

# Interferences in Atomic Absorption

## 1. Chemical interference:

Due to the **formation of a compound** which **cannot be decomposed in the flame**. The **results will always be low**.

General rule for suspecting chemical interferences  
A chemical interference may exist if **analyzing a polyvalent cation** in the presence of a **polyvalent oxyanion** or fluoride

Note the possibility of amphoteric element acting as polyvalent an ion, e.g., aluminum, silicon, boron, chromium, iron, vanadium, molybdenum, etc.

## 2. **Physical interference:**

Variations in viscosity or surface tension between samples and standards. Unequal rates of delivery of material to flame.

## 3. **Ionization interference:**

Caused by **ion formation in the flame**. Lack of recognition and control of this problem can produce either positive or negative errors in an analysis. This effect is responsible for **anomalous curvature in the calibration curve**.

**a.** All of the alkali metals show this interference in the acetylene-air flame.

**b.** Most elements show this interference in the acetylene-nitrous oxide flame.

#### 4. Background Absorption or Scatter interference:

Caused by molecular absorption at resonance wavelength or by **light scatter due to very small, un-volatilized particles** in the flame. This phenomenon is wavelength dependent (greater at short wavelength) and always gives a positive error in the analysis.

#### 5. Spectral Interferences

Spectral interferences arise when the **emission of an interfering species** either overlaps or lies so close to the analyte absorption that resolution by the monochromator becomes impossible.

# Cures for Interferences

## 1- Chemical Interferences:

### a. Use of a releasing agent.

- Tie up the interference chemically. Add between 0.1 and 0.2 % lanthanum chloride to samples and standards.
- Tie up the element to be analyzed with EDTA. This reaction is pH dependent so not as frequently used as lanthanum chloride.

## Note:

- High purity  $\text{La}_2\text{O}_3$  or  $\text{LaCl}_3$ , specified for AA must be used.
- EDTA should be recrystallized from acid several times before use.

b. Use the acetylene-nitrous oxide flame.

Few chemical interferences are ever found in this flame.

c. Isolate the element to be analyzed by extraction, precipitation, or volatilization from the interfering agent.

## **2- Physical Interferences**

- a. Dilution of samples and standards with a common solvent, commonly used for oil analysis.**
- b. Calibration by the method of **standard additions**.**

## **3- Ionization Interference**

**Use of an **ionization suppressor**. Add Between 0.1 and 0.2% of an alkali metal salt to all samples and standards.**

#### 4- **Background Interference:**

- It is the **signal observed** when the **element sought is absent**.
- The **light** at a specific wavelength (Analyte wavelength) is attenuated **by the effect of flame components or matrix components in the sample**.
- Thus **measured absorbance and analyte concentrations are too high**.
- If problem from flame, **blank aspiration will correct** for it.
- It is more serious at short wavelengths ( $< 430$  nm) and **with graphite furnace**.

# Sources of Background in atomic absorption

1. Absorption by flame itself (Serious at  $\lambda$  below 220 nm; e.g., As, Se, Zn )
  - **Water blank** can compensate for this flame absorption
  - In **flame** absorption, **background interference is insignificant at  $\lambda > 230$  nm.**
2. **Absorption by contaminant molecular** species originating from the matrix like NaX or solvents containing X (halogen) **like CCl<sub>4</sub>.**
  - **Halides absorb at  $\lambda < 300$  nm**



### 3. Scattering of radiation from the particulate material in the flame

- Particulate material: Un evaporated droplets; un evaporated refractory salt particles
- Scattering is more serious at short  $\lambda$
- 2 and 3 are most common with Electrothermal atomizer

# Specific Applications Require background correction

1. Graphite furnace
2. Flame determination of low concentrations of an element in the presence of high concentrations of dissolved salts
3. Flame analysis where sample matrix may show molecular absorption at  $\lambda$  of the resonance line
4. Flame determination of an element at  $\lambda$  where flame absorption is high

# Background correction methods

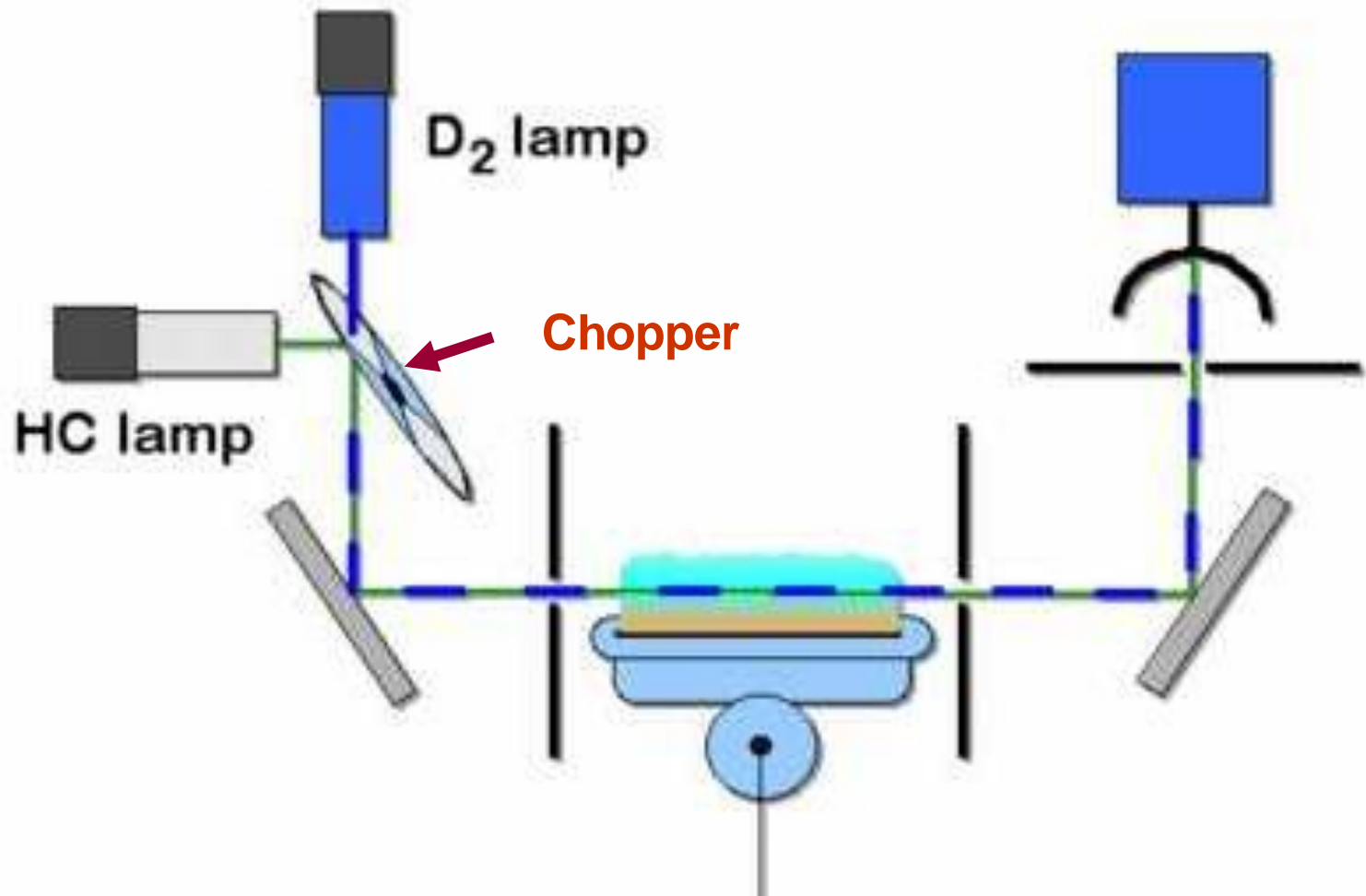
## 1. Using a blank

- **Measure the absorbance of the metal resonance line by both flame & blank (flame system)**
- **Measure the absorbance of the metal resonance line by sample and flame system (flame + blank)**
- **A is the difference**

## 2. Continuous-source correction method

- This method is an available option with most instruments
- **Deuterium lamp is used in conjunction with the HCL lamp**
- **The two lamps are observed by detector alternatively in time**
- **Background usually absorb radiation from D<sub>2</sub> lamp (Abs. D<sub>2</sub>) and HCL (Abs. HCL)**
- **Absorption of the analyte from D<sub>2</sub> lamp is negligible ( $A^a_{D_2} \approx 0$ )**
  - This method is based on the fact that;
    - Atomic bands are very narrow
    - Background bands are molecular in nature thus they are broad bands

# The continuous-source correction method



## Advantages and disadvantages of atomic absorption

**Prone to interferences, poor precision. Must take Step to control Precision:**

1. **Auto samplers** vs. Manual Injection - more precise.
2. **Duplicate analyses** for all samples (repeat if poor agreement).
3. **Standard addition method** - making standards up in sample.
4. **Background correction** for Molecular Absorption.)

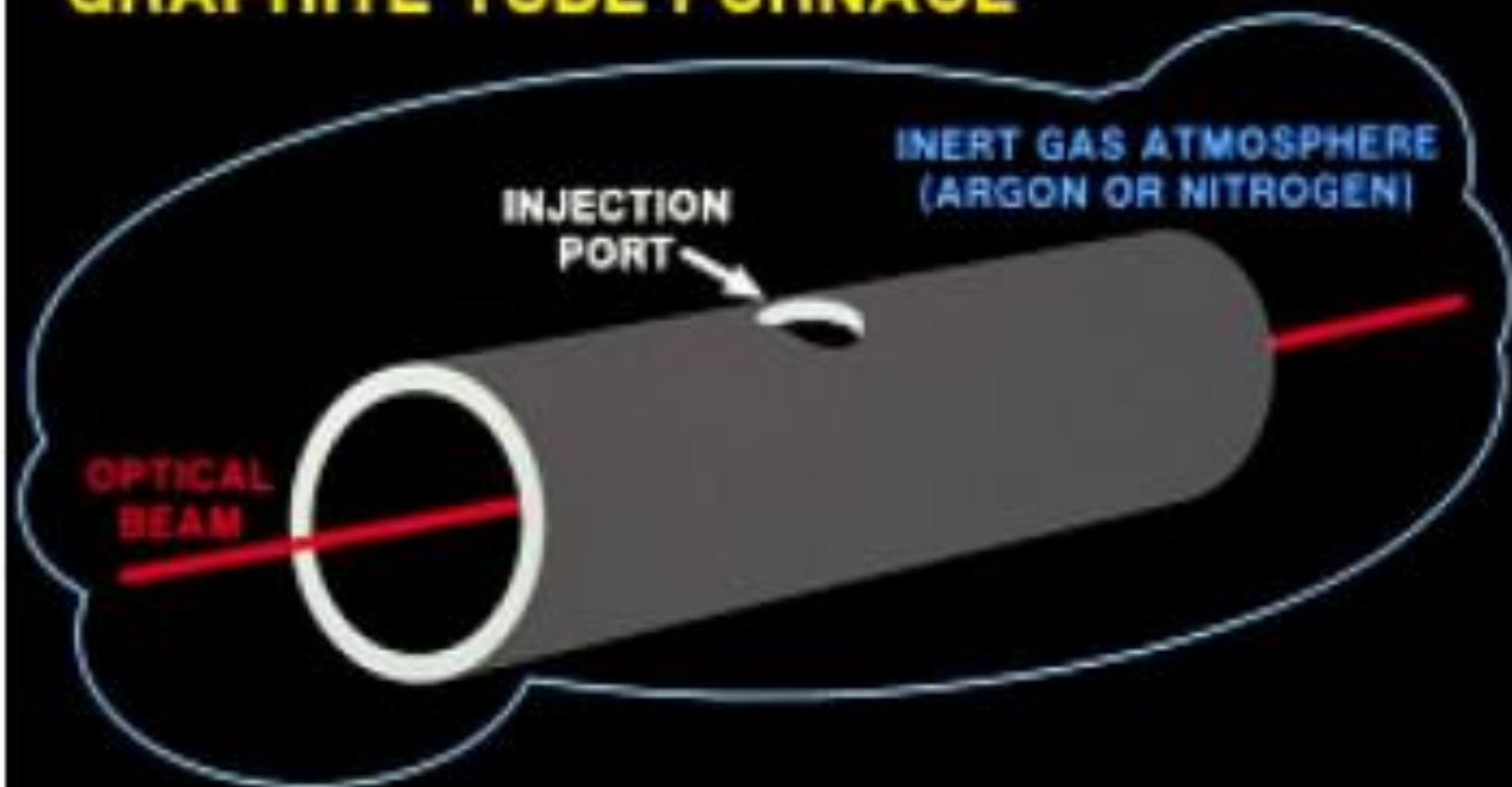
# Flameless atomization or Non-Flame atomization

## ➤ Electrothermal atomization(ET-AAS)

### (Graphite furnace)

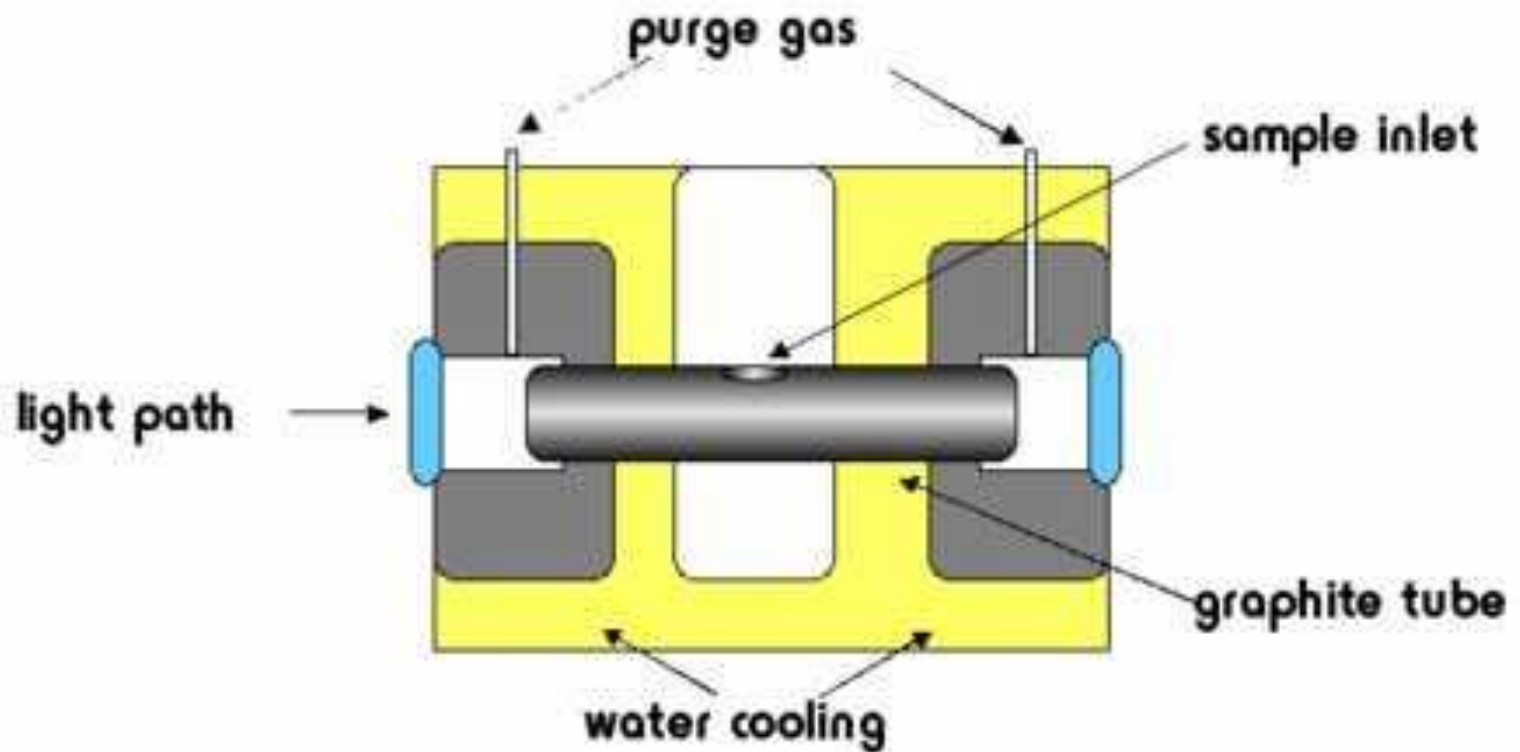
- ◆ Samples are placed in **carbon tubes** which is **heated electrically (graphite furnace)**
- ◆ A technique to **minimize dilution** during atomization of the analyte prior to its determination with atomic absorption spectrometry
- ◆ A technique with **more interferences** than the more reliable flame atomization
- ◆ A technique with **high sensitivity and very good detectability** but **not so good throughput and precision**

# GRAPHITE TUBE FURNACE





## Flameless atomization



## Advantages of GFA ( ET-AAS )

- Increase in the residence time thus more **sensitivity** will be obtained
- Possibility of analyzing samples of **various matrices**
- Analyzing **small size samples** even on the microliter scale
- **Avoiding the formation of refractory oxides** that cause serious interference sources

# **Why do we use an inert Argon gas with Flameless atomization?**

**Argon is often used as a purge gas to:**

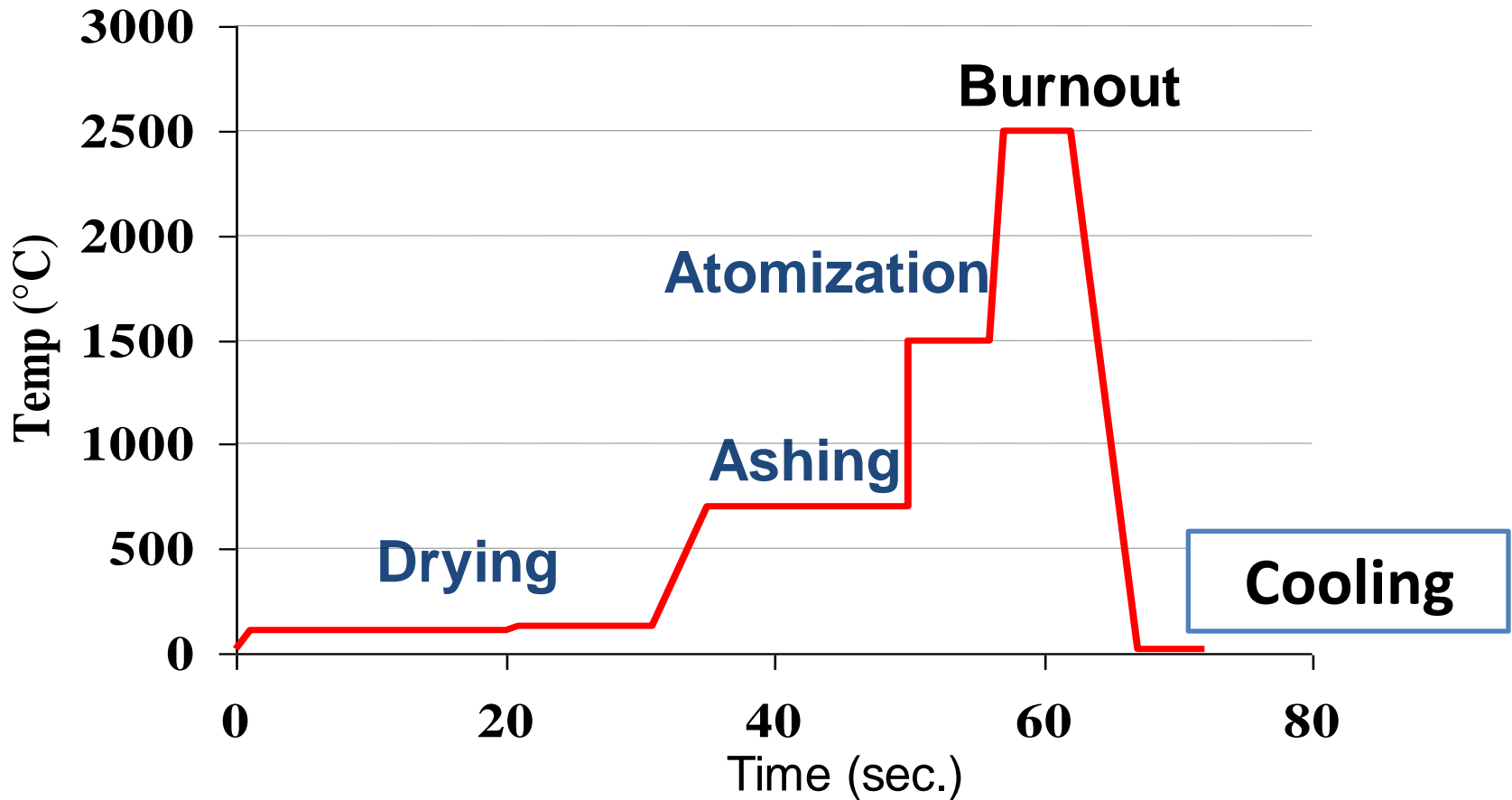
- Remove excess material during the dry and char phases and after atomization**
- Reduce oxidation of the tube.**
- Provides a protective blanket during atomization since high temperature carbon will react with nitrogen to produce cyanogen - you should always vent to a hood anyway.**

# Steps in graphite furnace atomization

- The steps of a GF atomization ( injection 5-100 $\mu$ l sample)
  - Drying
  - Ashing
  - Atomization
  - Burnout
  - Cool

# Steps in GF atomization

## temperature programme



- The sample is injected, usually between **5-30 $\mu$ l** but sometimes the range could be extended to **100 $\mu$ l**.
- The solution is preferably made up of **dilute nitric acid as matrix**
- Sometimes **solid samples** are introduced

- **The drying step**

- **To volatilize the sample solvent**

- **Use some degrees above the solvents boiling point (for water use 110°C) and about the same time in seconds as the injected volume in  $\mu\text{l}$**

- **Ashing of the sample**

May be the most important step

- **Remove** sample **matrix** without losing the analyte
- Highly dependent on both the **analyte and sample matrix**
- Conditions for **every new sample** type should be optimized
- **Inorganic matrix more difficult, because higher temperatures are needed**
- Temp may be in the range **200-500°C**
- Drying and ashing may take about **30-90 sec.**



- **The atomization step**

**This step is to vaporize and atomize the analyte**

- **Temp. is in the range of 2000 to 3000 °C**
- **It takes 3-5 sec.**
- **The vaporization pressure of the analyte dominate the supply of analyte atoms inside the tube**
- **Rapid heating is necessary for good sensitivity**

- **The burnout step**

it is used for taking away parts of the sample not completely volatilized during atomization

- temperatures in the range **2700-3000°C** is most often used
- if vaporization of the sample is achieved, completely, the **sensitivity** will slowly **decrease** and the **imprecision increase**

- **Cooling step**

- its purpose is to **cool down the furnace before next sample is added**

# AAS

## Advantages

- **sensitive**
- **selective**

## Disadvantages

- **lamps - one element at a time**
- **not easy for solids**
- **calibration curves nonlinear above  $Abs. > 0.5$**
- **more costly and less widely applicable than UV- vis.**
- **matrix effects - easy for some metals to be masked**

# Sample Preparation

Many materials of interest, such as soils, animal tissues, plants, petroleum products, and minerals are **not directly soluble** in common solvents, and **extensive preliminary treatment** is often required to obtain a solution of the analyte **in a form ready for atomization**.

## Organic Solvents

**Leaner fuel/oxidant ratios must be employed with organic solvents in order to offset the presence of the added organic material.**

# Calibration Curves

**In theory, atomic absorption should follow the Beer's law with absorbance being directly proportional to concentration.**

# Standard Addition Method

The standard addition method is widely used in atomic absorption spectroscopy **in order to partially or wholly counteract the chemical and spectral interferences** introduced by the **sample matrix**.

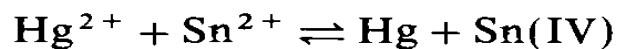
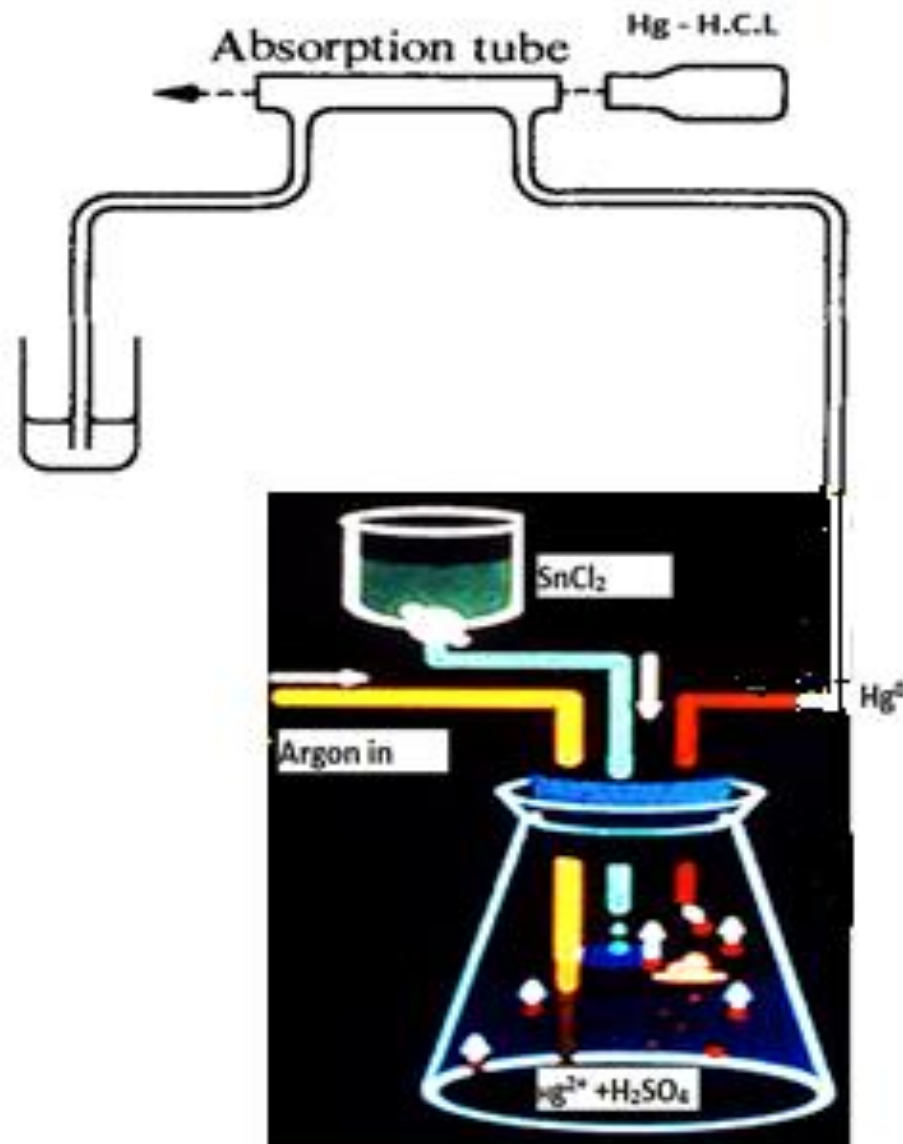
## Applications of Atomic Absorption Spectrometry

Atomic absorption spectrometry is a sensitive means for the quantitative determination of more than **60 metals** or metalloid elements. The resonance lines for the nonmetallic elements are generally located below 200 nm, thus preventing their determination by convenient, non-vacuum spectrophotometers.



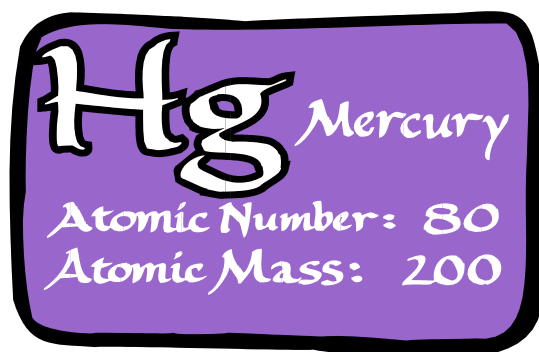
# Mercury - Cold Vapor Atomic Absorption spectrophotometer

- The method is excellent for **MERCURY**
- It concentrates” and “isolates” the Mercury from most any **Sample MATRIX**
- and it provide:
  - A Clean Abs.( high selectivity)
  - Signal at very low concentration levels



A diagram of a suitable apparatus is shown in Fig. The mercury vapour is flushed out of the reaction vessel by bubbling argon through the solution, into the absorption tube.

# Environment pollution by Mercury



- $\text{Hg}^{2+}$
- $\text{Hg}_2^{2+}$
- $\text{Hg}^0$



# Our Fish

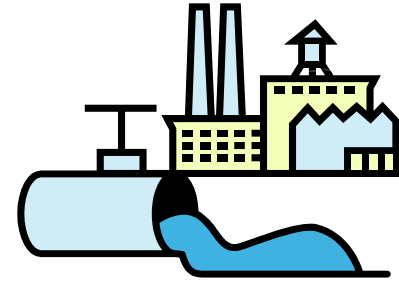


Fish-eating is a major route of **exposure to many pollutants** because fish are **good at accumulating chemicals in their bodies**. Other animals are also accumulators.

**(EPA) U.S. Environmental Protection Agency** reports that **75% of the average American's dioxin exposure is through consumption of meat and dairy products.**

- The **methyl mercury** compounds present in the **effluent wastes discharged** directly into **sea water** were gradually **bioconcentrated by fish and shellfish in the bay**, which provided the sea-food for many families along its shores.
- The disease known as "**Minamata disease**".

# Minamata disease



- **Minamata** disease was first discovered in Minamata village, Japan in 1956
- The disease was caused from the release of **mercury** in the industrial wastewater from the **Chisso** chemical factory

# Bioaccumilated of Mercury

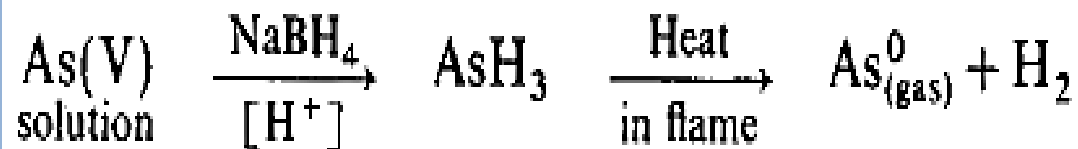
- Mercury accumulated in shellfish and fish which was then eaten by the people who live the area and the result mercury poisoning.
- **Shellfish can contain levels of mercury 100,000 times greater than those in the water in which they live.**
- 2,265 victims were recognized and 1,784 of them died.

# Hydride Generation – AAS ( HG-AAS )

- A number of elements such as arsenic, tellurium and selenium may be reduced by a suitable reagent, e.g. sodium borohydride in acidic solution, to their hydrides as follows..

**Ge, As, Se , Sn , Sb , Te , Pb & Bi**

The reaction sequence, in the case of arsenic, may be represented as follows:





<sup>51</sup> Sb — Atomic Number, Element  
 206.836 — Wavelength  
 I — Ionization States

Detection Limit Ranges

< 0.1 ppb  
 0.1-1 ppb  
 1-10 ppb  
 > 10 ppb

Wavelength (nm)

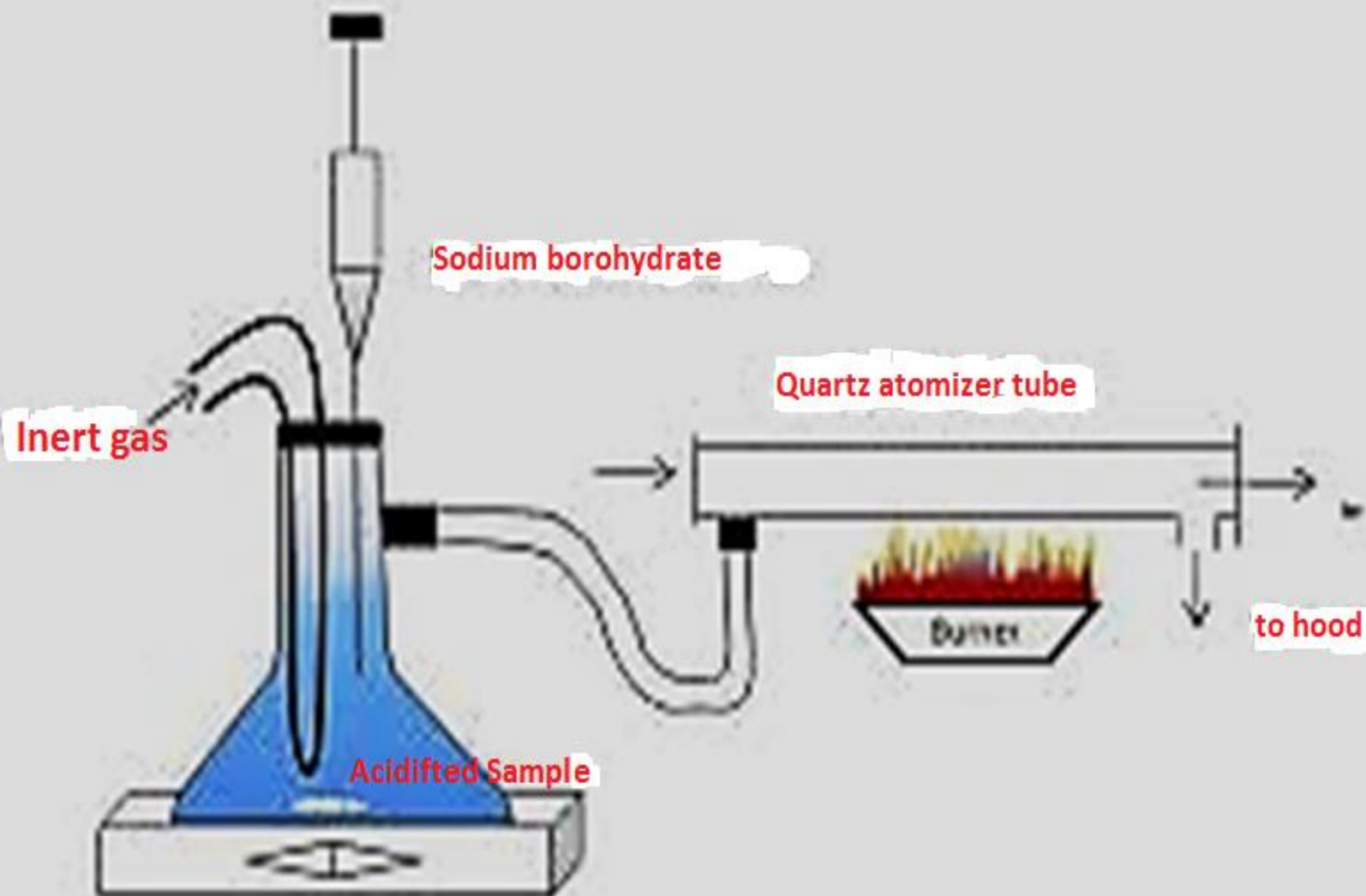
Ionization States

I = Neutral Atom  
 II = +1 ion

<sup>1</sup> H																	<sup>2</sup> He						
<sup>3</sup> Li 670.784 I	<sup>4</sup> Be 313.107 II																	<sup>5</sup> B 249.772 I	<sup>6</sup> C 193.030 I	<sup>7</sup> N	<sup>8</sup> O	<sup>9</sup> F	<sup>10</sup> Ne
<sup>11</sup> Na 589.592 I	<sup>12</sup> Mg 280.271 II																	<sup>13</sup> Al 396.153 I	<sup>14</sup> Si 251.611 I	<sup>15</sup> P 213.617 I	<sup>16</sup> S 180.669 I	<sup>17</sup> Cl 725.670 I	<sup>18</sup> Ar
<sup>19</sup> K 766.490 I	<sup>20</sup> Ca 393.366 II	<sup>21</sup> Sc 361.383 II	<sup>22</sup> Ti 334.940 II	<sup>23</sup> V 290.880 I	<sup>24</sup> Cr 267.716 II	<sup>25</sup> Mn 257.610 II	<sup>26</sup> Fe 238.204 II	<sup>27</sup> Co 228.616 II	<sup>28</sup> Ni 231.604 II	<sup>29</sup> Cu 327.393 I	<sup>30</sup> Zn 206.200 II	<sup>31</sup> Ga 417.206 I	<sup>32</sup> Ge 265.118 I	<sup>33</sup> As 188.979 I	<sup>34</sup> Se 196.026 I	<sup>35</sup> Br 863.866 I	<sup>36</sup> Kr						
<sup>37</sup> Rb 780.023 I	<sup>38</sup> Sr 407.771 II	<sup>39</sup> Y 371.029 I	<sup>40</sup> Zr 343.823 II	<sup>41</sup> Nb 309.418 II	<sup>42</sup> Mo 202.031 II	<sup>43</sup> Tc 249.677 II	<sup>44</sup> Ru 240.272 II	<sup>45</sup> Rh 343.489 I	<sup>46</sup> Pd 340.458 I	<sup>47</sup> Ag 328.068 I	<sup>48</sup> Cd 228.804 I	<sup>49</sup> In 230.606 I	<sup>50</sup> Sn 189.927 II	<sup>51</sup> Sb 206.836 I	<sup>52</sup> Te 214.281 I	<sup>53</sup> I 178.215 I	<sup>54</sup> Xe						
<sup>55</sup> Cs 455.531 I	<sup>56</sup> Ba 455.403 II	<sup>57</sup> La 408.672 II	<sup>72</sup> Hf 264.141 II	<sup>73</sup> Ta 226.230 II	<sup>74</sup> W 207.912 II	<sup>75</sup> Re 197.248 I	<sup>76</sup> Os 228.226 II	<sup>77</sup> Ir 224.268 II	<sup>78</sup> Pt 214.423 I	<sup>79</sup> Au 267.595 I	<sup>80</sup> Hg 194.168 II	<sup>81</sup> Tl 190.801 II	<sup>82</sup> Pb 220.353 II	<sup>83</sup> Bi 223.06 I	<sup>84</sup> Po	<sup>85</sup> At	<sup>86</sup> Rn						
<sup>87</sup> Fr	<sup>88</sup> Ra	<sup>89</sup> Ac																					

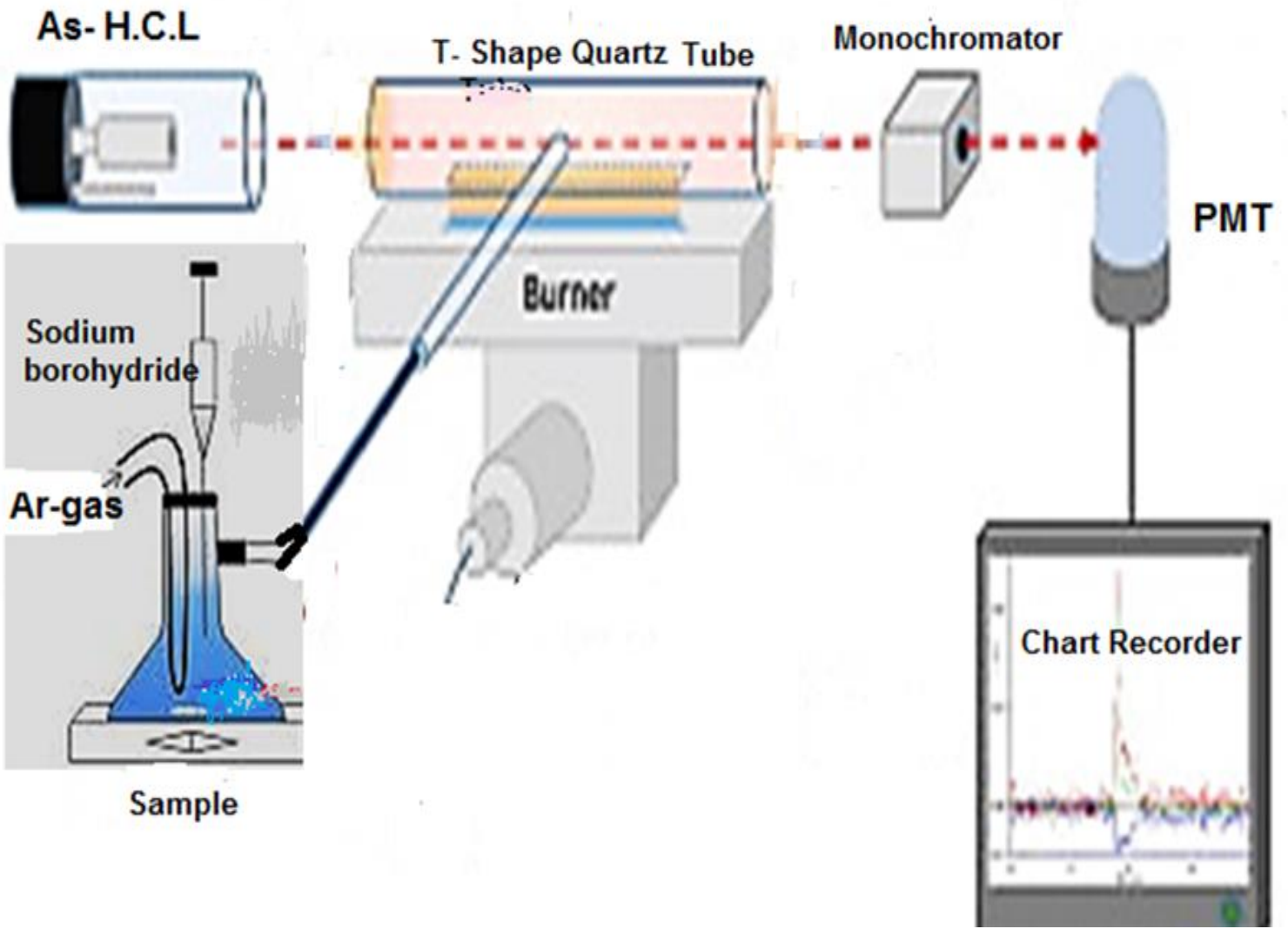
<sup>58</sup> Ce 413.764 II	<sup>59</sup> Pr 414.311 II	<sup>60</sup> Nd 406.109 II	<sup>61</sup> Pm	<sup>62</sup> Sm 442.434 II	<sup>63</sup> Eu 381.967 II	<sup>64</sup> Gd 342.247 II	<sup>65</sup> Tb 350.917 II	<sup>66</sup> Dy 353.170 I	<sup>67</sup> Ho 345.600 II	<sup>68</sup> Er 337.271 II	<sup>69</sup> Tm 313.126 II	<sup>70</sup> Yb 328.937 II	<sup>71</sup> Lu 261.542 II
<sup>90</sup> Th 283.730 II	<sup>91</sup> Pa 385.958 II	<sup>92</sup> U 385.958 II	<sup>93</sup> Np	<sup>94</sup> Pu	<sup>95</sup> Am	<sup>96</sup> Cm	<sup>97</sup> Bk	<sup>98</sup> Cf	<sup>99</sup> Es	<sup>100</sup> Fm	<sup>101</sup> Md	<sup>102</sup> No	<sup>103</sup> Lr

# A hydride generation and atomization system for AAS



# Hydride Vapour Generation Atomic Absorption Spectroscopy (HVG-AAS)

<b>Advantages</b>	<b>Disadvantages</b>
<ul style="list-style-type: none"><li>• Low detection limits.</li></ul>	<ul style="list-style-type: none"><li>• The specific chemical form of the analyte is required.</li></ul>
<ul style="list-style-type: none"><li>• Quite fast measurement.</li></ul>	<ul style="list-style-type: none"><li>• High chemical interference.</li></ul>
<ul style="list-style-type: none"><li>• Most of interferences disappear when the analyte is transferred to a gaseous state.</li></ul>	<ul style="list-style-type: none"><li>• A large excess of the hydride-forming element makes determination of traces of the other one impossible.</li></ul>



# Flow injection analysis- HG-AAS

