Trace and ultra trace analysis of metals Using atomic absorption spectrometry

Dr. J R Mudakavi
Department of Chemical Engineering
Indian Institute of Science, Bangalore

Lecture - 35
Methods, Nomenclature and techniques: Individual Elements

Greetings: from today onwards in the next 2 or 3 classes what we will do is we will talk about the analysis or analytical chemistical aspects of atomic absorption spectrophotometry.

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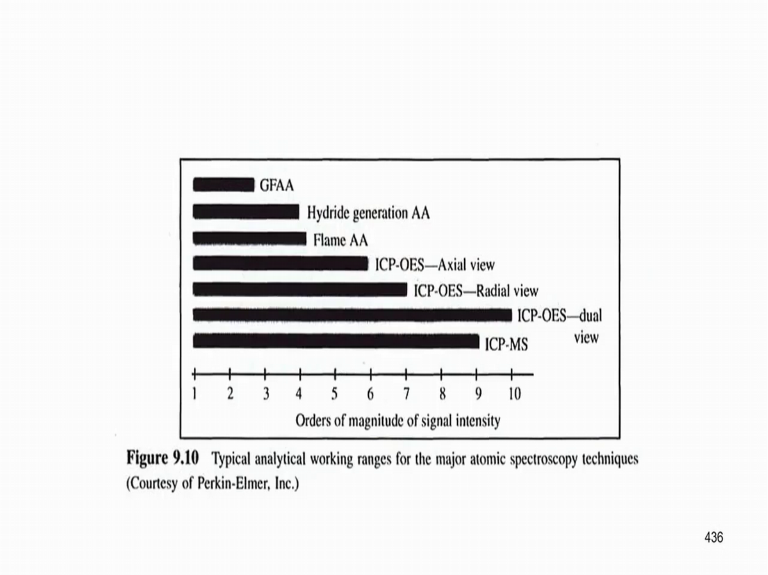

Figure 9.10 Typical analytical working ranges for the major atomic spectroscopy techniques (Courtesy of Perkin-Elmer, Inc.)

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So, here I am presenting you some of the nomenclatures detection limits methods and the application of atomic absorption that will complete the course. So, in general what we are going to do is we are going to see the atomization conditions analysis conditions compare them with other hydride generation cold vapor mercury and electro thermal atomic absorption etcetera followed by some nomenclature to. We should be very familiar if you want to work in atomic absorption spectrometry and then we will go to the applications in various diverse fields where atomic absorption is normally employed or preferably employed.

So, here is the comparison of the signal intensity. So, we can see I have plot the plotted 1 to signal intensities 1 to 10 these are the order of magnitude; that means, if I have a graphite signal atomic absorption signal about point about 25 percent the same signal will be approximately double if I use hydride generation, but you have to remember that hydride generation AAs is not suitable for all elements similarly flame is atomic absorption signal intensity is always higher than hydride generation AAs look at the ICP OES this is inductive couple plasma optical emission spectroscopy it is also known as ICP OES or ICP MS also there. So, if in ICP OES that is inductive couple plasma the signal handling can be up to 6 times that is this is about 3 times ICP OES is 6 times ICP OES radial wave is about 7 it is on around 7 and dual wave is about 10 and ICP MS is about 9.

So, this slide will show you the capabilities of signal handling in atomic absorption and other related techniques of elemental analysis metal analysis conditions.

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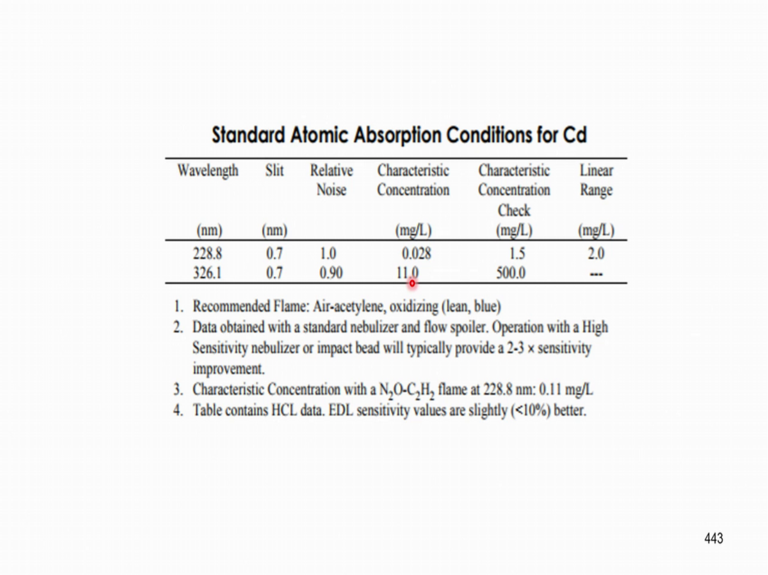

Standard Atomic Absorption Conditions for Cd

Wavelength (nm)	Slit (nm)	Relative Noise	Characteristic Concentration (mg/L)	Characteristic Concentration Check (mg/L)	Linear Range (mg/L)
228.8	0.7	1.0	0.028	1.5	2.0
326.1	0.7	0.90	11.0	500.0	---

1. Recommended Flame: Air-acetylene, oxidizing (lean, blue)
2. Data obtained with a standard nebulizer and flow spoiler. Operation with a High Sensitivity nebulizer or impact bead will typically provide a 2-3 × sensitivity improvement.
3. Characteristic Concentration with a N_2O-C_2H_2 flame at 228.8 nm: 0.11 mg/L
4. Table contains HCL data. EDL sensitivity values are slightly (<10%) better.

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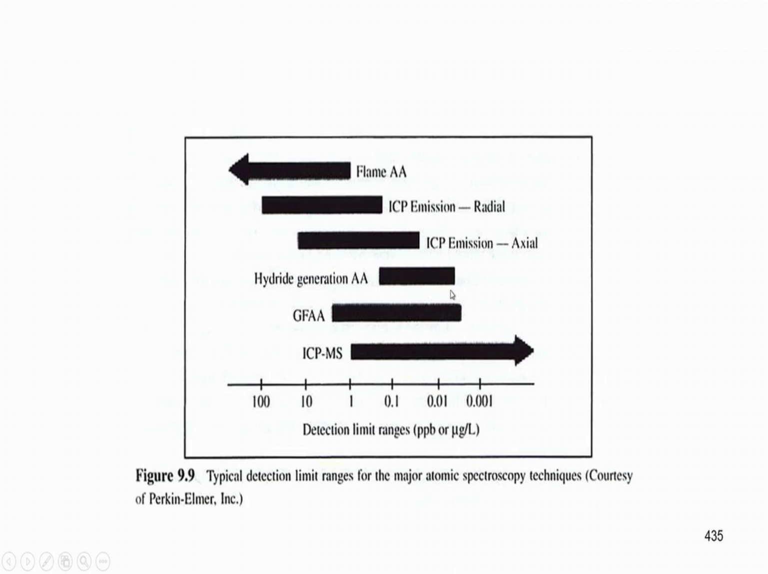

Figure 9.9 Typical detection limit ranges for the major atomic spectroscopy techniques (Courtesy of Perkin-Elmer, Inc.)

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Now this is the slide I wanted to show you in the flame (Refer Time: 03:28) detection limit ranges I am writing here in the detection limits what we have is flame atomic absorption limits. So, the minimum you can go is about 100 ppb that is the detection limit that is the back side you should see. So, up to 100 ppb you can work; that means, all the elements that can be determined using flame atomic absorption detection limits are of the order of 1 ppb to 100 ppb that is for flame detection limit; that means, the absorbance should correspond to 0.004.

So, that is the that is actually theoretical limit of signal handling, but determination limit would be approximately 100 times more than this similarly you look at ICP detection limit is approximately about 0.7 or 0.8 detection limit ppb 0.8 ppb and then it can handle up to 100 ppb the range of detection limits for all elements fall within 0.8 to 100 ppb minimum detection limit look for ICP emission it is about 0.02 or something like that up to 10 ppb look at hydride generation detection limit ranges from 0.001 approximately 0.005 that is 5 ppb that is 5 parts per trillion and then it goes up to 0.1 or 0.12 is the detection limit the all their detection limits of all the elements that is arsenic selenium tellurium and bismuth all the detection limits are in this range for graphite furnace it goes still further a little bit. So, it is about 0.001 ppb that is almost 1 ppb and then the maximum range of detection for the worst element would be somewhere between 1 to 10 ppb that is approximately 5 ppb for ICP MS there is the limit go still down that is it the range is from 1 ppb to 0.0001 ppb or something like that.

So, if you want to determine elements in parts per million I am taking 1000 times detection limit parts per million range flame is your technique preferred choice and then ICP emission still lower you can work and ICP radial excel hydride generation is stick only to arsenic, selenium, bismuth, tellurium, etcetera, hydride forming including lead and mercury nobody does this cold vapor mercury is only specific for atomic absorption graphite furnace of course, it is a for ppb quantitative determinations and then ICP MS would be quantitative in still lower range.

Now what we will see is a the practice of atomic absorption analysis these areas I had taken these. Next 10 to 20 slides I had taken from presently available manuals from the manufacturers I for reasons of copyright etcetera I will not reveal what are the which a instrument this data is taken from, but you can say that 99 percent of the information will be available whenever in as a manual or on the CD or in the data base in the computer when you buy an atomic absorption, but what information you should look for that is the most important thing.

So, I had taken an example may be about 10 elements I will talk about it. So, first thing is when you buy an atomic absorption they will give you a manual may be CD or it may be printed copy also, but there they will specify the conditions for atomic absorption for different elements for example, look at this; this is for silver. So, this is for silver. So, you will or the moment you look at it you will know that wavelength is 3.28 there are 2 resonance lines for the determination of silver 328.1 and 338.3 and the optimum slit width that is the hollow cathode lamp radiation should pass through this is the mechanical slit width relative noise is 1 and that is the electrical noise corresponding to this wavelength and then characteristic concentration this is the concentration where the determination is gives you point the absorbance of 0.054.

So, the use of characteristic concentration is if you take want to check whether the instrument is functional whether it is good are there they no problems with respect to your samples etcetera what you should do is prepare 2.5 ppm of milligram per liter 2.5 ppm of silver then you should get an absorbance of about 2.5 multiplied by 0.05 that is about 0.1 absorbance.

So, if you multiply characteristic concentration and concentration check this value should be multiplied by this and if everything is all right your solution is all right your sample is all right your standards are all right your instrument setting is all right your hollow cathode lamp is all right your gas is all right etcetera you should get about 0.1 absorbance for 2.5 ppm of silver the next range is it will tell you up to what ppm you can prepare your standard solutions the here it is written as four milligram per liter; that means, you can prepare your standards 1 2 3 4 or you can choose anything, but it should be below 4.

Similarly, for if you choose this line 338.3 you can see that the characteristic concentration is double; that means, this is not so sensitive the first preference is 328.1 if for some reason if you are not able to get this line from your monochromator in your from your hollow cathode lamp you can choose 338, but it will be at the cost of sensitivity. So, this 5 ppm is at that time you should prepare 5 ppm of silver concentration and it should give you 5 into 0.1 is approximately 0.5 absorbance and working range is approximately double than this.

So, this is how you should interpret the instrument conditions whenever you want to do an analysis; that means, they also give you what gas you should be use you should be using here they are recommending air acetylene oxidizing is the oxidizing means it should be lean blue color. So, you must adjust the gas fluorate in such a way that air should be more acetylene should be less and it must the flame must look blue when you are not aspirating anything.

So, data obtained with standard nebulizer etcetera this that is the concentration this sensitivity is characteristic concentrations are calculated using data obtained with standard nebulizer and flow spoiler. So, operation with high sensitivity nebulizer will increase sensitivity. So, it depends upon the nebulizer. So, for this instrument which I have chosen this these are the conditions. So, characteristic suppose you determine go for the determination of silver using nitrous oxide and acetylene flame at 328 the detection limit is 0.36 milligram per liter; that means, 0.36 multiplied by this concentration would be the approximate reading.

So, they will also tell you how to prepare your standard samples and standards they say use 5 percent volume by volume nitric acid to keep the element in solution some times what happens is you have to prepare the concentrations at low concentrations they precipitate in especially in parts per million ppb level they precipitate and after some time you will see that there is no signal. So, to keep the solution to keep the sample in solution or to keep the solutions table they recommend nitric acid as the standard component of the standard solutions.

So, once you prepare the solutions the samples will be stable for considerable length of time you do not have to prepare the standards again and again now the additional information.

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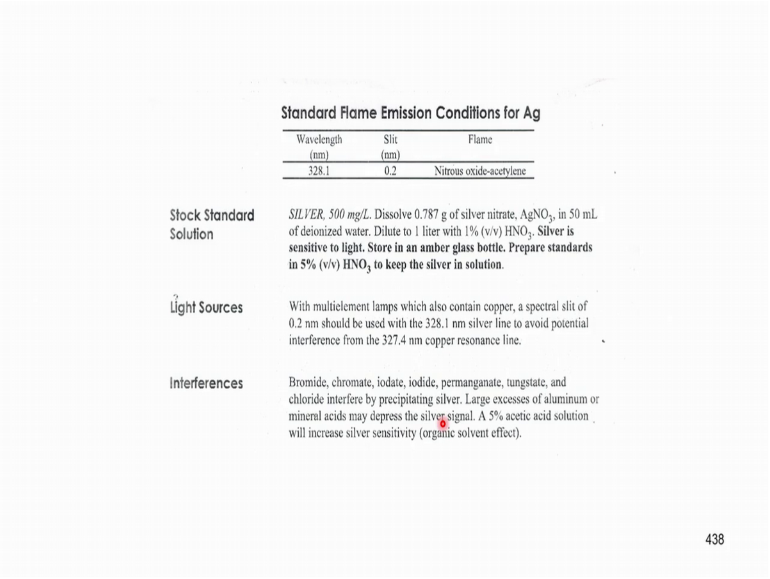

Standard Flame Emission Conditions for Ag

Wavelength (nm)	Slit (nm)	Flame
328.1	0.2	Nitrous oxide-acetylene

Stock Standard Solution *SILVER, 500 mg/L*. Dissolve 0.787 g of silver nitrate, $AgNO_3$, in 50 mL of deionized water. Dilute to 1 liter with 1% (v/v) HNO_3. **Silver is sensitive to light. Store in an amber glass bottle. Prepare standards in 5% (v/v) HNO_3 to keep the silver in solution.**

Light Sources With multielement lamps which also contain copper, a spectral slit of 0.2 nm should be used with the 328.1 nm silver line to avoid potential interference from the 327.4 nm copper resonance line.

Interferences Bromide, chromate, iodate, iodide, permanganate, tungstate, and chloride interfere by precipitating silver. Large excesses of aluminum or mineral acids may depress the silver signal. A 5% acetic acid solution will increase silver sensitivity (organic solvent effect).

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They give you this wavelength slit suppose you use 328 and 0.2 nanometer slit you should be using if you are using nitrous oxide acetylene flame for the same silver. So, all of this will be contained in one page. So, they will say how to prepare a stock standard solution and then we will see; what is stock standard solution etcetera after sometime. So, we have to dissolve so much of silver nitrate in 50 ml dilute to 1 liter all these details are available a in the manual.

And then light sources use they say you use multi element lamp or multi element lamp you can use or you can use other lamp silver dedicated silver, but they will also give you some information about bromide interferences bromide chromate iodide etcetera if they are there they will be precipitating silver large the excess of these are this is only to help you whenever you want to do signals some additional specific information they give you for example, large excess of aluminum or mineral acids may depress the silver signal. So, if you do not get the characteristic concentration or absorbance for a known standard look for such changes is there lot of aluminum in the sample like that you can check and then they also give you a some information organic solvent inter effect they say- if you prepare the solution in 5 percent acetic acid solution it will increase the sensitivity.

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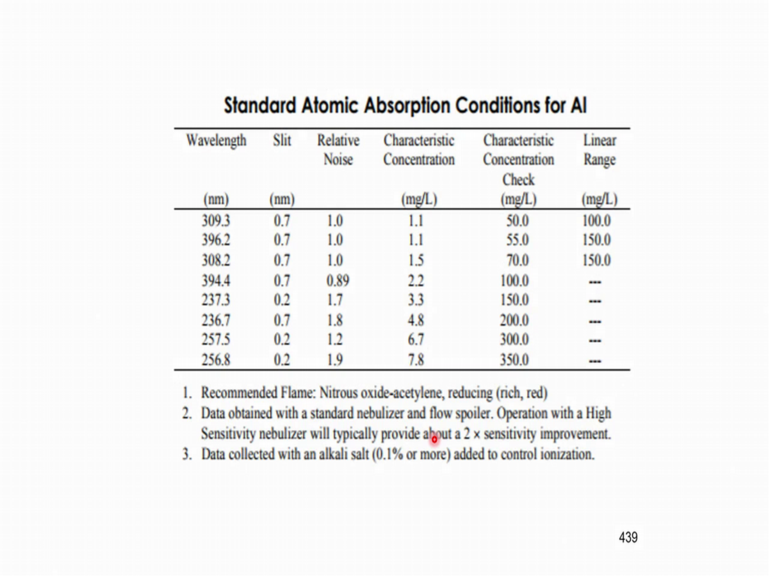

Standard Atomic Absorption Conditions for Al

Wavelength (nm)	Slit (nm)	Relative Noise	Characteristic Concentration (mg/L)	Characteristic Concentration Check (mg/L)	Linear Range (mg/L)
309.3	0.7	1.0	1.1	50.0	100.0
396.2	0.7	1.0	1.1	55.0	150.0
308.2	0.7	1.0	1.5	70.0	150.0
394.4	0.7	0.89	2.2	100.0	---
237.3	0.2	1.7	3.3	150.0	---
236.7	0.7	1.8	4.8	200.0	---
257.5	0.2	1.2	6.7	300.0	---
256.8	0.2	1.9	7.8	350.0	---

1. Recommended Flame: Nitrous oxide-acetylene, reducing (rich, red)
2. Data obtained with a standard nebulizer and flow spoiler. Operation with a High Sensitivity nebulizer will typically provide about a 2 × sensitivity improvement.
3. Data collected with an alkali salt (0.1% or more) added to control ionization.

So these are the standard atomic conditions for aluminum you can see that there are about 5 plus 5 about 10 resonance lines for atomic absorption, but their sensitivity characteristic concentration is almost comparable in the first 3, but lower in the remaining.

But their recommended curve flame would be nitrous oxide because it forms a refractory oxide. So, they say use reducing flame that is rich and red it should be flame should look reddish. So, that is how you must adjust your nitrous oxide and acetylene. So, all other things will remain the same and sometimes data they will give you this information data collected with an alkali salt containing 0.1 percent that is to adjust the ionic concentrations in your sample to control ionization.

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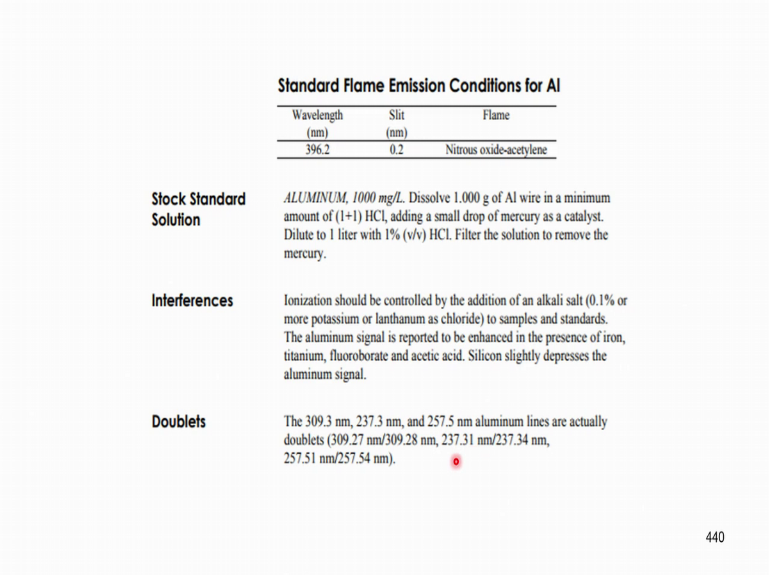

Standard Flame Emission Conditions for Al

Wavelength (nm)	Slit (nm)	Flame
396.2	0.2	Nitrous oxide-acetylene

Stock Standard Solution *ALUMINUM, 1000 mg/L.* Dissolve 1.000 g of Al wire in a minimum amount of (1+1) HCl, adding a small drop of mercury as a catalyst. Dilute to 1 liter with 1% (v/v) HCl. Filter the solution to remove the mercury.

Interferences Ionization should be controlled by the addition of an alkali salt (0.1% or more potassium or lanthanum as chloride) to samples and standards. The aluminum signal is reported to be enhanced in the presence of iron, titanium, fluoroborate and acetic acid. Silicon slightly depresses the aluminum signal.

Doublets The 309.3 nm, 237.3 nm, and 257.5 nm aluminum lines are actually doublets (309.27 nm/309.28 nm, 237.31 nm/237.34 nm, 257.51 nm/257.54 nm).

Now, similarly we can continue they will tell you stock solution interferences etcetera you can see that ionization is in a big interference in most of the nitrous oxide acetylene flames they will also give information about doublets etcetera for aluminum.

Now, for arsenic is one of the most difficult elements to do because the resonance line is 193 that is almost UV here the problem is many of the organic compounds will give you molecular absorbance around 193 that is pi sigma to sigma star or pi to pi star contributions and n to pi star also. So, this signal is very difficult to handle, but and more over the arsenic lamp the intensity of the lamp also is not very good with respect to hollow cathode lamp. So, pre people prefer EDL that is electrode less discharge lamps HCL sensitivity hollow cathode lamp sensitivity data are about 25 percent poorer; that means, these intensity of the radiation coming out from EDL is about 20; is about 25 percent better than hollow cathode lamp. So, any element which has got wavelength resonance wavelength below 200 you must go for EDL that is electrode less discharge lamp.

So, characteristic concentration also seems to be quite high that is 45 etcetera. So, flame is not really good for arsenic hydride yes you will see the better sensitivity almost up to parts per billion level.

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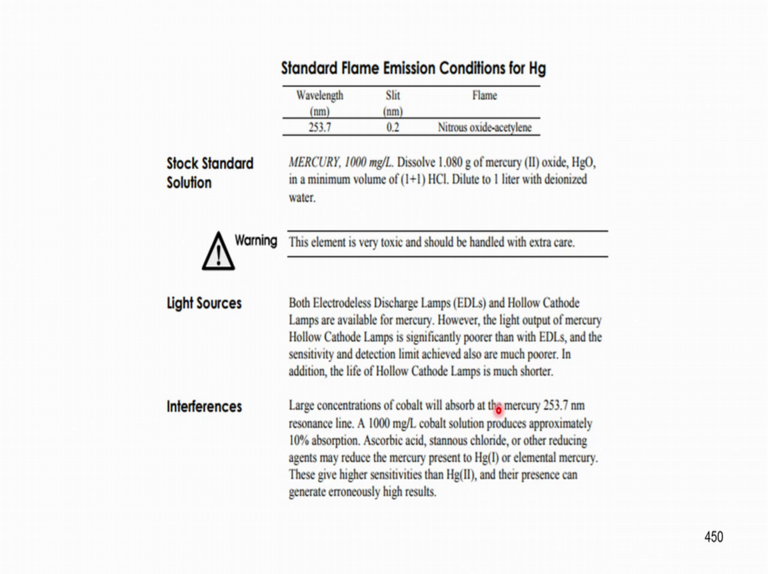

Standard Flame Emission Conditions for Hg

Wavelength (nm)	Slit (nm)	Flame
253.7	0.2	Nitrous oxide-acetylene

Stock Standard Solution *MERCURY, 1000 mg/L.* Dissolve 1.080 g of mercury (II) oxide, HgO, in a minimum volume of (1+1) HCl. Dilute to 1 liter with deionized water.

⚠ **Warning** This element is very toxic and should be handled with extra care.

Light Sources Both Electrodeless Discharge Lamps (EDLs) and Hollow Cathode Lamps are available for mercury. However, the light output of mercury Hollow Cathode Lamps is significantly poorer than with EDLs, and the sensitivity and detection limit achieved also are much poorer. In addition, the life of Hollow Cathode Lamps is much shorter.

Interferences Large concentrations of cobalt will absorb at the mercury 253.7 nm resonance line. A 1000 mg/L cobalt solution produces approximately 10% absorption. Ascorbic acid, stannous chloride, or other reducing agents may reduce the mercury present to Hg(I) or elemental mercury. These give higher sensitivities than Hg(II), and their presence can generate erroneously high results.

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So, then the other information is same stock standard solution they will give you a warning that it is arsenic is toxic air acetylene flame absorbs or scatters more than sixty percent so, the some problem explanation for arsenic. So, you should be very careful they say use of background correction is recommended quite often we do not need background correction because the; if the matrix is very simple foe example if you want to determine elements in water you do not need a background correction not many elements will be there any way.

So, light sources HCL and EDL etcetera some interferences and there is non specific absorption that is what I was telling you about the molecular absorption peaks from organic compounds in UV range that is around 183.7 all right. So, this is how we interpret the manual in the this atomic absorption I have about another 6 or 7 slides for different elements anything specific I will keep on I will mention that for example, cadmium seems to be one of the best element for the determination using flame atomic absorption the you can see that detection limit characteristic concentration is 0.028 ppm. So, that is fantastic.

So, you do not need really you know graphite furnace or something for detection of cadmium and 326.1 line is fairly not. So, sensitive and the detection limit or characteristic concentration should be about 500 ppm. So, it is not very nice, but other things will remain the same. So, you given a choice you should choose 228.8 nanometer range from for cadmium and they say HCL data is better is, but EDL sensitivity values are slightly better. So, if you have EDL for cadmium use it otherwise go ahead with the HCL data hollow cathode lamp data.

So, you can see here even this linear range is only up to 2 ppm. So, you can determine really cadmium concentrations up to 2 ppm which is good because cadmium is a carcinogenic element cadmium causes a disease known as Itai, Itai in Japanese which corresponds to approximately IIO. So, cadmium is good for flame similarly other conditions are there light sources interferences you can study these this kind of information at your; or whenever you want to determine cadmium go through this manual or you can go through any other manual available the specific to cadmium.

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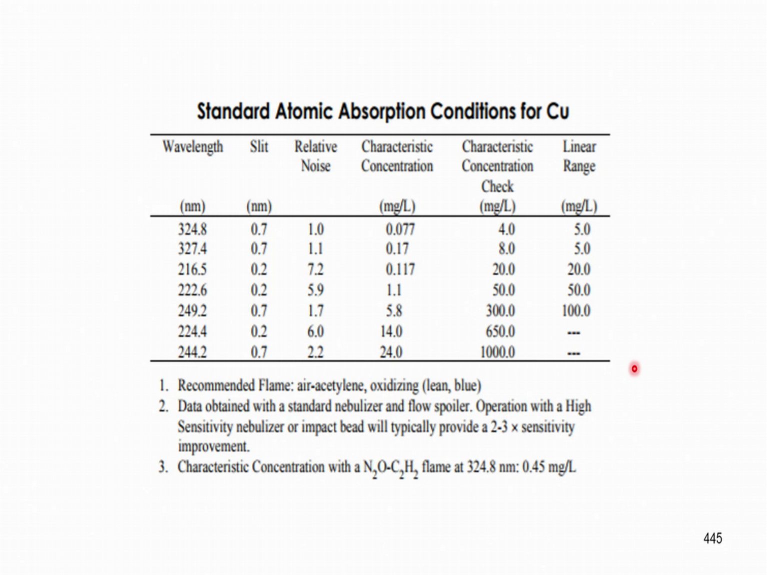

Standard Atomic Absorption Conditions for Cu

Wavelength (nm)	Slit (nm)	Relative Noise	Characteristic Concentration (mg/L)	Characteristic Concentration Check (mg/L)	Linear Range (mg/L)
324.8	0.7	1.0	0.077	4.0	5.0
327.4	0.7	1.1	0.17	8.0	5.0
216.5	0.2	7.2	0.117	20.0	20.0
222.6	0.2	5.9	1.1	50.0	50.0
249.2	0.7	1.7	5.8	300.0	100.0
224.4	0.2	6.0	14.0	650.0	---
244.2	0.7	2.2	24.0	1000.0	---

1. Recommended Flame: air-acetylene, oxidizing (lean, blue)
2. Data obtained with a standard nebulizer and flow spoiler. Operation with a High Sensitivity nebulizer or impact bead will typically provide a 2-3 × sensitivity improvement.
3. Characteristic Concentration with a N_2O-C_2H_2 flame at 324.8 nm: 0.45 mg/L

Now, for copper there are. So, many lines nut sensitivity relative noise is much better only for 324.8327 and detection limit is 0.077 and air acetylene oxidizing flame that is it basically.

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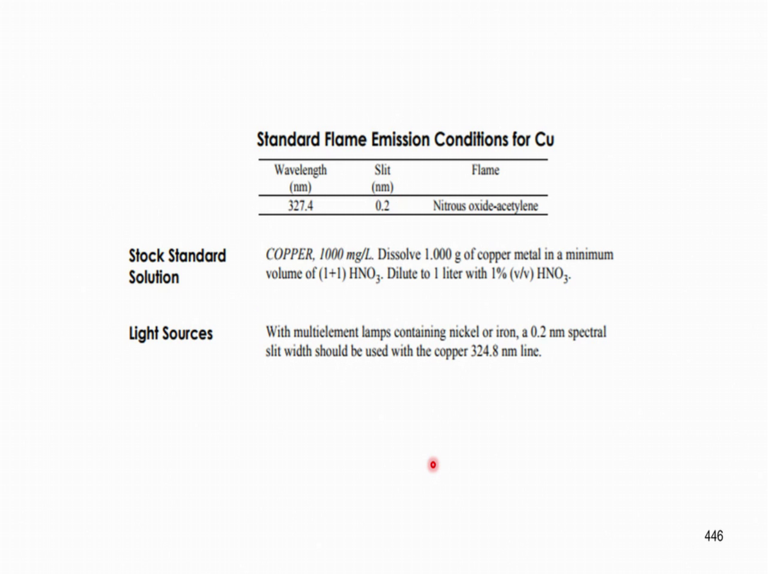

Standard Flame Emission Conditions for Cu

Wavelength (nm)	Slit (nm)	Flame
327.4	0.2	Nitrous oxide-acetylene

Stock Standard Solution *COPPER, 1000 mg/L.* Dissolve 1.000 g of copper metal in a minimum volume of (1+1) HNO_3. Dilute to 1 liter with 1% (v/v) HNO_3.

Light Sources With multielement lamps containing nickel or iron, a 0.2 nm spectral slit width should be used with the copper 324.8 nm line.

Standard flame emissions they say dissolve 1 gram etcetera light sources hallow cathode lamp should be good you can use multi element lamp also.

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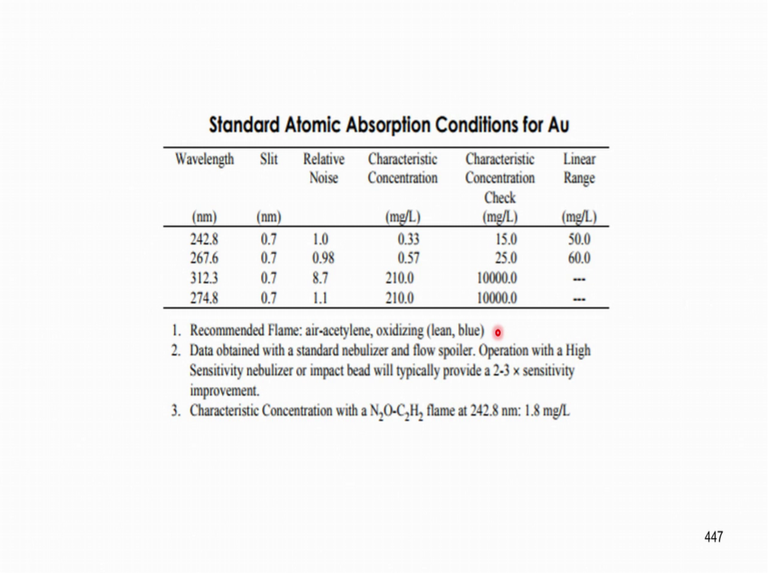

Standard Atomic Absorption Conditions for Au

Wavelength (nm)	Slit (nm)	Relative Noise	Characteristic Concentration (mg/L)	Characteristic Concentration Check (mg/L)	Linear Range (mg/L)
242.8	0.7	1.0	0.33	15.0	50.0
267.6	0.7	0.98	0.57	25.0	60.0
312.3	0.7	8.7	210.0	10000.0	---
274.8	0.7	1.1	210.0	10000.0	---

1. Recommended Flame: air-acetylene, oxidizing (lean, blue)
2. Data obtained with a standard nebulizer and flow spoiler. Operation with a High Sensitivity nebulizer or impact bead will typically provide a 2-3 × sensitivity improvement.
3. Characteristic Concentration with a N_2O-C_2H_2 flame at 242.8 nm: 1.8 mg/L

So gold; these are the 242.28 is the most ideal wavelength and characteristic concentration is 0.33 and characteristic concentration check is 15 ppm that is 15 into 0.3 is about 15 3 za 45. So, approximately 0.45 is the check characteristic concentration check and then linear range is up to 50 ppm air acetylene is advised and sometimes if you want to determine at lower level you should go to nitrous oxide acetylene, but ninety percent of the time people do not want to work with air acetylene unless it is necessary people prefer air sorry nitrous oxide acetylene.

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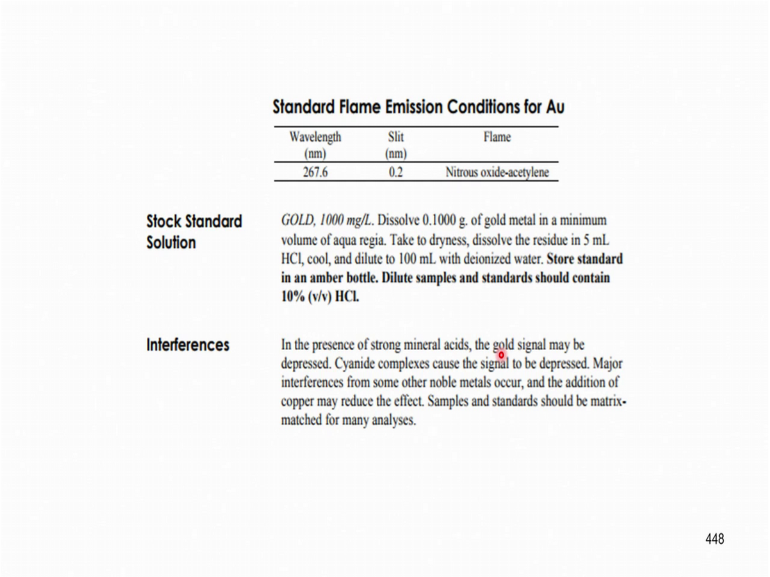

Standard Flame Emission Conditions for Au

Wavelength (nm)	Slit (nm)	Flame
267.6	0.2	Nitrous oxide-acetylene

Stock Standard Solution

GOLD, 1000 mg/L. Dissolve 0.1000 g. of gold metal in a minimum volume of aqua regia. Take to dryness, dissolve the residue in 5 mL HCl, cool, and dilute to 100 mL with deionized water. **Store standard in an amber bottle. Dilute samples and standards should contain 10% (v/v) HCl.**

Interferences

In the presence of strong mineral acids, the gold signal may be depressed. Cyanide complexes cause the signal to be depressed. Major interferences from some other noble metals occur, and the addition of copper may reduce the effect. Samples and standards should be matrix-matched for many analyses.

Nitrous oxide acetylene they prefer only when there is oxide formation sensitivity is a if the sensitivity is very low you do not need if the sensitivity is bad you should go for higher this thing now other conditions are all there in gold they say- you can use strong mineral acids also and they say you maintain your standards in 10 percent HCL as for as gold. And other noble metals are concerned and for actual good analysis, because gold is a very precious element you have to choose samples and standard should be matrix matched. That means, suppose there will be a allowing elements etcetera you have to add the allowing elements to see the correct signal.

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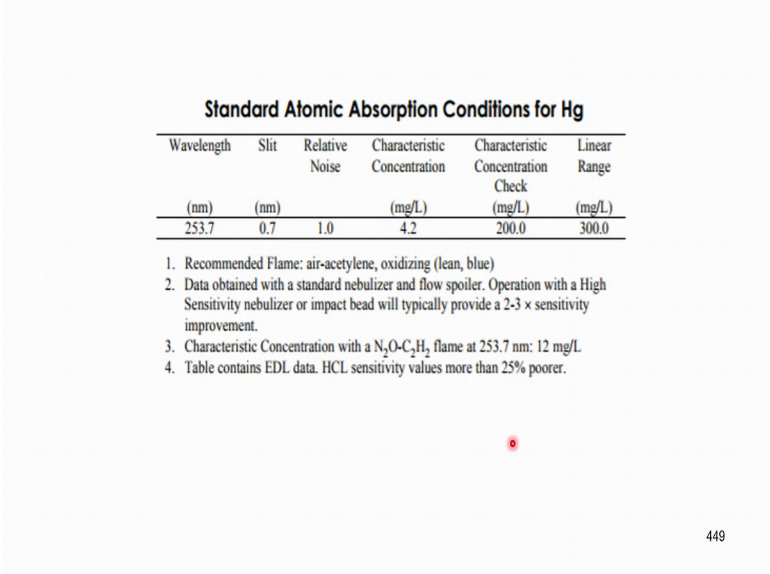

Standard Atomic Absorption Conditions for Hg

Wavelength (nm)	Slit (nm)	Relative Noise	Characteristic Concentration (mg/L)	Characteristic Concentration Check (mg/L)	Linear Range (mg/L)
253.7	0.7	1.0	4.2	200.0	300.0

1. Recommended Flame: air-acetylene, oxidizing (lean, blue)
2. Data obtained with a standard nebulizer and flow spoiler. Operation with a High Sensitivity nebulizer or impact bead will typically provide a 2-3 × sensitivity improvement.
3. Characteristic Concentration with a N_2O-C_2H_2 flame at 253.7 nm: 12 mg/L
4. Table contains EDL data. HCL sensitivity values more than 25% poorer.

So, mercury the usually hydride generation, but if you do want to do with air acetylene characteristic concentration is 4.2 milligram per liter and for 0.2 absorbance you should use 200 ppm.

And they say use EDL for mercury and because the HCL sensitivity is poorer by about 25 percent so, but if you choose this nobody likes to determine mercury by atomic absorption flame atomic absorption because gold vapor gives you analysis of at ppb levels straight away. So, mercury other conditions are there here I must say that you must be very careful whenever you are handling mercury. Mercury is a toxic element mercury is a carcinogenic element it affects the nervous system, it causes a disease known as nervous disease known as Minamata disease.

You can look up the additional information from the text books. We will continue our discussion.