	NA
Selenium	Se	196.09	I	0.05

So, similarly, I have put magnesium, and then manganese, mercury, etcetera. You can see here, mercury determination is up to 0.2 ppb, and manganese is 0.0005 ppb. So, the detection limits, in general, are comparable with ICP with respect and in electro thermal atomic absorptions. So, the choice is left to you. If you want to determine the elements at parts per billion levels for most of the elements using the electro-thermal atomic absorption or ICP; the choice falls between the two. So, if you want to determine in PPM level, then the choice is between atomic emission, atomic absorption, flame atomic absorption, nitrous oxide atomic absorption or electro-thermal, as well as the ICP.

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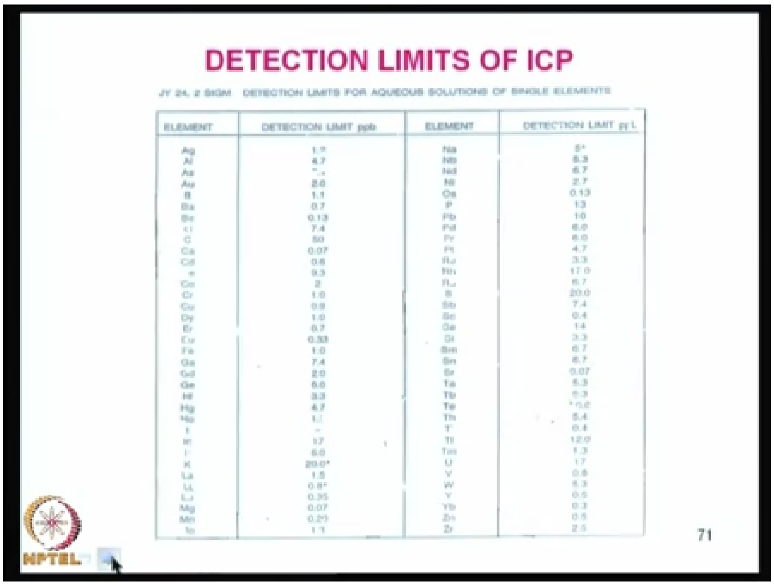

DETECTION LIMITS OF ICP

JY 24, 2 SIGMA DETECTION LIMITS FOR AQUEOUS SOLUTIONS OF SINGLE ELEMENTS

ELEMENT	DETECTION LIMIT ppb	ELEMENT	DETECTION LIMIT µg L
Ag	1.7	Na	5*
Al	4.7	Nb	8.3
As	[illegible]	Nd	6.7
Au	2.0	Ni	2.7
B	1.1	Os	0.13
Ba	0.7	P	13
Be	0.13	Pb	10
Bi	7.4	Pd	6.0
C	50	Pr	6.0
Ca	0.07	Pt	4.7
Cd	0.8	Re	3.3
Ce	9.3	Rh	17.0
Co	2	Ru	6.7
Cr	1.0	S	20.0
Cu	0.9	Sb	7.4
Dy	1.0	Sc	0.4
Er	0.7	Se	14
Eu	0.33	Si	3.3
Fe	1.0	Sm	6.7
Ga	7.4	Sn	6.7
Gd	2.0	Sr	0.07
Ge	6.0	Ta	5.3
Hf	3.3	Tb	5.3
Hg	4.7	Te	[illegible]
Ho	1.0	Th	5.4
I	-	Ti	0.4
In	17	Tl	12.0
Ir	6.0	Tm	1.3
K	20.0*	U	17
La	1.5	V	0.8
Li	0.8*	W	5.3
Lu	0.35	Y	0.5
Mg	0.07	Yb	0.3
Mn	0.2	Zn	0.5
Mo	1.1	Zr	2.5

71

So, the detection limits of ICP also I have put it here; again the same thing, what I have shown you earlier. Because, it contains the... this comes along with the comparison; you can even take a print out of this and have a ready reference. Most of the industry equipments come with this kind of data loaded in the computer, so, you will not have much difficulty in working out which method is the best one to determine any element in parts per billion level.

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FLAME ATOMIC ABSORPTION SPECTROMETER

Here, I am showing you a commercial instrument of atomic absorption. This is flame, this is the nebulizer, and this is the place where the flame comes, and then gases etcetera are all connected, and then, here is the computer which will control most of the operations, and then there is computer mouse etcetera most of the operations can be controlled here.

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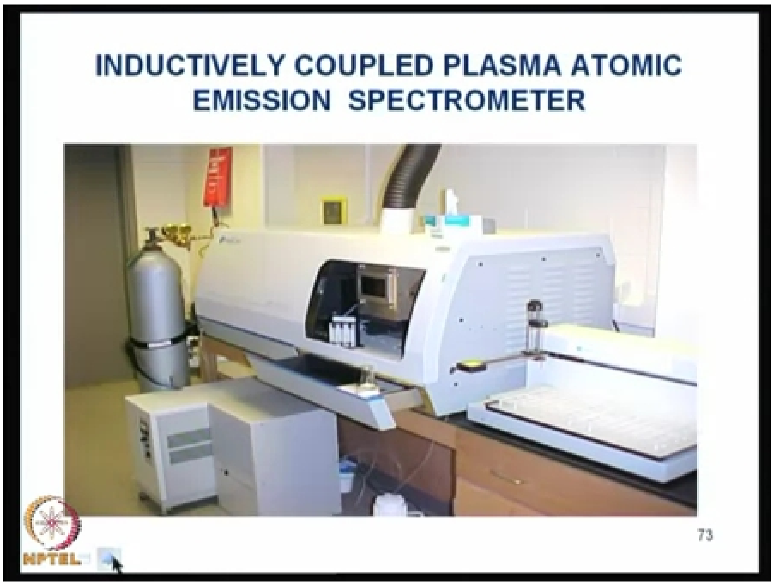

INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETER

And then, this is for inductively coupled plasma, a bench-top instrument, which can be used in an ordinary laboratory. This is not portable nor is it easy to keep it in a small lab.

Most of such instruments are therefore centralized in any institute.

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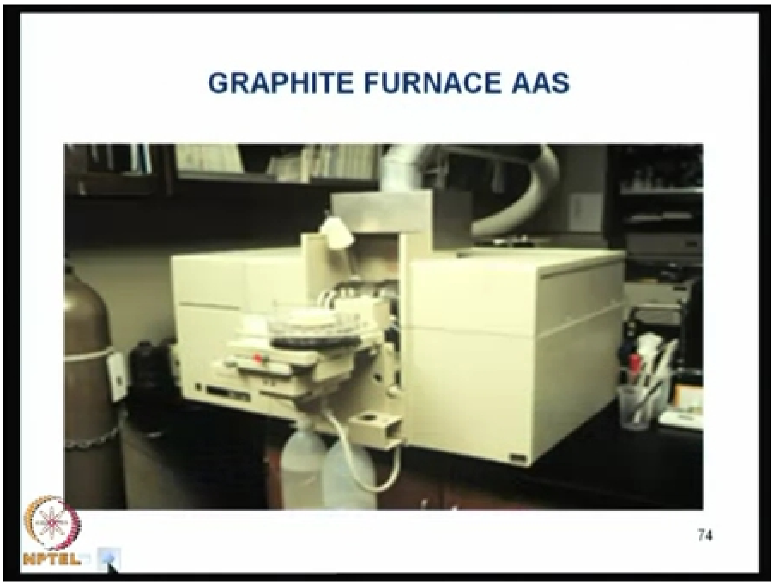

GRAPHITE FURNACE AAS

Now, this is a graphite furnace AAS, here you can see the sample carousel; and then, graphite tube would be somewhere here, in this range; and then, rest of the instrument will remain the same, just like flame photometer. Now, I would like to close our discussion with respective ICP and flame atomic emission as well as electro-thermal atomic absorption with this presentation. And then, I would like to proceed to another technique which we had discussed in the beginning, and that is infrared spectroscopy.

Now, this infrared spectroscopy is entirely different from what we have discussed; because, infrared spectroscopy is used for the determination of organic compounds, but not necessarily quantitative determination, but qualitative. The use of maximum use of infrared spectrometry is in the use of a qualitative identification of the functional groups that are present in a molecule. So, the discussion here would concentrate on what types of functional groups are there, how to integrate the IR frequencies for the characterization of a compound.

This is mainly the domain of organic chemist; but for the sake of brevity, we should also be knowing quite a lot about the infrared spectroscopy, mainly because, some of the environmental samples and several other situations will arise, where you may have to use pass-fail test to determine whether a compound is present or not. It may be in the environment, it may be in an affluent, it may be in a given matrix, production unit in a pharmaceutical company or it may be present in some other matrix, such as consumer consumable cosmetics and several other places where infrared spectroscopy, would be very useful to identify the various types of organic compounds present in a given sample.

So, with this introduction, I would like to take you to the discussion on infrared spectrometry. Now, what is the major difference in infrared and other spectrums, other spectroscopic techniques? The main difference is, you can compare, forget about element determination, inorganic elements; but among the organic compounds, so far, we have discussed the ultraviolet spectroscopy, for the determination of organic compounds; afterwards, we have not discussed, but spectrophotometry can also be used for the determination of organic substances present in a given matrix.

But taking a look at the ultraviolet and photospectrophotometry in contrast to ultraviolet spectroscopy, the infrared spectrum provides a rich array of absorption bands which can provide a wealth of structural information; that is, how the molecule is there, what type of functional groups are there etcetera, in a given molecule. So, it provides methods for studying materials in all three types of physical states; that is, either it can be gas, it can be a liquid or it can be a solid. Analytically useful IR spectrum covers the range of 15000 to 670 centimeters inverse; that is, after the after the visible spectral photometry, if you take a, remember, our discussion on the electromagnetic spectrum, starting from cosmic rays to micro waves and radio waves etcetera, this infrared range comes after the spectrophotometry; then we have a near infrared range, and then infrared range, and then far infrared range.

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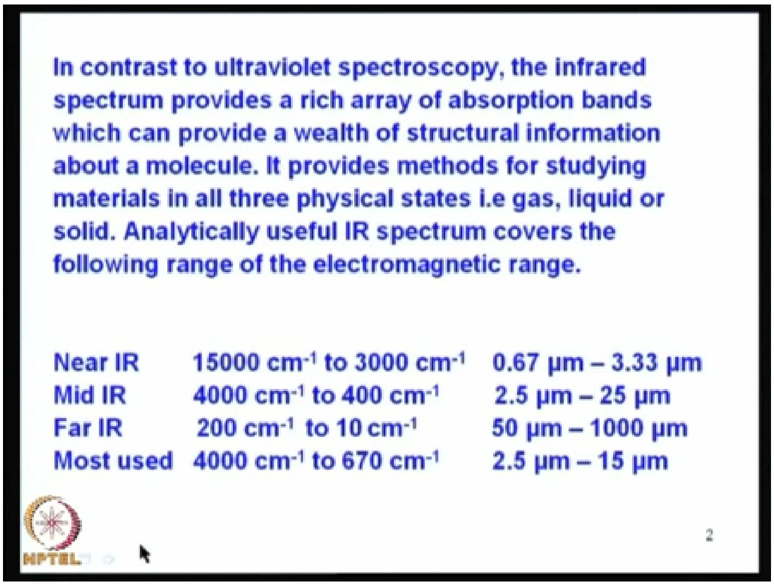

In contrast to ultraviolet spectroscopy, the infrared spectrum provides a rich array of absorption bands which can provide a wealth of structural information about a molecule. It provides methods for studying materials in all three physical states i.e gas, liquid or solid. Analytically useful IR spectrum covers the following range of the electromagnetic range.

Near IR	15000 cm^{-1} to 3000 cm^{-1}	0.67 μm – 3.33 μm
Mid IR	4000 cm^{-1} to 400 cm^{-1}	2.5 μm – 25 μm
Far IR	200 cm^{-1} to 10 cm^{-1}	50 μm – 1000 μm
Most used	4000 cm^{-1} to 670 cm^{-1}	2.5 μm – 15 μm

So, if you want to specify different ranges in the spectrum of infrared, you can see that, near infrared ranges is from 15000 centimeters inverse to 3000 centimeters inverse; and in terms of micrometers it is 0.67 to 3.33 micrometers. And the conversion, we have already discussed from centimeters inverse to 3.33 in the micrometers, earlier in our discussion on the spectroscopy. And, mid IR range is the one which starts from 4000 centimeters to 400 centimeters, inverse this is the range for mid IR. Most of the organic determinations infrared cover this range. Commercial instruments are available and maximum use corresponds to mid IR region, and in terms of micrometers, it is from 2.5 to 25 micro meters.

Then, there is a far infrared region, 200 centimeters inverse to 10 centimeters inverse; and this covers, this is equivalent to 50 micrometers to 100 micrometers; 1000 micro meters, not 100. And, this is used for coordinate complexes, metal and organic complexes, metal organic compounds; and most used is the 4000 to 670 centimeters inverse, you can even go up to 200 centimeter also some times, and this is the one range 2.5 to 15 micro meters.

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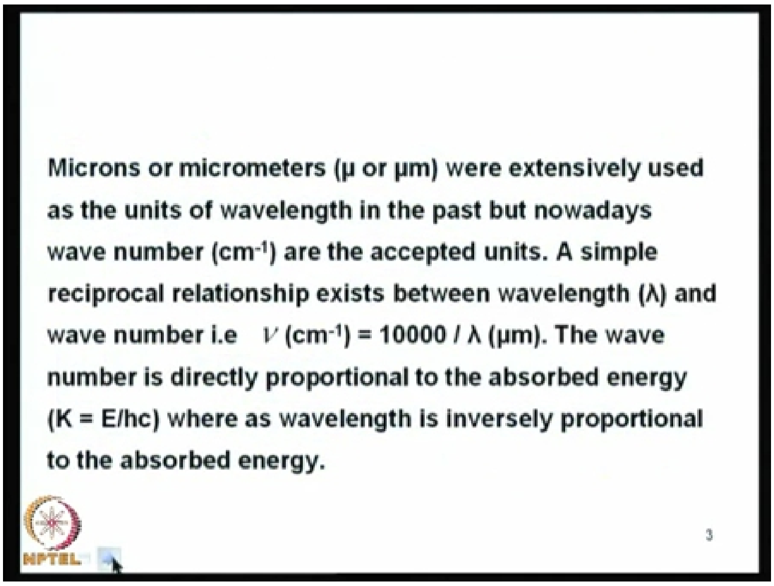

Microns or micrometers (μ or μm) were extensively used as the units of wavelength in the past but nowadays wave number (cm^{-1}) are the accepted units. A simple reciprocal relationship exists between wavelength (λ) and wave number i.e ν (cm^{-1}) = 10000 / λ (μm). The wave number is directly proportional to the absorbed energy (K = E/hc) where as wavelength is inversely proportional to the absorbed energy.

So, the microns or micrometers were extensively used as the unit of as the unit of wavelength in the past, but nowadays, it is the wave numbers that are the excepted units. And, everybody understands a wave numbers; it is more easy to remember; the ranges a good organic chemist usually remembers about 400 to 500 functional group frequencies automatically. But, for others, it may be slightly difficult, but still, we can take a look at different functional groups and form an idea about what sort of compounds it could it can be. A simple reciprocal relationship exists between the wavelength and wave number. So, what is that? That is, centimeter inverse is equal to 10000 divided by wavelength in micrometers; so, micrometers can be converted into centimeters and vice versa. The wave number is directly proportional to the absorbed energy, that is, K is equal to E by H C, that is a very standard formula; whereas, wavelength is inversely proportional to the absorbed energy, because, both these are reciprocal reciprocally related.

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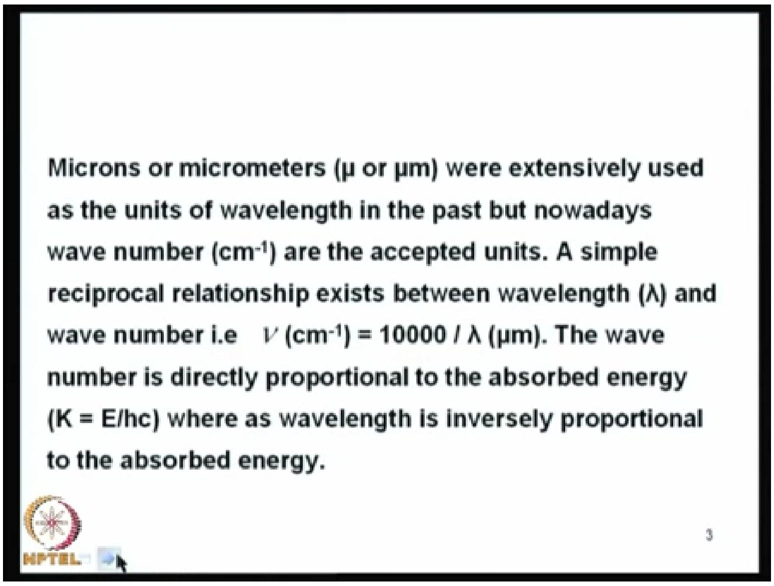

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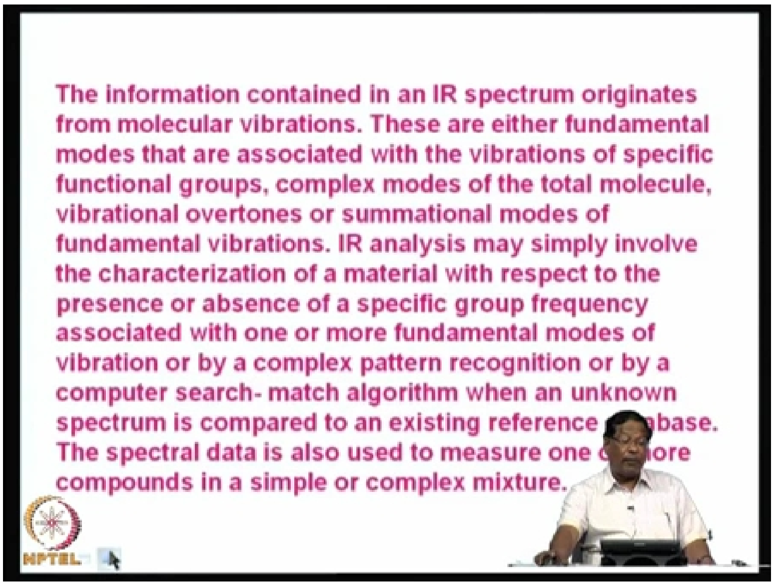

The information contained in an IR spectrum originates from molecular vibrations. These are either fundamental modes that are associated with the vibrations of specific functional groups, complex modes of the total molecule, vibrational overtones or summational modes of fundamental vibrations. IR analysis may simply involve the characterization of a material with respect to the presence or absence of a specific group frequency associated with one or more fundamental modes of vibration or by a complex pattern recognition or by a computer search- match algorithm when an unknown spectrum is compared to an existing reference base. The spectral data is also used to measure one o ore compounds in a simple or complex mixture.

So, there is nothing much to worry with respect to; you can choose either wave centimeters or centimeters inverse or the micro micrometers for depending upon your convenience and you can use; I personally prefer the micrometer range, I personally prefer not the micrometer but centimeters inverse, I personally prefer for my work. So, the information content in an infrared spectrum originates from the molecular vibrations; you can imagine a molecule containing different, different balls connected with springs; that is how a molecule should be imagined. So, the molecular the springs will keep on expanding and contracting, expanding and contracting, depending upon the amount of energy that is absorbed by the organic compounds.

So, there you will find a number of fundamental modes, they can be bonds, can be can be vibrating in different fashions; for example, they may be they may be stretching and contracting in the same plane or they may be moving back and forth like this; and then, these are all. Then, there could be complex modes of total molecular vibrational overtones; two vibrations can overlap, can combine to give another peak at double the wavelength or half the wavelength.

So, such things are also possible. So, IR analysis may simply involve the characterization of a material with respect to the presence or absence of a specific group frequency. If you get an IR peak at a non-position which is there, the compound is there, functional group is there. If you do not have IR spectra peak at a known position which corresponds to a particular functional group, that functional group is absent; that is how we go about using infrared. So, each frequency or absorption peak, what you obtain in IR is associated with one or more fundamental modes of vibration by a complex pattern recognition or by computer search match algorithm also you can use.

I have to tell you, that most of the commercial instruments, also have a computer data stored, so that, the given compound will automatically show, what are the peaks expected and where are the peaks expected. And, you can record the spectrum and simply submit it to the computer for just match matching or not non-matching; and the computer can give you use this search-match algorithms, when an unknown spectrum is compared to the existing reference data. So, there are a lot of databases which contain information about the spectrums of thousands and thousands of organic compounds. These databases are sometimes incorporated in the commercial instruments; otherwise, one can look for specific frequencies, what you would like to see.

So, when an unknown spectrum must be compared to the existing reference data, if it matches, you do not have to worry at all; you can say confidently that the given compound matches with such a known IR spectrum, and therefore, the curve, the compound what you are analyzing is that compound, if it matches exactly. The spectral data is also used to measure one or more compounds in a simple or a complex mixture, if the functional groups are different. Suppose, you have a mixture, where they have the similar functional groups, then you will not be able to use the search and match algorithms. So, one has to be slightly careful in determining this IR spectrum, where you are able to obtain the different peaks.

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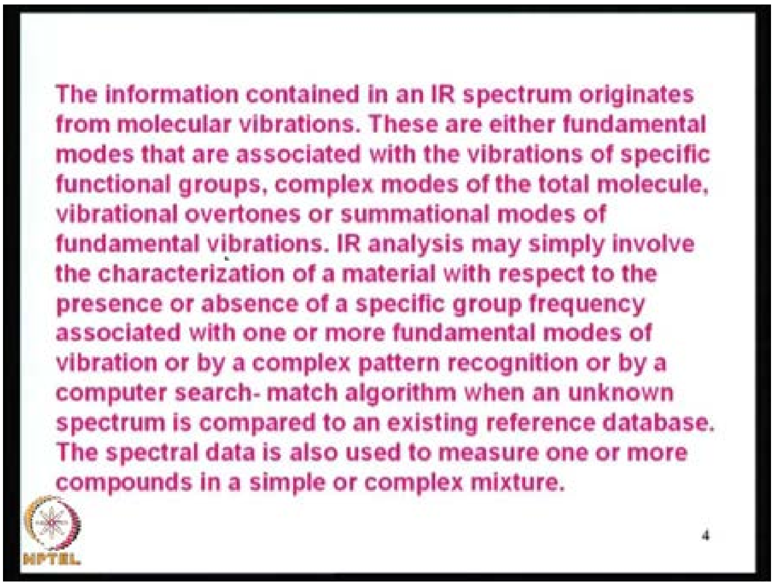

The information contained in an IR spectrum originates from molecular vibrations. These are either fundamental modes that are associated with the vibrations of specific functional groups, complex modes of the total molecule, vibrational overtones or summational modes of fundamental vibrations. IR analysis may simply involve the characterization of a material with respect to the presence or absence of a specific group frequency associated with one or more fundamental modes of vibration or by a complex pattern recognition or by a computer search- match algorithm when an unknown spectrum is compared to an existing reference database. The spectral data is also used to measure one or more compounds in a simple or complex mixture.

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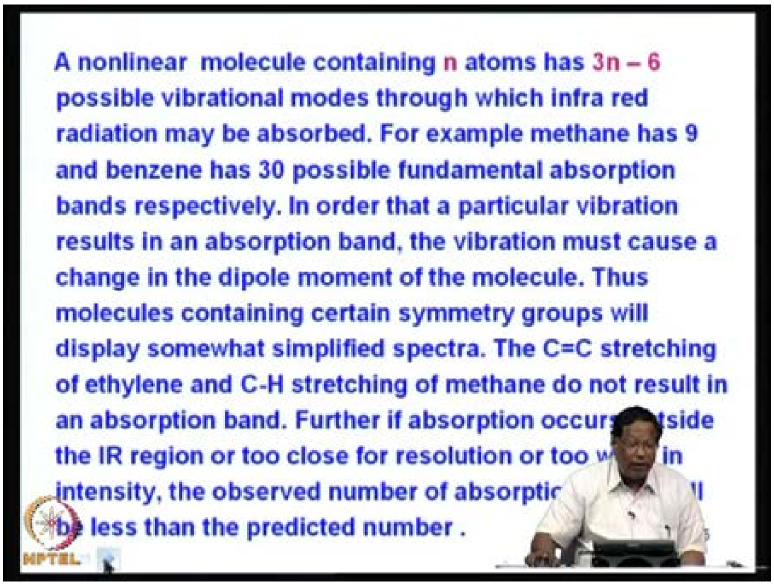

A nonlinear molecule containing n atoms has 3n – 6 possible vibrational modes through which infra red radiation may be absorbed. For example methane has 9 and benzene has 30 possible fundamental absorption bands respectively. In order that a particular vibration results in an absorption band, the vibration must cause a change in the dipole moment of the molecule. Thus molecules containing certain symmetry groups will display somewhat simplified spectra. The C=C stretching of ethylene and C-H stretching of methane do not result in an absorption band. Further if absorption occurs tside the IR region or too close for resolution or too w in intensity, the observed number of absorptic ll be less than the predicted number .

So, if you take a look at a non-linear molecule, I would like to remind you that a molecule containing n number of atoms will have 3n minus 6 possible degrees of freedom; that is, vibrational modes, through which infrared radiation may be absorbed. That means the degrees of freedom in which a molecule can vibrate, is 3n minus 6, if there are n number of molecules.

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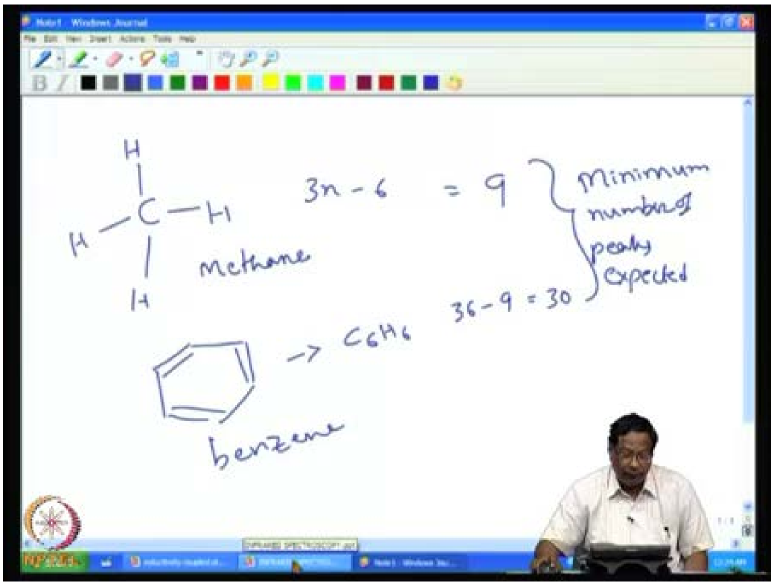

So, for example, methane 9 bands and benzene has got 36 peaks. For example, if you write methane like this, how many elements are there? 1, 2, 3, 4, 5. So, 3n minus 6, this works out to 9; so, 9 modes of vibration. Similarly, if you write benzene molecule, the formula for this is C 6 H 6. So, 12 atoms are there, so, 12 into 3 is thirty six. So, 36 minus 9 is 30. So, these are the minimum number of peaks expected. This is benzene, this is methane.

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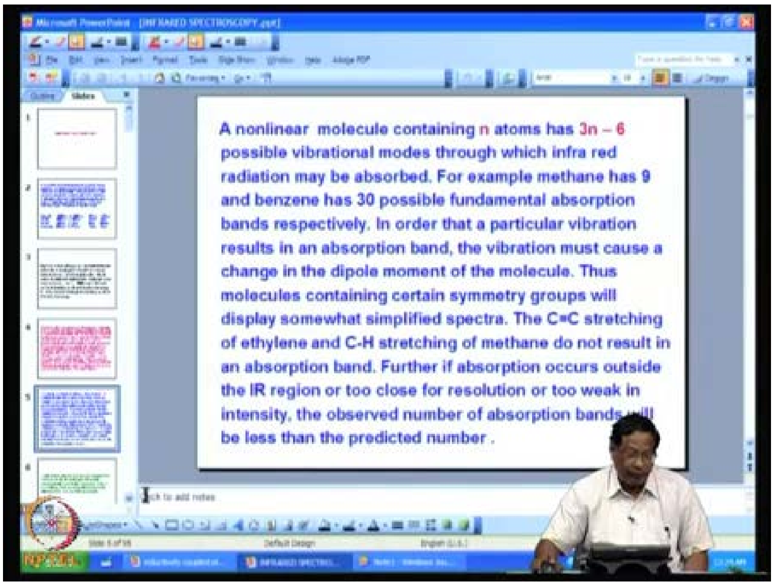

A nonlinear molecule containing n atoms has 3n – 6 possible vibrational modes through which infra red radiation may be absorbed. For example methane has 9 and benzene has 30 possible fundamental absorption bands respectively. In order that a particular vibration results in an absorption band, the vibration must cause a change in the dipole moment of the molecule. Thus molecules containing certain symmetry groups will display somewhat simplified spectra. The C=C stretching of ethylene and C-H stretching of methane do not result in an absorption band. Further if absorption occurs outside the IR region or too close for resolution or too weak in intensity, the observed number of absorption bands will be less than the predicted number .

So, similarly, as the complexity increases, you can see that, more number of atoms means more number of peaks expected for a given system. So, in order that a particular vibration results in an absorption band, the vibration must cause a change in the dipole moment of the molecule. If there is no change in the dipole moment of the molecule, there is no infrared absorption.

So, molecules containing certain symmetric groups will display somewhat simplified spectra; for example, the carbon-carbon stretching frequency, that is, in ethylene group, that is, carbon-carbon double bond present in ethylene and the carbon hydrogen stretching frequency of methane, they do not result in an absorption band; because, all the C-H bonds in methane are equivalent. So, they will all be stretching simultaneously, and then contracting simultaneously, when IR radiation impinges on the molecule, and there is no change in the dipole moment, because, the change in dipole moment occurs only when there is the asymmetric stretching; that is, one should be more, one should be less etcetera, the molecule must undergo some sort of a structural change in which the dipole moment must change.

So, further, if absorption occurs outside the IR region or too close for resolution or if it is too week, there are three possibilities; outside the IR region, it may occur; too close to each other, it may occur or the resolution may be too weak in intensity, the absurd number of absorption bands will be less than the predicted number. So, you could always say that, even though the minimum number is expected for methane is 9 and benzene is 30, the actual number of IR peaks, what you would see, would be much less if there is, if there is a possibility for the absorption bands occurring, some other occurring at outside the region or if it is too weak etcetera.

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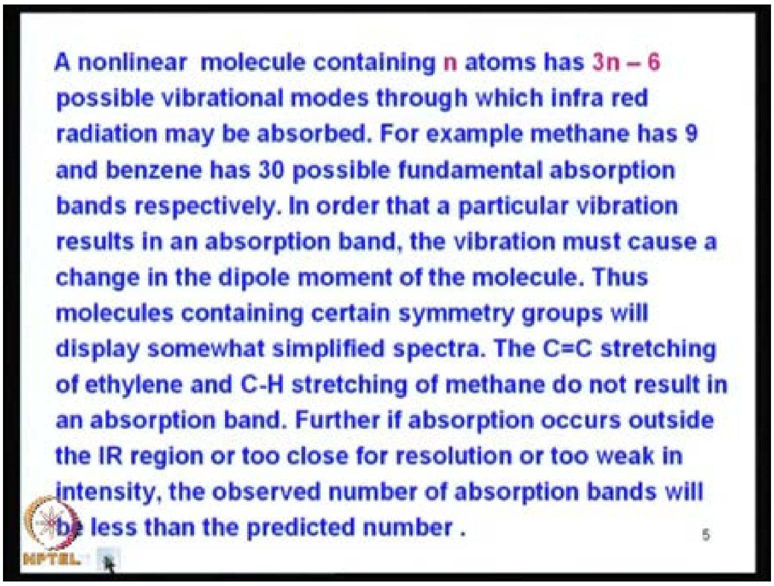

A nonlinear molecule containing n atoms has 3n – 6 possible vibrational modes through which infra red radiation may be absorbed. For example methane has 9 and benzene has 30 possible fundamental absorption bands respectively. In order that a particular vibration results in an absorption band, the vibration must cause a change in the dipole moment of the molecule. Thus molecules containing certain symmetry groups will display somewhat simplified spectra. The C=C stretching of ethylene and C-H stretching of methane do not result in an absorption band. Further if absorption occurs outside the IR region or too close for resolution or too weak in intensity, the observed number of absorption bands will be less than the predicted number .

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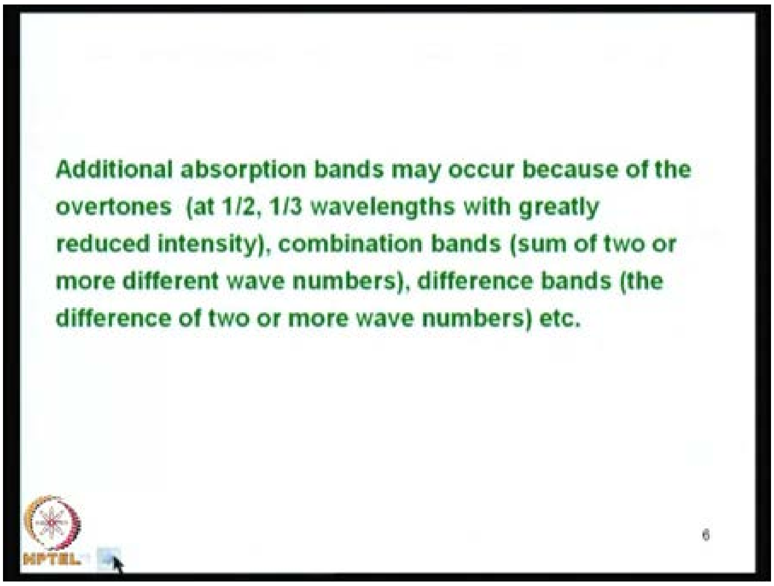

Additional absorption bands may occur because of the overtones (at 1/2, 1/3 wavelengths with greatly reduced intensity), combination bands (sum of two or more different wave numbers), difference bands (the difference of two or more wave numbers) etc.

So, you may also see additional absorption bands may occur because of the overtones; that is, suppose, we have discussed this presence of overtones earlier, because, when we were discussing gratings, and you will see that an overtone band may appear at one-third and one-half wavelengths with greatly reduced to intensity; such combination bands sometimes do fall in the IR region itself, giving you some amount of confusion, arae, where is this peak coming from? Even though it is not expected, suddenly, you will see an overtone band which is of lower intensity, you will not be able to assign. So, if the overtone if the overtone is possible, one has to be careful.

Then, we may have combination bands; that is, sum of two or more different wave numbers. Suppose, there are some of the compounds which are which will reduce the IR frequency absorption; like in ultraviolet, we have discussed a similar situation, where conjugation in diens and dinons and then aldehydic groups etcetera, they do result in the reduced appearance of a wavelength at longer wavelength appearance of a peak at longer wavelengths.

So, such possibility is there. Then, there are there is a possibility for different band, difference bands; that is, two or more wave numbers, the difference; that also may appear as a consequence of infrared absorption. So, the molecular vibrations, what we have been taking about since such a since last few minutes, I would like to say, that a molecule, you should always remember, that in infrared, in the infrared region, a system, a molecule must essentially resemble a system of balls of varying masses; that is, hydrogen is 1, and then oxygen is 8, carbon is 12 and like that different atomic masses of elements combine to give you an organic compound. So, the range in which the wavelength, in which they are, the atoms are organized in a given organic compound, depends upon the bond length; and the bond length, the strength of the bond also varies depending upon the functional groups.

So, there are two kinds of fundamental vibrations in a given molecule. One is stretching frequency; just like what I was trying to tell you in the same axis, it is just like pulling a rubber band, holding it in your hand and pull it both sides, that is known as stretching frequency. And then, you take you take a spring on which put a ball and then shake it, and then it will be moving above; that is in the vertical plane. So, there are basically two types of infrared frequencies which you will be able to recognize in infrared spectrum.

For example, one is stretching, in which the distance during stretching, what happens? The distance between the two atoms increases or decreases, but the atoms remain in the same bond axis; that is stretching frequency. And then, bending frequency is the one in which the position of the atoms changes with respect to a predetermined axis; that is bond axis.

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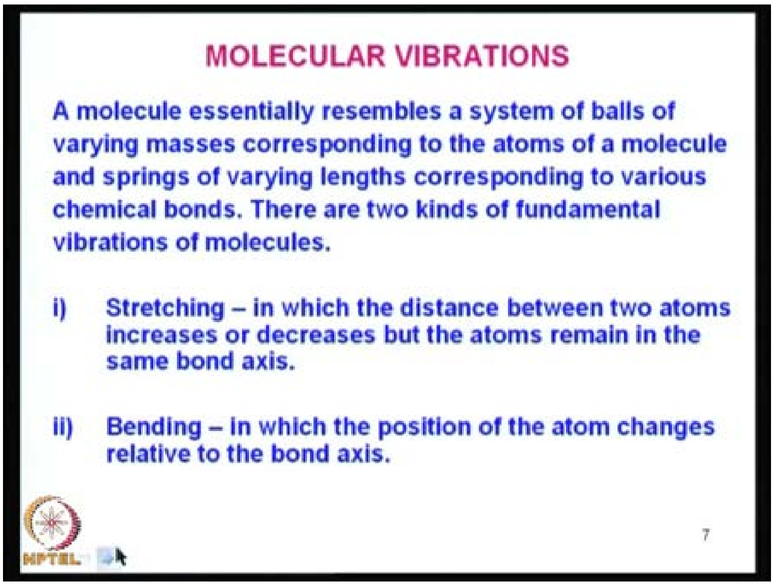

MOLECULAR VIBRATIONS

A molecule essentially resembles a system of balls of varying masses corresponding to the atoms of a molecule and springs of varying lengths corresponding to various chemical bonds. There are two kinds of fundamental vibrations of molecules.

i) Stretching – in which the distance between two atoms increases or decreases but the atoms remain in the same bond axis.

ii) Bending – in which the position of the atom changes relative to the bond axis.

So, you can see that the bond axis, in general, you will see that changes during bending operations.

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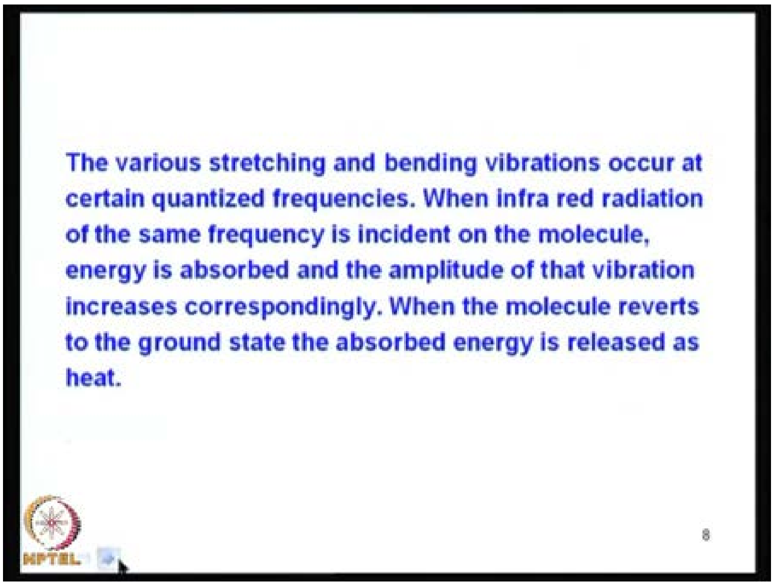

The various stretching and bending vibrations occur at certain quantized frequencies. When infra red radiation of the same frequency is incident on the molecule, energy is absorbed and the amplitude of that vibration increases correspondingly. When the molecule reverts to the ground state the absorbed energy is released as heat.

So, the various stretching and bending vibrations occur always at some certain quantized frequencies. This, you should never forget, because, in most of the spectroscopic techniques are put on a great foundation of quantum mechanics; so, when infrared radiation of the same frequency is incident on the molecule, the energy is absorbed and the amplitude of the vibration increases correspondingly. When the molecule reverts to the ground state, what happens? The absorbed energy is released as heat; there is no other way the absorbed energy can be used up.

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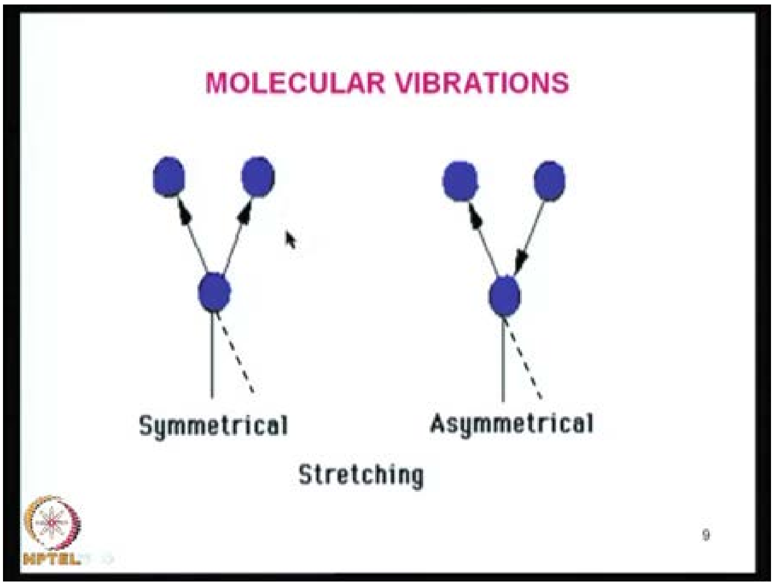

MOLECULAR VIBRATIONS

Symmetrical

Asymmetrical

Stretching

So, if you look, take a look at the molecular vibrations, take a look at the slide, I have, we have, I have 3 atoms here, 3 balls. Of course, you have to assume that they could be of the same element or they could be of the different elements, and this is known as stretching frequency. These two are known as stretching frequencies, in which the atoms could be stretching at the simultaneous, simultaneously. That is, for example, if you look at my hand operations, for example, if I pull them, both stretching and both could be stretching simultaneously. But another possibility exists, that one could be stretching, another could be contracting. So, two possibilities are there during stretching operations.

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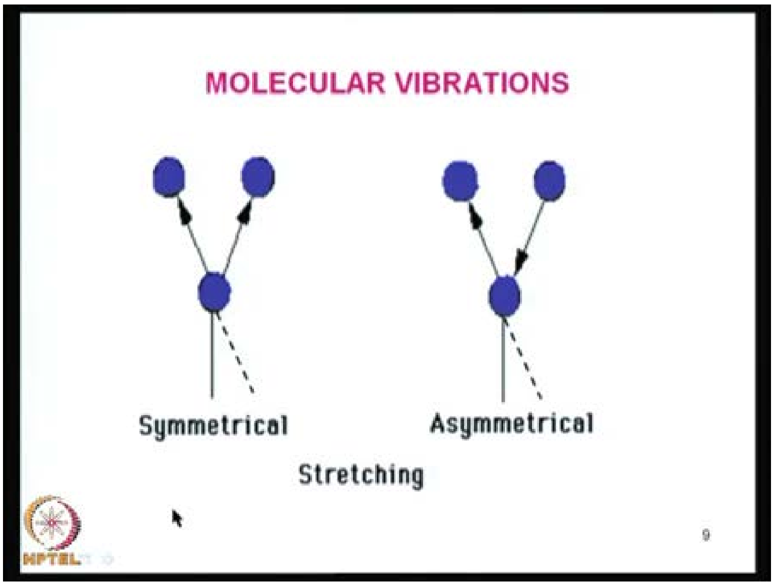

MOLECULAR VIBRATIONS

Symmetrical

Asymmetrical

Stretching

So, when you when you take a look at this slide again; here, both molecules are stretching away from the central molecule; whereas, in this case, one is stretching away and another is stretching towards; so, these two possibilities always exist in infrared spectrum.

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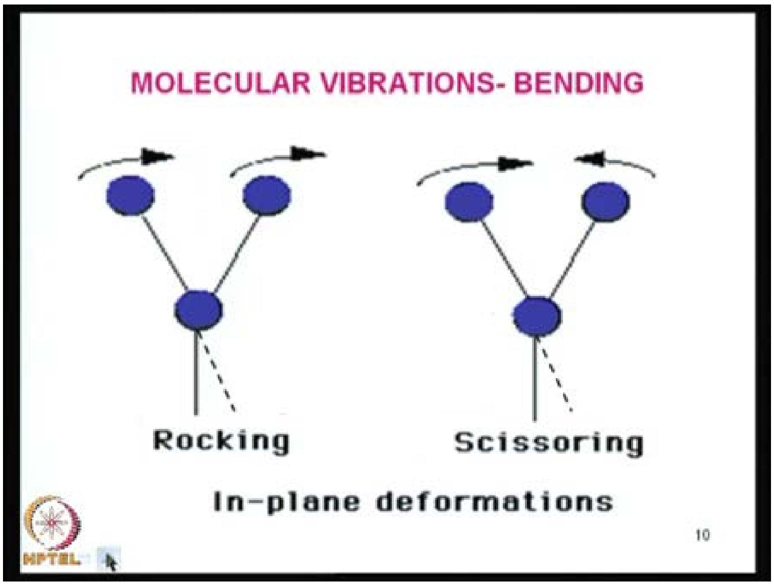

MOLECULAR VIBRATIONS- BENDING

Rocking

Scissoring

In-plane deformations

Now, I come to bending vibrations. So, they could be in plane deformations, for example, if you take a look at my hand moments, you will see that they are they could be stretching in the same plane, that is, vertical plane. They could be stretching in same way, so, they could be going towards both of the molecules or they could be going like this or one could be going like this; one could be coming out, one could be stretching, another could be contracting.

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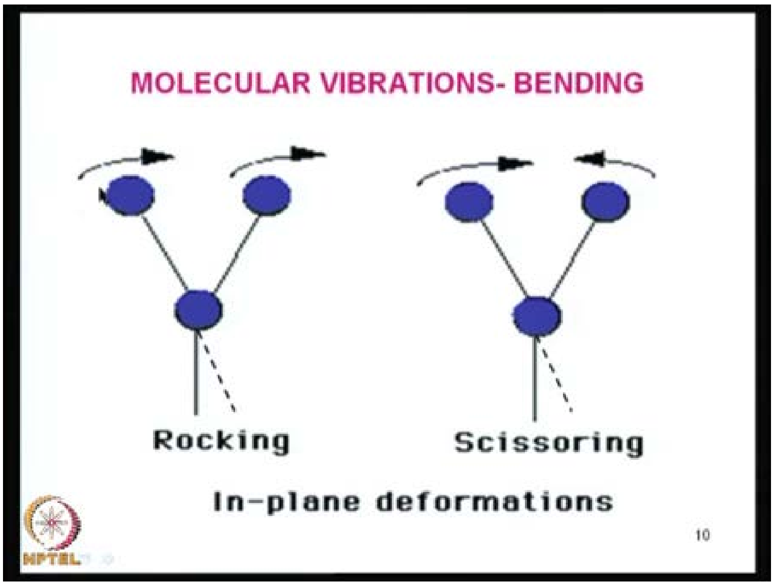

MOLECULAR VIBRATIONS- BENDING

Rocking

Scissoring

In-plane deformations

10

So, the again there are two possibilities; here, one is, this is known as rocking; when both elements, both the atoms are moving in the same direction, but there are all in the same plane; and here, they are trying to come nearer; one is stretching, another is contracting.

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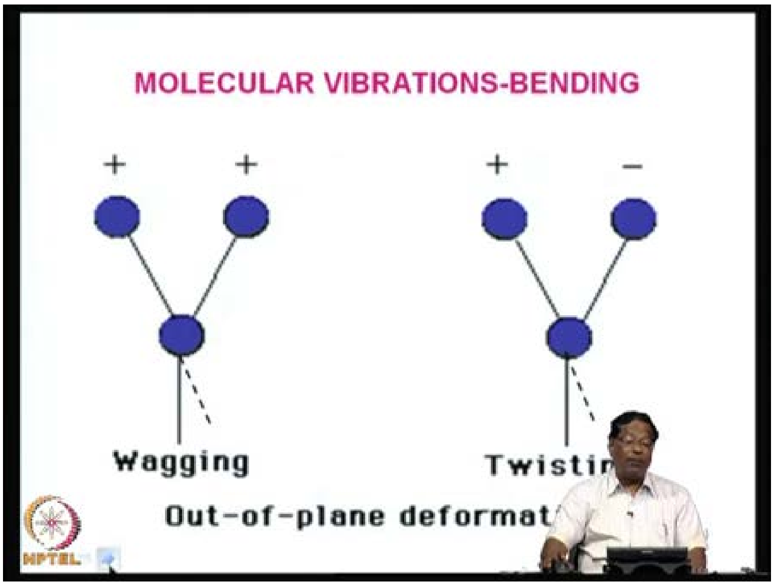

MOLECULAR VIBRATIONS-BENDING

Wagging

Twisti

Out-of-plane deformat

So, these two possibilities are there. And, another possibility is like this; that is, if I show you by hand, like this, that what you would be observing not in plane, but out of plane; that is, both of them could be going back and forth. Earlier, I had shown you like this, stretching is like this; and in plane, by an in-plane is like this, they are going in the same plane; and out of plane is, they could be coming towards, you are towards you. As an observer or they could be going back or one could be coming towards you, and one could be going away from each other.

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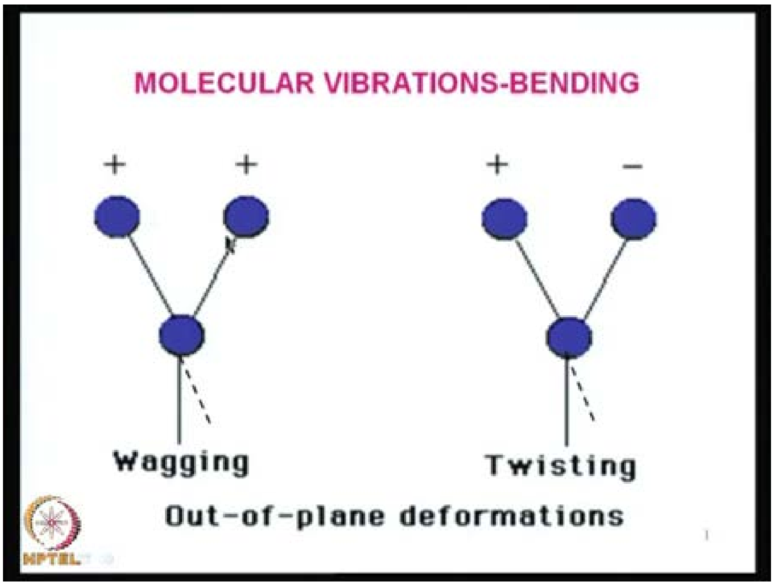

MOLECULAR VIBRATIONS-BENDING

Wagging

Twisting

Out-of-plane deformations

So, this is known as wagging. When both are approaching the observer in the same, in the different planes; and here, it could be, one could be coming towards you and one could be going away from you.

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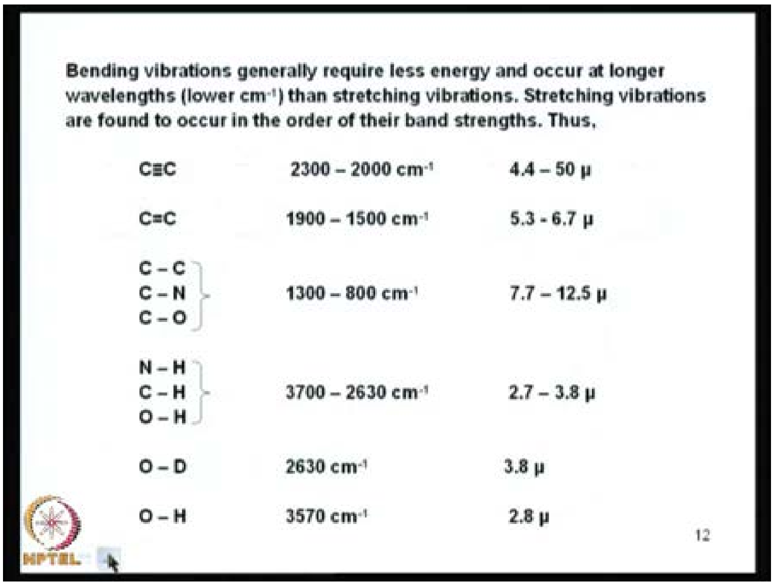

Bending vibrations generally require less energy and occur at longer wavelengths (lower cm^{-1}) than stretching vibrations. Stretching vibrations are found to occur in the order of their band strengths. Thus,

C≡C	2300 – 2000 cm^{-1}	4.4 – 50 μ
C=C	1900 – 1500 cm^{-1}	5.3 - 6.7 μ
C – C C – N C – O	1300 – 800 cm^{-1}	7.7 – 12.5 μ
N – H C – H O – H	3700 – 2630 cm^{-1}	2.7 – 3.8 μ
O – D	2630 cm^{-1}	3.8 μ
O – H	3570 cm^{-1}	2.8 μ

So, these are the different kinds of bending vibrations. In general, bending vibrations require less energy than stretching frequencies, because, for stretching, you need more energy to pull them; but bending energy requires very less energy. So, if they require less energy, where should the bond occur? Towards the longer wavelength region. If it energy intensive process will occur towards the shorter wavelength region.

So, the stretching vibrations, in general, require, appear, that is, stretching frequencies will appear at shorter wavelengths, and then bending vibrations will occur at the longer wavelength in a given infrared spectrum. So, the stretching frequency vibrations are also found to occur in the order of their bond strength. A single bond, you can imagine different types of bonds present in a given molecule; that could be a single bond, double bond, triple bond etcetera.

So, in general, triple bond means molecules are the, inter-molecular distances are very less; that means, the molecules or atoms are held very, very strongly; and compared to that, a double bond would be held less strongly and single bond would be held; bond length would be longer, so, they would be held still less strongly.

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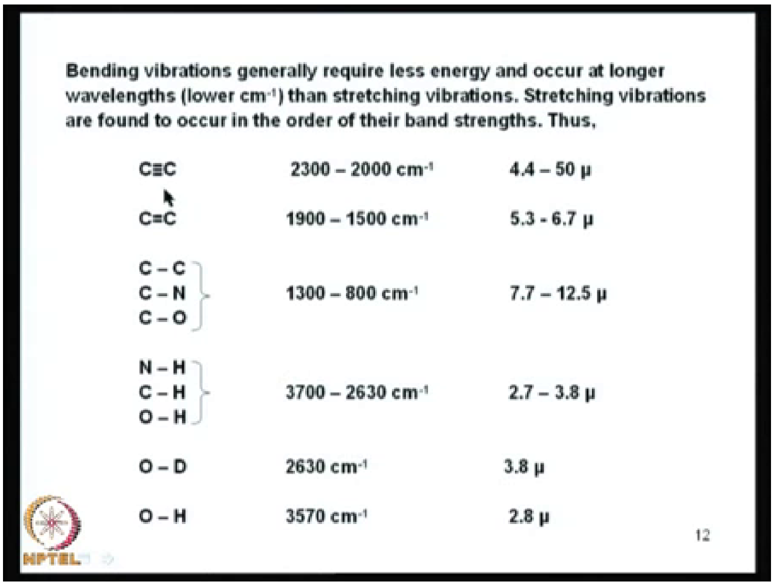

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So, if you take a look at carbon-carbon triple bond, here you can see that the wavelength is 2300 to 2000 centimeters inverse. In this range, carbon-carbon triple bond frequency is expected. Compared to that, look at carbon-carbon double bond; here, it appears at 1900 to 1500 centimeters inverse. So, if you have a compound in which a stretching frequency appears in this range 1900 to 1500 range, you can see that it could be a, you can infer actually, that it is a double bond; it is not, it is an ethelenic compound; it is not an acetylenic compound.

Similarly, if you take stretching frequencies of carbon-carbon single bond, carbon-nitrogen, double bond, single bond and carbon-oxygen single bond, you can see that the range is 1300 to 800 centimeters inverse, still lower longer wavelengths; and then, if you take hydrogen, here, I am putting all the hydrogen in as common, and here, I am changing nitrogen, carbon and oxygen; this stretching frequencies occur around 3700 to 2063 centimeters inverse.

You do not have to remember all these numbers, but with practice, it will come; but it will be good to know that stretching frequencies are always more energy intensive. So, suppose, I change this hydrogen to deuterium, then what happens? The range is 2630 and O-H stretching frequency actually is 3570 centimeters inverse. You can see that it is the heavier atom and it could be more symmetrically matched, and less energy is required;

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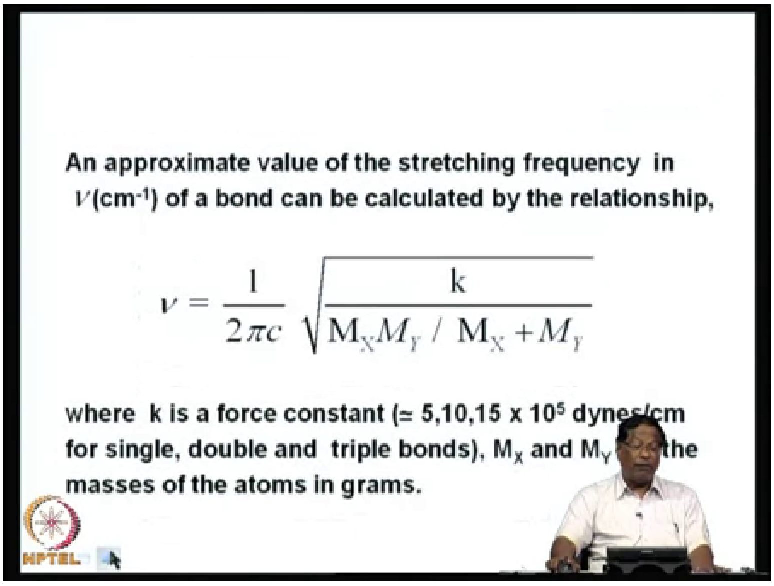

An approximate value of the stretching frequency in ν(cm^{-1}) of a bond can be calculated by the relationship,

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{k}{M_X M_Y / M_X + M_Y}}$$

where k is a force constant ($\simeq$ 5,10,15 x 10^5 dynes/cm for single, double and triple bonds), M_X and M_Y the masses of the atoms in grams.

Like that, we can infer lot of, you can, information. You can get lot of information depending upon the presence of peaks either due to stretching frequency or due to bending frequency single bond, double bond and then, same atom different atom. So, it is always like this, that you keep on getting lot of information. So, where is the bottom line? The bottom line is an approximate value of the stretching frequency; is it possible for us to calculate or not? To know, by theory, the answer is, yes. You can calculate where a frequency is expected provided you use this formula.

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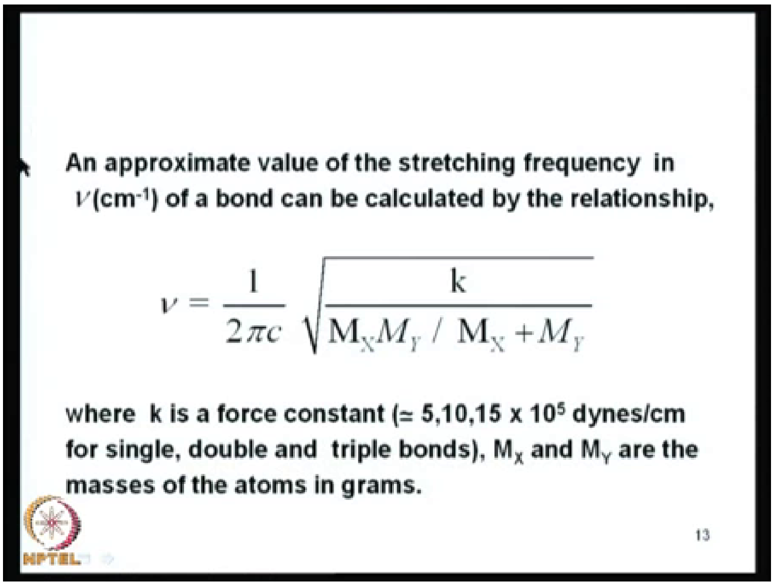

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where k is a force constant ($\simeq$ 5,10,15 x 10^5 dynes/cm for single, double and triple bonds), M_X and M_Y are the masses of the atoms in grams.

The frequency is given by 1 over 2pi c square root of k divided by Mx My divided by Mx plus My. Here, it may look very complicated to you, but actually it is not. Here, k represents a force constant, that is the strength of the bonds, approximately for single bond, double bond and triple bond, it is about 5, 10, 15 into 10 raised to 5 dyne per centimeter. For single bond, it is 5, for double bond it is 10 and for triple bond it is 15; and 10 raised to 5 dynes per centimeter is common. And, you know the other numbers; this is frequency, and pi is 3.142, and C is the velocity of light, and this Mx and My are the atomic masses present in the compound. So, Mx My and Mx divided by Mx plus My; this quantity is known as reduced mass.

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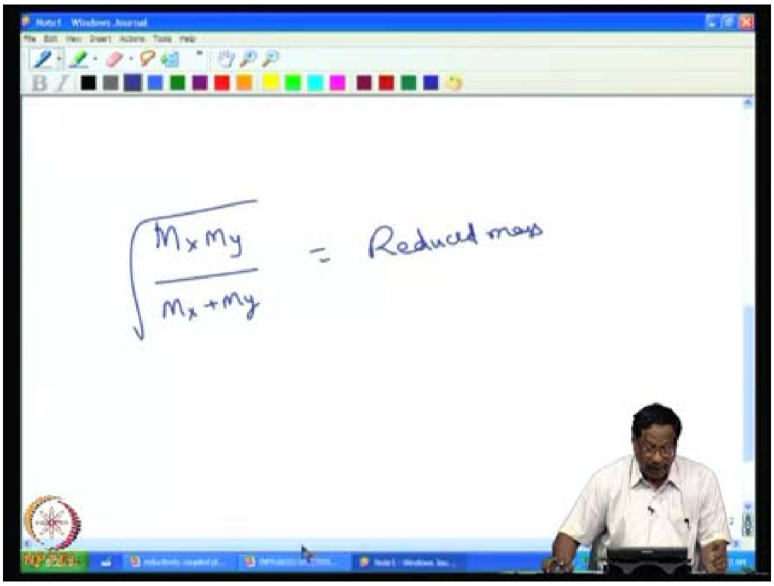

$$\sqrt{\frac{M_x M_y}{M_x + M_y}} = \text{Reduced mass}$$

You can write like this; Mx My divided by Mx plus My square root; this is known as reduced mass, this is a consequence of the quantum mechanical calculations and information.

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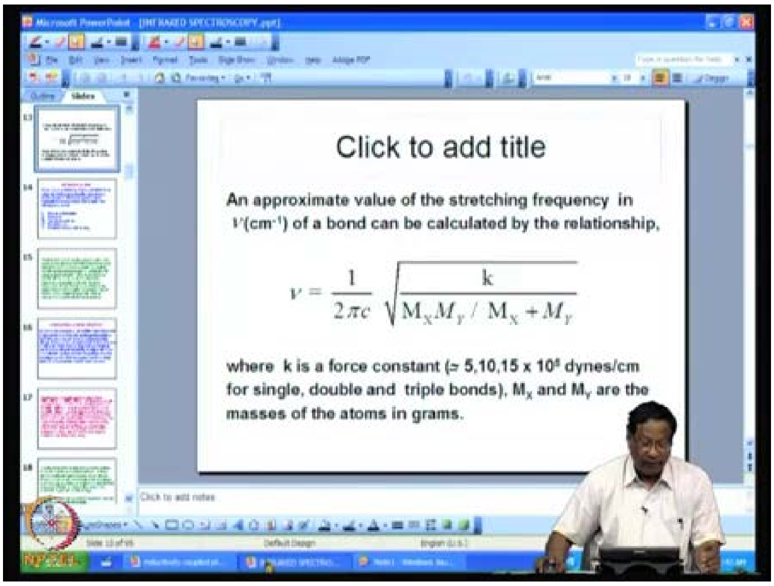

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An approximate value of the stretching frequency in $\nu(\mathrm{cm}^{-1})$ of a bond can be calculated by the relationship,

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{k}{M_X M_Y / M_X + M_Y}}$$

where k is a force constant ($\approx$ 5,10,15 x 10^5 dynes/cm for single, double and triple bonds), M_X and M_Y are the masses of the atoms in grams.

You can simply calculate using the atomic numbers, and then you can see that the reduced masses must be used to approximately guess or exactly guess the infrared spectrum. But, of course, it is not always at the expected place because of several other constraints like the presence of solvents and interactions; solvent-solvent interactions, solute-solvent interactions etcetera. But, in general, you can guess where a compound or a given bond should absorb infrared region frequency.

Now, let us come to the instrumentation. In most of the modern commercial instruments, infrared instrument fall into three categories. One is grating dispersive, another is filter dispersive and another is Fourier transform infrared spectrometer. These are different kinds of commercial instruments. Whatever be the type of instrument, what you need essentially are the main optical system is what you need; and then, you need a source of infrared energy, and you need a separate sample compartment in which to place your sample take it out etcetera, and a you need a detector to gauze the changes in the infrared spectrum energy and the electronics and data handling, nowadays, part and parcel of most of the equipment.

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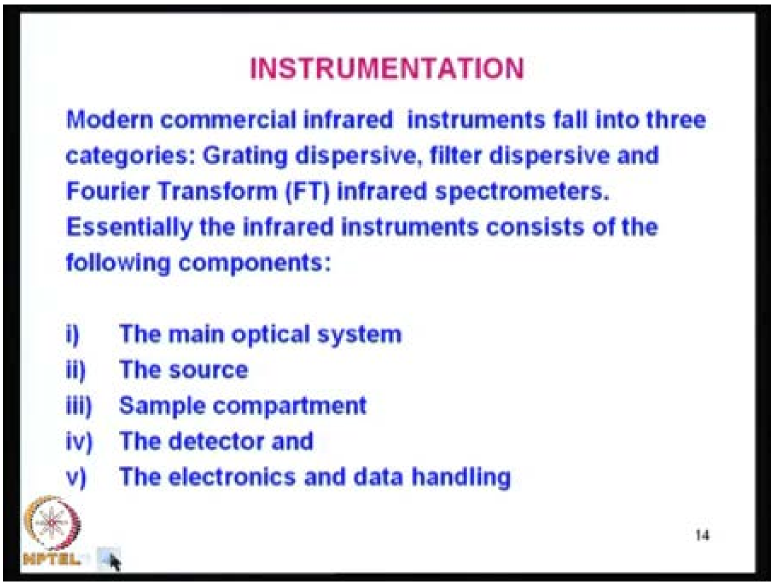

INSTRUMENTATION

Modern commercial infrared instruments fall into three categories: Grating dispersive, filter dispersive and Fourier Transform (FT) infrared spectrometers. Essentially the infrared instruments consists of the following components:

i) The main optical system
ii) The source
iii) Sample compartment
iv) The detector and
v) The electronics and data handling

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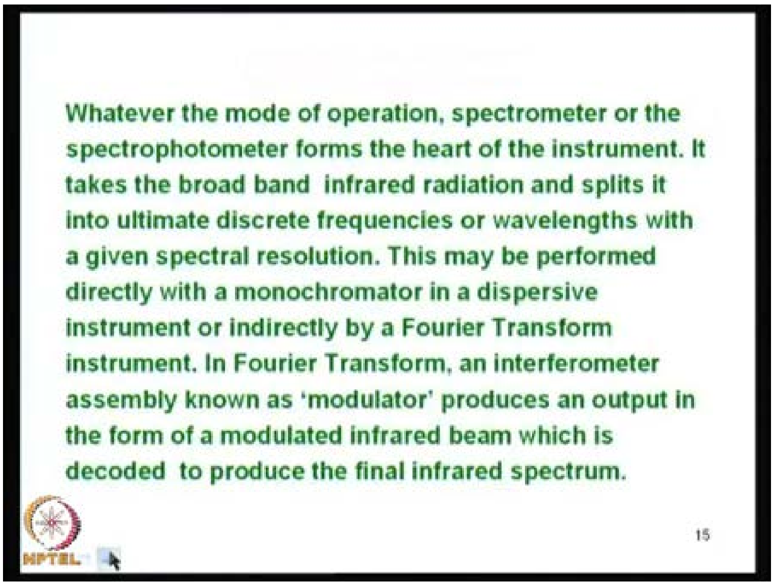

Whatever the mode of operation, spectrometer or the spectrophotometer forms the heart of the instrument. It takes the broad band infrared radiation and splits it into ultimate discrete frequencies or wavelengths with a given spectral resolution. This may be performed directly with a monochromator in a dispersive instrument or indirectly by a Fourier Transform instrument. In Fourier Transform, an interferometer assembly known as 'modulator' produces an output in the form of a modulated infrared beam which is decoded to produce the final infrared spectrum.

So, whatever the forms of operation, mode of operation, the spectrometer forms the heart of the instrument. It takes the broadband infrared radiation, and spectrometer cuts into different wavelengths, so that, you can tune the different wavelengths and then choose what wavelength range goes through your sample.

So, it splits into ultimate discrete frequencies or wavelengths with a given spectral resolution. This may be performed directly with a monochromator; you can do it in a dispersive monochromator in a dispersive instrument or you can do indirectly by Fourier transform instrument. We will see in, we will see what is Fourier transform instrument, after a short while in Fourier transform, what you use is, an interferometer assembling, that is, it is known as modulator, it produces an output in the form of a modulated infrared beam, which is decoded to produce the final infrared spectrum. It is more of a mathematical operation, but nevertheless, it is a great advance in the IR instrumentations. So, among the monochromator instrumentation - we will come back to Fourier transform once again after some time - among the monochromator instruments, the monochromator’s range, from simple filter based instruments, you can just use source filters, and then, infrared sample compartment and optics; and you can use double prism grating instruments, double prism grating- grating, two grating instruments you can use.

And then, both Litro and Czerny-Turner mountings are useful. Although, the former is more useful, because Litro is more compact, and which is, provided, the earlier instruments were mostly prism based, which provided simple wavelength scan in micrometer; that is, that is, linear scale, basically, non-linear scale in a prism. And, nowadays, Litro designs with one or more diffractions grating we are using, and the gratings are driven by very small, small increments using a stepper motor, which is programmed into non-linear fashion to produce a linear output in wave numbers. That means, you move the motor non-linearly to see that, with every movement of the motor, you get a linear increment in the wavelength; it is possible.

Very simple and commercial instruments, they all do this very routinely and the full range of a grating spectrometer may be 4000 to 6600 centimeters inverse. You can buy an instrument from 4000 to 6600 centimeters inverse or 500 to 200, 5000 to 200 centimeters inverse; both are useful for infrared spectrum. Gratings are normally operated in second or third order; usually spectrums in 4000 to 2000 centimeters inverse are operated always in the second order; whereas, 2000 to 400 centimeters inverse wavelength range, you should operate in the first order.

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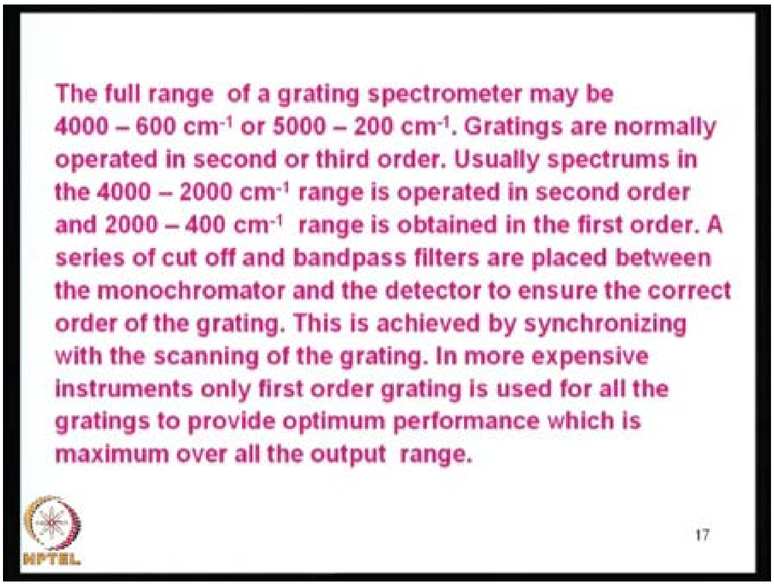

The full range of a grating spectrometer may be 4000 – 600 cm^{-1} or 5000 – 200 cm^{-1}. Gratings are normally operated in second or third order. Usually spectrums in the 4000 – 2000 cm^{-1} range is operated in second order and 2000 – 400 cm^{-1} range is obtained in the first order. A series of cut off and bandpass filters are placed between the monochromator and the detector to ensure the correct order of the grating. This is achieved by synchronizing with the scanning of the grating. In more expensive instruments only first order grating is used for all the gratings to provide optimum performance which is maximum over all the output range.

A series of cut offs and band pass filters are placed between the monochromator and the detector to ensure that the correct order of the wavelengths is maintained; that means, if you have from 5000 to 200 centimeters inverse, you should automatically change from second order rating to first order rating output. So, this is achieved automatically by synchronizing with this canning of the grating; the grating will be moving slowly in the second order; the moment it comes to a particular wavelength, it will change to first order, so that, you can have a good control over the wavelength accuracy. In more expensive instruments, only first order rating is used, because, that is the most accurate for all the gratings to provide optimum performance, which is maximum over all the output range; because, in the first order, only you will get the maximum output range.

So, a grating blazed at two angles perform as two gratings. You do not have two have two different gratings, but you can blaze them at two different angles, and a dry wage reproducible by 0.01 centimeters inverse.

So, will continue our discussion on this, after, in the next class.

Thank you very much.