

Trace and ultra trace analysis of metals Using atomic absorption spectrometry
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Lecture - 36
Technology and Applications

So, we were discussing about the determination of mercury. As I told you mercury can be determined using flame as well as nitrous oxide flame.

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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.

Inferences 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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But everybody prefers to do it by cold vapour technique, and you only if the concentration is very high, you can go for flame or nitrous oxide. But otherwise everybody would like to do it by this thing. So, if there is you can look at the interference data is more important here, for their right is large concentration of cobalt will absorbed at 253.7 this is the spectral interference. So, one has to be careful you should also know with it whether cobalt is there or not, in the sample whenever you are determining mercury.

And suppose there are reducing agents like, ascorbic acid, stannous chloride, hydroxyl I mean, hydro chloride etcetera, they were reduce the mercury present to elemental mercury or mercury one also. These give higher sensitivity than mercury 2, but their presence can generate erroneously high results also.

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Wavelength (nm)	Slit (nm)	Relative Noise	Characteristic Concentration (mg/L)	Characteristic Concentration Check (mg/L)	Linear Range (mg/L)
283.3	0.7	0.43	0.45	20.0	20.0
217.0	0.7	1.0	0.19	9.0	20.0
205.3	0.7	1.4	5.4	250.0	---
202.2	0.7	1.8	7.1	350.0	---
261.4	0.7	0.35	11.0	500.0	---
368.3	0.7	0.40	27.0	1200.0	---
364.0	0.7	0.33	67.0	3000.0	---

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 283.3 nm: 2.7 mg/L
4. Table contains HCL data. EDL sensitivity values approximately the same.

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So, one has to be careful with respect to matrix components. So, similarly for lead look at the wavelength for lead is 280.3 nanometers relative noise is 0.3 recommended slit is 0.7 characteristic concentration is 0.45 for 0.2 absorbance. And characteristic concentration check should be 20, and linear range is up to 20 ppm. 20 milligram per liter is 20 ppm. So, air acetylene is fine lower determinations 2.7 ppm you can determine, with nitrous oxide acetylene flame and EDL is the preferred light source instead of hollow cathode lamp. Because EDL are more stable than hydro than hollow cathode lamps, but sensitivity values remain the same.

Similarly continuing our discussion nitrous oxide if you do it, your detection limit will be slightly lower, and interferences are large interferences definitely you must avoid. Normally whenever you do atomic absorption when you prepare ppm level standard solutions or if this sample is also ppm level the interfering element will be very less, 99 percent of the time ok.

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(1) FAAS instrumentation
FAAS analysis is performed on a PerkinElmer Model 5000 or 5100 atomic absorption spectrometer using an EDL power supply or HCL source lamp. The wavelength setting for Pb is 283.3 nm. Line pressure settings are preset at approximately 50–64 for air and 20–30 for acetylene. Manual aspiration of the samples is performed.

(2) GFAAS instrumentation
The analysis for Pb in floor-dust wipe samples is performed on a Perkin-Elmer Model 5100 graphite-furnace atomic absorption spectrometer with Zeeman background correction. The system is microcomputer controlled with a CRT display, keyboard, and AS-70 Autosampler. Virtually all operating parameters and functions for the spectrometer and the graphite-furnace are entered via the keyboard. The following program is used for the analysis of Pb in dust-wipe samples by graphite-furnace:

Wavelength (nm):	283.3	Max sig. figures:	5
Slit width:	0.7	Read Time (sec):	3.0
Signal type:	Zeeman	Read delay (sec):	0.0
Signal Measurement:	Peak area	BOC time (sec):	2.0
Pb linear, calculated intercept		Calibration units:	ppb
Sample units:	ppb	Max decimal places:	4

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So, sometimes the same cookbook will also tell you that o flame AAS instrumentation, you can choose graphite furnace also. And they will give you similar conditions for graphite furnace. So, the information what you get for graphite furnace analysis is wavelength that is the that is same as the flame. Because resonance line you need and then slit width is recommended by the company, because there are only fixed slit widths either 0.2 or 0.7 and then signal type is zeeman effect.

They say preferably you do peak area and calculated go for linear calibration and sample unit should be in ppb and retime should be approximately 3 seconds. Read delay there should be no need for delay; that means, signal will start coming the moment you reach the atomization temperature and then calibration unit is are in ppb, maximum decimal places should be 0.4 ppm, 0.4 milligram per liter.

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Furnace Conditions						
Step#	Temp(°C)	Ramp Time	Hold Time	Flow Time	Gas Type	Read Step
1	120	1	20	250	Normal	
2	140	5	30	250	Normal	
3	900	10	20	250	Normal	
4	1700	0	5	0	Normal	X
5	2400	1	2	250	Normal	

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So furnace conditions also they will recommend sometimes, but you are free to change the furnace conditions. Here the recommended furnace condition is they say heat it to 120 degrees ramp time is 1 that in; that means, in 1 1 second you should go to 120 degrees, hold it for 20 seconds at that time flow time should be about 250 and gas type should be normal that is argon. And read you can choose other gases also. So, they say normal means argon in graphite furnace.

And read step you are not reading the signal here because you are removing only the moisture. At 140 degrees you will remove some more organic crystalline organic crystalline compounds, and higher boiling organic compounds. And 900 all organic is gone. And only the inorganic salts will be there and 1700 is the atomization temperature they are recommending, and you will get a you say read the absorbance. This is the atomization step. Then blow out step final cleaning 2400 and that is you should not be reading it just to clean out the graphite tube.

Like that they will give you conditions, but for every matrix every element you have to optimize you can optimize your own method, ramp time hold time flow time depending upon the sample ok.


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CALIBRATION AND CALIBRATION VERIFICATION PROCEDURES

Dust-wipe sample digestates are analyzed using either a Perkin-Elmer Model 5000 or 5100 Flame Atomic Absorption Spectrometers (FAAS). Working standards are prepared from standard solution stocks using a 1 M HNO₃ matrix. A midrange control standard and a calibration blank are evaluated no less than every 10 samples during a run. If there is more than a 5% relative percent difference to the previous standard, the entire set of standards is re-examined. If necessary, the subset of samples subject to the disagreement is re-run after a review of methods and procedures, and after corrections have been made so that standards are verified within 5% RPD. Reagent blanks, controls and NIST standards are incorporated into each preparation of samples. The concentration of all controls must be within +10% of the established value. If not, the samples are re-analyzed.

The actual run order of samples analyzed by FAAS or GFAAS follows:

Sample No.	Sample ID	Description
1	ICB	Calibration Blank
2-4	Low Std. - High Std.	Calibration Standards
5	ICB	Calibration Blank
6	ICV	Different stock, Conc. Near mid-point
7	High Std.	Calibration Std.
8	CCB	Calibration Blank
9	ICS (ICP)	Interference check sample
10	CCB	Calibration Blank
11	CCV	Intermed. Calibration Std.
12	CCB	Calibration Blank
13-22	Samples	Digestates
23	CCV	Intermed. Calibration Std.
24	CCB	Calibration Blank
25-34	Samples	Digestates
35	ICS (ICP)	Interference check sample
36	CCB	Calibration Blank
37	CCV	Intermed. Calibration Std.
38	CCB	Calibration Blank



Now, calibration and calibration verification procedures are there these. Are internal standards ICB calibration blank and CCB is calibration blank like that you can introduce, whenever you want to prepare a calibration curve first you must put a blank and then (Refer Time: 06:45) to use you have to aspire, or determine low standard and high standard both. That will give you calibration standard. And then again you put ICB that is internal calibration blank, because to remove the high standard memory. So, once you have the blank then you can introduce your standards etcetera, after every calibration standard you have to introduce blank water for some time. So, that the memory effects are removed.

So, that is why the give a typical procedure for samples etcetera and if you study these you will understand what I am talking about, it may take a little time for you to understand. But the basic principle is in between 2 measurements you put blank. So, that this instrument comes to the normal. That is the whole idea, and this procedure is to be followed whether it is flame or graphite furnace. Including even for hydride generation same procedure can be followed. That means, first blank, then standard then blank then another standard then blank, then another standard like that until you finish all your standards, prepare the calibration curve then you introduce your unknown again after the blank and then unknown you can repeat 2 or 3 times to get the average value etcetera, and all those things belong to the rim of analytical science.

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PROCEDURE OPERATING INSTRUCTIONS; CALCULATIONS; INTERPRETATION OF RESULTS

A. SAMPLE DIGESTION PROCEDURE

- (1) Remove the wipe from its container and place into a 50–100 ml glass beaker. Quantitatively rinse the container transferring the contents to the beaker. Add DDW to cover the wipe (~10 ml). Use a glass rod and stir the wipe to open it. Rinse the glass rod with DDW and add to the beaker.
- (2) Add two ml of concentrated HNO_3 and 2 ml of concentrated HCL.
- (3) Gently heat at 100°C for 20–30 minutes under reflux.
- (4) Cool and transfer all contents to a 50-ml graduated tube. Rinse any bulk material several times and gently squeezing with a glass rod while pouring the solution over into graduated tube.
- (5) Add DDW to 50 ml, cap and mix well.
- (6) If need be, prior to analysis filter a portion of the sample through ashless filter paper into a clean tube or centrifuge the original sample at 9000 rotations per minute (rpm) for 20 minutes.
- (7) The final digestate is analyzed by either FAAS or GFAAS.

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So, sometimes they will give you operating instructions, calculations etcetera, in the manual and then the sample digestion procedure also they will recommend, for you normal recommendation procedure. But again it depends upon your experience and your requirement. So, here they say that remove and wipe the container place in 100 ml add ddw to cover the wipe use a glass rod stir the wipe to open it and all these things. And then add concentrated nitric acid heat for 100 degrees they add it these and then dilute to 50 ml like that.

So, before you proceed with the analysis you must your sample must be ready apart from these standards. So, this is a procedure recommended for sample handling. Sometimes you may find them or you may not find them in the cookbook in that case what you should be doing is, you should go to literature available literature either in the internet or in the text books, or in the research papers etcetera, depending upon your requirement you can definitely go for this.

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ANALYSIS PROCEDURE

(1) FAAS

- (a) Turn the instrument on and light the hollow cathode lamp or electrodeless discharge lamp. Allow the instrument to warm up for 45 minutes prior to use.
- (b) Adjust the wattage on the HCL to that recommended on the lamp and allow it to warm up for 20 minutes prior to use. Adjust the milliamps to the proper level.
- (c) Tweak up the wavelength (283.3nm) for maximum light throughput (energy).
- (d) Check the following line pressures: air = 50-64; acetylene = 20-30. Ignite the burner and allow a 5-minute warm-up time.
- (e) Optimize the burner position for maximum absorbance while aspirating a 10 ppm solution of lead in 1 M HNO₃.
- (f) If applicable start the chart recorder (20 mm/min, 10 mv).
- (g) Start analyzing standards and samples according to standard run order. Allow enough time in between samples to achieve baseline.
- (h) The standard analyzed after every 10 samples should agree within 5% of the previous one. If not, re-calibrate.
- (i) Any samples over 9 ppm should be set aside for dilution.
- (j) An analytical duplicate should be analyzed after every 25 samples. One sample should be selected for recovery after every 20 samples.

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Now, analysis procedure again flame analysis, what they say is let the instrument warm up for 45 minutes; that means, hollow cathode lamp should warm up, and then lamp should stabilize. And then adjust the wattage on HCL, you have to give the voltage to HCL and allow it to warm up for 20 minutes. Adjust the milliamps, there this they recommend for the hollow cathode lamp each hollow cathode lamp, you have to give 16 millivolts etcetera, and then wavelength you have to adjust to the resonance wavelength 280.3.

This you will be adjusting for the detector, not for the hollow cathode. Hollow cathode lamp will give you the radiation anyway, resonance and all other radiations also. But the point is the detector should detect 280.3 nanometers, because that comes from the hollow cathode lamp, you detector should not detect any other radiation that is why you need a monochromator at after the flame.

So, then you can optimize the burner position and all these things with a 10 ppm solution of lead etcetera. And standard samples and an any samples over 9 ppm should be set for dilution; that means, do not aspirate more than 9 ppm it may lead to memory effect or contamination later. So, this kind of resolution this kind of suggestions they will make it. And analytical duplicate should be analyze after every 25 sample suppose you have 100 or 200 samples what happens is over some time, you will see that the there will be some amount of drift from the optimal signal. So, what we say is after about 25 samples run a

standard once again. See whether there is a you get the same reading otherwise adjust it in such a way that you get the a right absorbance.

And again continue for another 20 to 25 samples, like that you can run it. And graphite furnace similarly similar procedures are described; you can go through this or develop your own procedure, ok.

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CALCULATIONS AND REPORTING

- (1) Sample concentration is derived using a linear regression equation of the standards and their absorbance readings.
- (2) The correlation coefficient for the standard curve must be 0.995 or better.
- (3) Specimens are repeated if their analytical duplicates differ by more than +10 RPD.
- (4) All samples whose results are greater than 9 ppm are diluted and re-analyzed.
- (5) The Method Detection Limit (MDL) is 2 µg by FAAS and 0.16 µg for GFAAS. Results below the MDL are reported, however, qualified to indicate that they are lower than the MDL.

REPORTABLE RANGE OF RESULTS

All window dust wipe results are analyzed by FAAS. For samples are first analyzed by GFAAS. If the result is greater than or equal to 5 µg, the sample is re-analyzed by FAAS and that value reported. All results by FAAS greater than 9 ppm are diluted and re-analyzed.

REFERENCE RANGES (NORMAL VALUES)

According to the 1995 Guidelines for the Evaluation and Control of Lead-Based Paint Hazards in Housing, the Federal Lead Standards are defined as 100 µg/ft² for floors and 500 µg/ft² for interior window sills. New guidelines have not been officially set at this time; however, it is expected that the floor standard will be lowered to 40 µg/ft².

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And calculations reporting range all these things the manual will tell you, otherwise analytical good analytical scientist will work their own way depending upon the samples.

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Standard Atomic Absorption Conditions for Se


Wavelength (nm)	Slit (nm)	Relative Noise	Characteristic Concentration (mg/L)	Characteristic Concentration Check (mg/L)	Linear Range (mg/L)
196.0	2.0	1.0	0.59	30.0	200.0
204.0	0.7	0.61	2.9	150.0	--
206.3	0.7	0.44	12.0	600.0	---
207.5	0.7	0.43	40.0	2000.0	---

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 N₂O-C₂H₂ flame at 196 nm: 2.7 mg/L.
4. Table contains EDL data. HCL sensitivity values are more than 25% poorer.
5. Use 0.7 nm slit on Models 3100 and 3110.

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So, this is the standard atomic absorption conditions for selenium. You can again see that the resonance line is around 196 for maximum sensitivity, anything above that the up to 30 ppm you can do it by flame, and any other resonance line you have to work only in 150, 600 like that ppm range it is not very nice. But selenium by flame is again a bad decision. Because the linear range is up to 200 ppm and air acetylene and oxidizing etcetera, but EDL is slightly better, but again nobody determine selenium by atomic absorption; the we do it by hydride generation, there it the detection limit can extend up to ppb levels ok.

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Stock Standard Solution	<i>SELENIUM, 1000 mg/L.</i> Dissolve 1.000 g of selenium metal in a minimum volume of concentrated HNO ₃ . Evaporate to dryness, add 2 mL water and evaporate to dryness 2 or 3 additional times. Dissolve in 10% (v/v) HCl and dilute to 1 liter with 10% (v/v) HCl.
 Warning	This element is toxic and should be handled with extra care.
Light Sources	Both HCL and EDL sources are available for Se. EDLs, which are more intense, provide better performance and longer life.
Interferences	The air-acetylene flame absorbs or scatters more than 50% of the light source radiation at the 196.1 nm selenium line. Flame absorption is reduced with the use of the nitrous oxide-acetylene flame, although sensitivity is reduced also. Use of background correction is recommended, as it will correct for flame absorption and thus improve the signal to noise ratio. It will also correct for nonspecific absorption caused by samples with high total salt content.

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Similarly, now the remaining conditions they will mention here like this that prepares how to prepare standards, and how to this thing interferences they will mention. You can go through this; I do not want you to remember anything like this for examination, or a test if you want to take. But the information should be analyzable for by you, useful for you.

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Wavelength (nm)	Slit (nm)	Relative Noise	Characteristic Concentration (mg/L)	Characteristic Concentration Check (mg/L)	Linear Range (mg/L)
286.3	0.7	1.0	3.2	150.0	400.0
224.6	0.2	3.3	1.7	80.0	300.0
235.5	0.7	2.8	2.2	100.0	---
270.7	0.7	1.5	4.1	200.0	---
303.4	0.7	0.90	5.0	200.0	---
219.9	0.2	4.4	7.3	350.0	---
300.9	0.7	0.98	9.2	400.0	---
233.5	0.7	6.7	9.2	450.0	---
254.7	0.7	2.8	9.4	450.0	---
266.1	0.7	3.8	37.0	1500.0	---

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. Table contains EDL data. HCL sensitivity values slightly (<10%) poorer.

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So, similarly for tin is another important element, because it is carcinogenic it is toxic and wavelength is 286.3, but fairly in the ultra violet not much problem, but the sensitivity is very low. Rather sensitivity is very high. Detection limit is very high, 150. Normally tin is a hydride generation element, and we do not do it by flame. Nitrous oxide again if you want to determine tin you should use nitrous oxide, and acetylene flame rather than acetylene and air.

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Wavelength (nm)	Slit (nm)	Flame
284.0	0.2	Nitrous oxide-acetylene

Stock Standard Solution *TIN, 1000 mg/L.* Dissolve 1.000 g of tin metal in 100 mL of concentrated HCl and dilute to 1 liter with deionized water. **Dilute tin standards should contain 10% (v/v) HCL.**

Other Flames An air-acetylene flame can also be used to determine tin. However, interference will be greater when using this flame. With air-acetylene, tin sensitivity is 3.5 mg/L for 1% absorption at the 286.3 nm line.

Light Sources Both Electrodeless Discharge Lamps (EDLs) and Hollow Cathode Lamps are available for tin. EDLs provide greater light output and longer life than Hollow Cathode Lamps. For tin, both EDLs and Hollow Cathode Lamps provide approximately the same sensitivity and detection limit.

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And again EDL is ideal similarly you can remaining information is available here. And please understand that any information that you get normally for atomic absorption may vary from instrument to instrument. So, it is your job to optimize conditions depending upon which instrument you have bought and what the cookbook says. So, one has to be careful to make sure that the procedures followed are as recommended in the respective cookbooks.

So, the basically the idea is the gas flow rate and other things will be common, slit width will be common, wavelength will be common, but all other conditions may vary a little bit from instrument to instrument, and software to software there will be differences. So, you should typically follow the conditions given in the manual or cookbook for proper analysis. So, here selection of proper atomic spectroscopic technique is also very important. One has to choose a technique by the merit of the method.

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Atomic Spectroscopy for Metal Analysis

Selection of the Proper Atomic Spectroscopic Techniques

Comparison of Interferences and Other Considerations

Interference

- Three types:
- (i) spectral,
- (ii) chemical,
- (iii) physical

Table 9.2 Atomic spectroscopy interferences

Technique	Type of interferences	Method of compensation ^a
FAA	Ionization	Ionization buffer
	Chemical	Releasing agent or nitrous-acetylene flame
	Physical (self-absorption)	Dilution, matrix matching, or method of additions
GFAA	Physical and chemical	Stabilized temperature platform furnace (STPF) condition
	Molecular absorption	Zeeman or continuum source background correction
	Spectral	Zeeman background correction
ICP-OES	Spectral	Background correction or the use of alternative analytical lines, IECs or MSF
	Matrix	Internal standardization
ICP-MS	Mass overlap	Interelement correction, use of dynamic reaction cell (DRC) technology, use of alternate mass values or higher mass resolution
	Matrix	Internal standardization

^aDetails of these compensation methods can be found in Skoog et al. (1997). IEC = Interfering element correction; MSF = Multicomponent spectral fitting. Zeeman background correction = A method to correct for background absorption in furnace AA that uses a magnetic field around the atomizer. The field splits the energy levels of the absorbing atoms and allows discrimination of atomic absorption from other sources of absorption. (Courtesy of Perkin-Elmer, Inc.)

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Now, if I ask you to prepare to determine mercury or some element first you should know which instrumental technique is most ideal. It may be flame atomic absorption like cadmium I do not need to do anything more than flame. But should you go for flame or graphite furnace? That becomes a big question. Again if you want to determine in parts per billion level go for graphite. If you want to determine parts per million level go for flame.

So, also you should understand what could be the type of interferences and other considerations are there with respect to chemical analysis that determines the technique which you want to use. So, as far as elemental metal analysis is concerned you have 3 or 4 choices, one is flame atomic absorption, another is graphite furnace another, is ICPOES that is ICP optical emission spectrometry which I have not thought you and ICPMS is another technology you can chose.

So, among these 3, among these 4 which one should be ideal? The ideality is defined by interferences. One is spectral interference, chemical interference and physical interference. And so, depending upon the interferences background correction or compensation is required. So, if you are using flame you can see that there are lot of ionization; that means, you should be using a buffer. So, if there is chemical reagent required you should know that whether you are at add a releasing agent or not etcetera. This kind of information is available for graphite furnace they say go for STPF stabilize temperature applied from furnace which we have discussed earlier, and if it is molecular absorption go for zeeman source or background correction, because zeeman source corrects for molecular continuous absorption.

So, spectral interference definitely by a zeeman is best. Similarly for ICP etcetera, you can use all this kind of all this information to choose the right method to get the optimum sensitivity; that means the detection limit should be as low as possible and determination limit also should be as low as possible, to have higher reliability.

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Detection limits for Atomic Spectroscopic Techniques

Element	Flame AAS (ppb)	GFAAS (ppb)	ICP AAS (Total) (ppb)	ICP AAS (Excl) (ppb)	ICPMS (Total) (ppb)
Ag	2	0.05	2	0.5	0.01-0.1
Al	30	0.25	6	1.5	0.1-10
As	300	0.33	12	2	1-10
Au	8	0.15	4	0.6	0.01-0.1
B	500	43	0.5	0.2	10-100
Ba	30	0.4	0.2	0.04	0.01-0.1
Be	1	0.025	0.2	0.06	0.1-1
Bi	50	0.3	18	2	0.01-0.1
C			50		
Ca	1	0.04	0.03	0.03	1-100
Cd	1.5	0.02	1	0.1	0.01-0.1
Ce	100,000		8		0.01-0.1
Co	5	0.5	2	0.5	0.1-1
Cr	6	0.025	2	0.4	0.1-1
Cs	4	0.3	2000		0.01-0.1
Cu	3	0.07	2	0.3	0.1-1
Dy	40	1.8	0.3		0.01-0.1
Er	35	3.8	0.7		0.01-0.1
Eu	1.5	0.8	0.3		0.01-0.1
Fe	6	0.06	1	0.3	0.1-100
Ga	65	23	7		0.1-10
Gd	2000		3		0.01-0.1
Ge	100	0.5	10		1-10
Hf	2000		4		0.01-0.1
Hg	145	18	9	1.2	1-10
Ho	60	18	0.5		0.01-0.1
In	40	0.3	18		0.01-0.1
Ir	500	4	4		0.01-0.1
K	2	0.02	6.5	0.5	0.1-100
La	2000		0.02		0.01-0.1
Li	2	0.1	1		0.01-1
Lu	300		0.05		0.01-0.1

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Now here I am showing you a comparison of the detection limits. Here first column it is an first column is element and this is flame next column, this column is graphite furnace, and this is ICPAES, and next is ICPAES excel. And ICP last is ICPMS. So, depending upon the detection limit you can choose the correct analytical technique. For example, silver if you use you can determine up to 2 ppm, 2 ppb. If it is graphite furnace the limit goes to 0.05 and ICPAES is 2 ppb and ICPAES excel is 0.5 and ICPMS is 0.01 to 0.1. So, a comparison of this table shows you where your sample should fit for analysis. Similar this covers most of the elements of the periodic table which are normally determined by AAS, for example, you can see aluminum is 30 here, and if you do it by ICPMS it is 0.1 ppb.

So, normally nobody likes this, ICP nobody likes flame, because 30 pp ppb is not very good. Similarly for gold it is 8 it is 0.1 5 in graphite furnace and 0.01 to 0.1 in ICPMS, that is inductive couple plasma mass spectrometry the last one. Similarly you can see for example, carbon nobody does determination except in ICPAES you get a signal for about 50 ppb. And then there are detection limits, these will serve as a ready reference for you to go for which analytical technique you should be going for.

So, you can see that most of the elements are in detection limit is are in ppb except for some elements like arsenic it is 0.3 and cerium is very bad 100000 ppb and gadolinium is

2000, hafnium is around 2000 nobody likes to determine using AAS and lanthanum is around 2000 etcetera ppb. That is 2 milligrams, that should give you 0.2 absorbance.

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Element	Flame AAS (ppb)	GFAAS (ppb)	ICP-AES (solid) (ppb)	ICP-AES (liquid) (ppb)	ICP-MS (ppb)
Nb	2000		4		0.01-0.1
Nd	850		2		0.01-0.1
Ni	10	0.24	6	0.4	0.1-10
Os	100		5		0.01-0.1
P	4000	100	18	13	>1,000
Pb	10	0.04	14	1	0.01-0.1
Pd	10	0.5	2		0.01-0.1
Pr	5000		0.8		0.01-0.1
Pt	75	4.5	20		0.01-0.1
Rb	5	0.06	35		0.01-0.1
Re	800		11		0.01-0.1
Rh	3	0.4	5		0.01-0.1
Ru	100	0.75	4		0.01-0.1
S			20	28	>1,000
Sb	40	0.35	18	2	0.01-0.1
Sc	30		0.2	0.05	1-10
Sr	500	0.65	20	5	1-100
Si	200	0.8	5	2	>1,000
Sm	750		7		0.01-0.1
Sn	95	0.6	0.1	0.01	0.01-0.1
Sr	2	0.1	0.1	0.01	0.01-0.1
Ta	1500		9		0.01-0.1
Tb	700	0.2	5		0.01-0.1
Tc	30	0.5	27		1-10
Th			17		0.01-0.1
Ti	70	1.6	0.6	0.09	0.1-1
Tl	20	0.75	16	3	0.01-0.1
Tm	20		1.5		0.01-0.1
U	40000		3.5	0.4	0.01-0.1
V	30	0.7	2	0.5	0.01-10
W	750		17		0.01-0.1
Y	350		0.2		0.01-0.1
Yb	4	0.15	0.3		0.01-0.1
Zn	1.0	0.0075	1	0.06	0.1-10
Zr	1500		0.8		0.01-0.1

* Information combined from a number of sources; not indicative of any one instrument.

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Similarly, I had listed other things, you can chose depending upon this will serve as a guide for you to chose the information, this information is combined from a number of sources, but not indicate you of any one instrument.

So, you should treat this table, as a guide rather than absolute recommendation. It will serve you only as a guide.

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Summary of elemental analysis techniques

	Flame AAS	GFAAS	ICP-AES	ICP-MS
Detection limits	Very good for some elements	Excellent for some elements	Very good for most elements	Excellent for most elements
Sample throughput	10-15 wcs per element	3-4 mins per element	1-40 elements/minute	All elements in <1 minute
Dynamic range	10 ⁴	10 ⁴	10 ⁴	10 ⁶
Precision	short term: 0.1-1.0% long term: 2-beam 1-2% 1-beam < 10%	0.5-5% 1-10% (tube lifetime)	0.1-2% 1-5%	0.5-2% 2-4%
Interferences	Spectral: Very few Chemical (matrix): Many Physical (matrix): Some	Very few Very many Very few	Many Very few Very few	Few Some Some
Dissolved solids in solution	0.5-5%	> 20% (slurries)	0-20%	0.1-0.4%
Elements applicable to	68+	50+	73	82
Sample volumes required	Large	Very small	Medium	Very small to medium
Semiquantitative analysis	No	No	Yes	Yes
Isotopic analysis	No	No	No	Yes
Ease of use	Very easy	Moderately easy	Easy	Moderately easy
Method development	Easy	Difficult	Moderately easy	Difficult
Unattended operation	No	Yes	Yes	Yes
Capital costs	Low	Medium to high	High	Very high
Cost per elemental analysis				
High volume - few elements	Low	High	Medium	Medium
High volume - many elements	Medium	High	Low-Medium	Low-Medium

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So, this is the summary of elemental analysis techniques. You can go through this these are all related to pro related to procedures, and I will not go into detail except or the columns here. One is sample through put it says 10 to 15 seconds per element. Whereas, graphite furnace it is 3 to 4 minutes and ICPAES is 1 to 60 elements per minute, that is the sample through put; that means, how many samples you can analyze in a given time, that is what you sample through put. Dynamic range is in what range calibration holds good.

So, precision is how good they are, how near the readings, without any problems. Now reproducibility, and interferences of course, I need not tell more about it. And dissolved solids in solution they say there is certain amount of limit. So, be very careful whenever you have to may need dissolved salts. So, elements applicable to etcetera are there sample volumes required large very small medium, very small to medium, etcetera. isotope analysis except ICPMS none of the none of the things you can do the isotope analysis. And is of use mostly you can see that flame is very easy, graphite is moderately easy, and the ICPAES is easy, and ICPMS is moderately easy. So, like that these are guidelines for you to choose atomic absorption whenever there is a requirement.

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Methods, Nomenclature and Techniques

- **Reference**
International Union of Pure and Applied Chemistry (IUPAC) and International Organization for Standardization ISO6955- Analytical Spectroscopic methods-Flame Emission, Atomic Absorption and Atomic Fluorescence.
- Solid samples can be directly analyzed by AAS but the majority of samples are presented as liquids or solutions.
- Sample solution – A solution suitably made up from a test portion submitted for analysis.
- Stock solution – A solution of known concentration ~1.000g/L.
- Reference solution – a series of known concentration of the analyte element in a solvent. Synthetic reference solution also contains other chemicals that are required for analysis.
- Blank solution – a zero member compensation solution containing all other chemicals in the same solution concentration except the analyte.

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Now, I will talk about the methods nomenclature and techniques of atomic absorption. So, some of the technical terms you may be familiar, but quite often I see that people are not familiar with the, they get confused. So, coming back to the methods nomenclature,

what is a reference? I am giving you the international union of pure and applied chemistry that is IUPAC. And international organization for standardization, that is ISO 6955 you will find much more details than what I am giving you in this course, but it relates to analytical spectroscopic methods of flame emission, atomic emission and atomic fluorescence. So, they say that solid samples can be directly analyzed by AAS, but majority of the samples are presented as liquids and solutions.

Sample solution, it is a it is defined as a solution suitably made of from a test portion submitted for analysis, that is the sample. Stock solution, earlier we have seen stock solutions are recommended by the manufacturers but it is air. What is a stock solution? That is a solution of known concentration from which dilutions are made, for regular analysis. So, this stock solution you can make and keep in your laboratory for 1 or 2 years depending upon the shelf life. Then there is a term known as reference solution; that means a series of known concentration of the analyte element in a solvent. So, reference solution synthetic reference solution also contains other chemicals that are required for analysis. This I have explained to you that whenever we have been doing gold in sea water for example, I said except gold make a solution of 3.5 percent of sodium chloride magnesium chloride etcetera, that is a known as matrix matching.

So, it this is essentially same as reference solution. Then we want to say; what is the blank solution? A blank solution is a 0 member compensation solution, containing all other elements except the analyte. So, the blank solution serves you to standardize the instrument make it ready for the next analysis. So, that is why I was saying in between any standard you keep on adding the blank, run a system but do not measure ok.

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- Analytical Curve – Calibration Curve A graphical plot of the measured absorbance (A) to the concentration C or mass (m) of the analyte element.
- Characteristic Concentration – characteristic mass – this is the concentration of the analyte element corresponding to a net absorption of 1% or an absorbance of 0.0044 when integrated absorbance peak area is used for evaluation, the unit is 0.0044 A.s (Absorbance seconds).
- Sensitivity – the slope of the analytical curve is termed as sensitivity $\frac{\partial A}{\partial C}$ or $\frac{\partial A}{\partial m}$
- Accuracy – Relates to the closeness of the agreement between true value of an element in a sample and the mean value. It can be calculated by the difference between the true value and the measured values.

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So, you should know about a term known as analytical curve. And analytical curve is the curve calibration curve and a graphical plot of the absorbance versus concentration; C or mass m of the analyte element. So, characteristic concentration we have already said that it is the substance it is the absorbance corresponding to 0.0044 absorbance or a net absorbance of 1 percent. So, this permit is you to measures to compare the different analytical techniques for the same signal.

So, if you are using peak area then the unit is 0.044 absorbance seconds. Then the sensitivity is the slope of the analytical curve that is delta absorbance by delta concentration or delta absorbance by delta mass, instead of concentration I can use mass also. And accuracy relates to the closeness of the agreement between true value of an element in a sample; that means, whenever we are talk we are talking about accuracy, we want to say that the aim of any chemical analysis is to determine accurately what is there in the sample right. So, accuracy obtained in an instrument relates to the closeness of the actual value, that is what it means.

So, the actually true value is never known, true value of a of an element in the sample is never known, and accuracy is only a probability value which approaches the true value; that means, if you do number of determinations and the take an average you may get the accurate. You may get nearer to the accurate value not the exactly to the accurate value. So, true accuracy relates to the closeness of the actual value, what is the actual

difference? So, if people say that they have a determined accurately only means that it is closeness to the actual value and the sample. So, it can be calculated by the difference between true value and the measured value.

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- **Precision** – Precision relates to the closeness of the agreement between the results obtained by applying the analytical procedure repeatedly even though the results are incorrect. It is determined by 2.83 times the standard deviation (σ) for 30 or more measurements or t sigma where t is the Student's factor. (2 sigma or 3 sigma).
- **Standard Deviation (SD)**

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So, precision, what is a precision? Precision relates to the closeness of your measurement. Suppose you determine absorbance for a copper solution we got 0.245, 0.246 0.243 you say precision is good, but a good precision need not be an accurate precision. Because there may be a constant source of error, and you might be incorporating the error, but your precision is good. So, what we say is imagine a guy shooting an arrow to the center of a board, but he misses it, and every time if he misses it by only 0.3 centimeter to the right, then out of 5 times if he hit is it about 5 centimeter to the right 4 times you say our precision is good, but it is not accurate. I will show you an example in the next class.

So, basically what we want to say is, the precision is determined by 2.83 times standard deviation for 30 or more elements or the t sigma. Where t is the student's values, sigma is the standard deviation. T , you multiply it by a student's factor, that is a probability factor by 2 that gives you the precision.

So, we will study about other terms and applications of atomic absorptions in the next class.