



Analysis of heavy elements in food and environmental samples: principles behind atomic absorption spectrometry

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Heavy elements are considered as serious inorganic pollutants because of their toxic effects for life humans.





- ✚ Heavy elements can be classified as:
 - highly toxic (arsenic, cadmium, lead, mercury),
 - ✚ probably essential (vanadium, cobalt)
 - ✚ and essential (iron, copper, zinc, manganese, etc.).



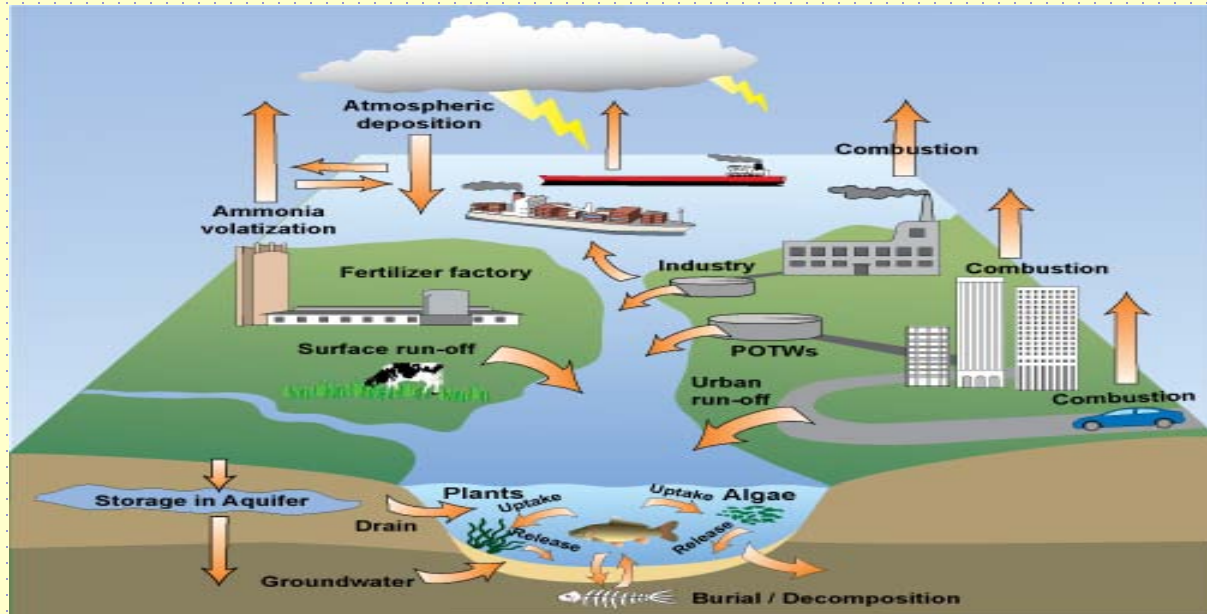
Toxic elements can be very harmful even at low concentration when ingested over a long time period.



The essential elements can also produce toxic effects when the element intake is excessively elevated.

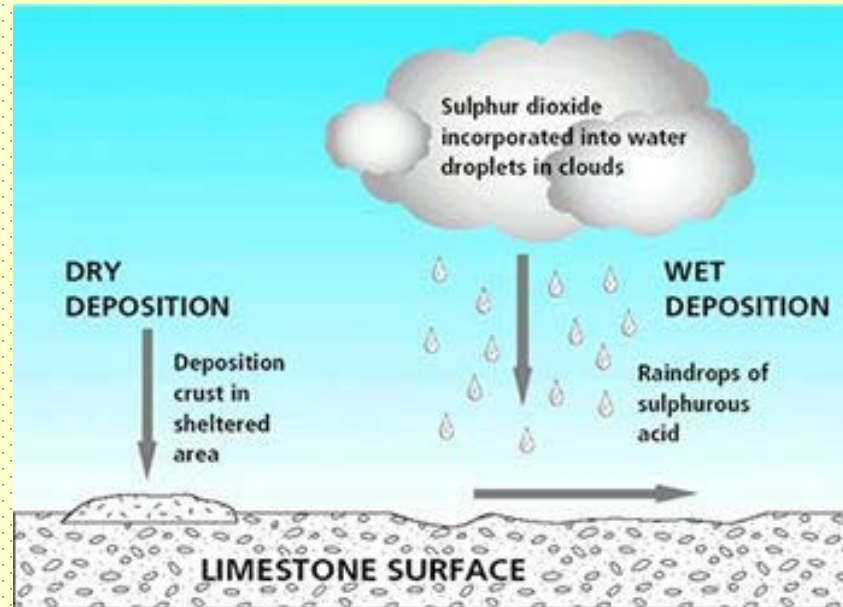


Elevated levels of heavy element concentrations in urban area are results of a wide range of human activities, as well as natural geochemical processes.



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Through wet and dry atmospheric deposition heavy elements contaminate the surface of all environmental compartments such as soil, water and vegetation.

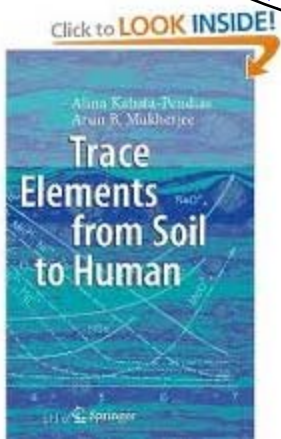


Heavy elements contamination in agricultural environments can come from atmospheric fall-out, pesticide formulations, contamination by chemical fertilizers and irrigation with water of poor quality.





The ecological importance of heavy elements in the environment is closely related to human health due to their high ecological transference potential.



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Indirect consequences of metal contamination of the environment include their subsequent migration to receiving bodies of water via urban runoff, affecting the quality of aquatic organisms through bioaccumulation and biomagnifications, potentially causing metal contamination of food chain.



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Food consumption had been identified as the major pathway of human exposure to toxic elements, compared with other ways of exposure such as inhalation and dermal contact.



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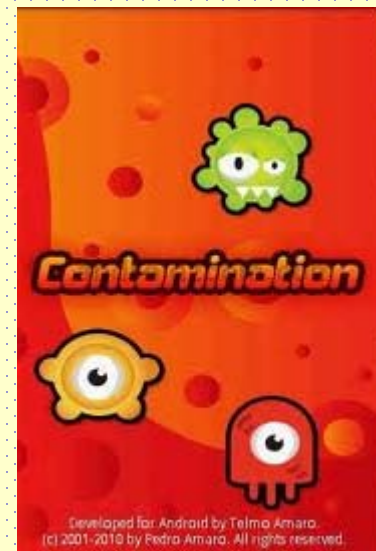
The presence of elements in food depends on several factors.

They might come from:

- ✓ the soil,
- ✓ environment,
- ✓ genotype of the plant,
- ✓ fertilizers and/or metal-containing pesticides,
- ✓ introduced during the production process or by contamination from the metal processing equipment.

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It is necessary to assess the levels of heavy elements in food and environmental samples to investigate possible contamination that would represent a health hazard.



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Commission Regulation (EC) 1881/2006 set maximum levels of lead, cadmium, mercury and tin in different foodstuffs...

20.12.2006

EN

Official Journal of the European Union

L 364/5

COMMISSION REGULATION (EC) No 1881/2006

of 19 December 2006

setting maximum levels for certain contaminants in foodstuffs

(Text with EEA relevance)



EUROPEAN
COMMISSION



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...and the latest Official Bulletin of the Republic of Serbia, No 28/11 (26 April 2011) establishes the maximum level for these elements (Pb, Cd, Hg, Sn) in different foodstuffs in line with this EU regulation.



Foodstuffs analyzed in the CEFSER Lab	Maximum levels (mg/kg) <u>EC regulation 1881/2006</u>		
	Pb	Cd	Hg
Cereals, legumes and pulses	0.2	0.10	-
Vegetables	0.1	0.05	-
Cultivated fungi	0.3	0.20	-
Fruit	0.1	0.05	-
Infant formulae and follow-on formulae	0.02	-	-
Fat and oil	0.1	-	-

Foodstuffs analyzed in the CEFSER Lab	Maximum levels (mg/kg) <u>Serbian regulation No 28/11</u>						
	Pb	Cd	Hg	As	Fe	Ni	Cu
Flour and other cereal products	0.4	0.05-0.1	0.03	0.5	-	-	-
Vegetable	0.1	0.1	0.02	0.3	20	-	-
Cultivated fungi	0.3	0.2	0.5	0.3	20	-	-
Fruit	0.1	0.05	0.02	0.3	30	-	-
Fat and oil	0.1	0.05	0.3	0.1	1.5	0.5	0.4-0.1

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Analysis of heavy metals

In order to determine the content of heavy elements in the samples either food or the environmental, it is necessary to prepare the samples, **i.e. to remove all the organic material and to obtain acid solution of the inorganic matter.**

This can be performed by digestion, either **wet or dry.**

After the digestion, the obtained solutions could be analyzed on heavy elements content with different technique:

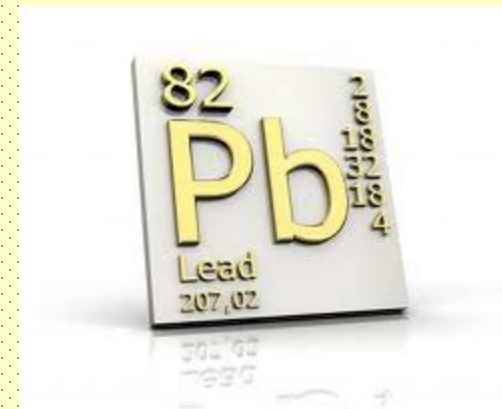
- Flame Atomic Absorption Spectroscopy (FAAS)
- Graphite Furnace Atomic Absorption Spectroscopy (GFAAS)
- Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)
- Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

According to the phenomenon used, these instrumental techniques could be divided into:

- ✚ Optical absorption methods
- ✚ Optical emission methods

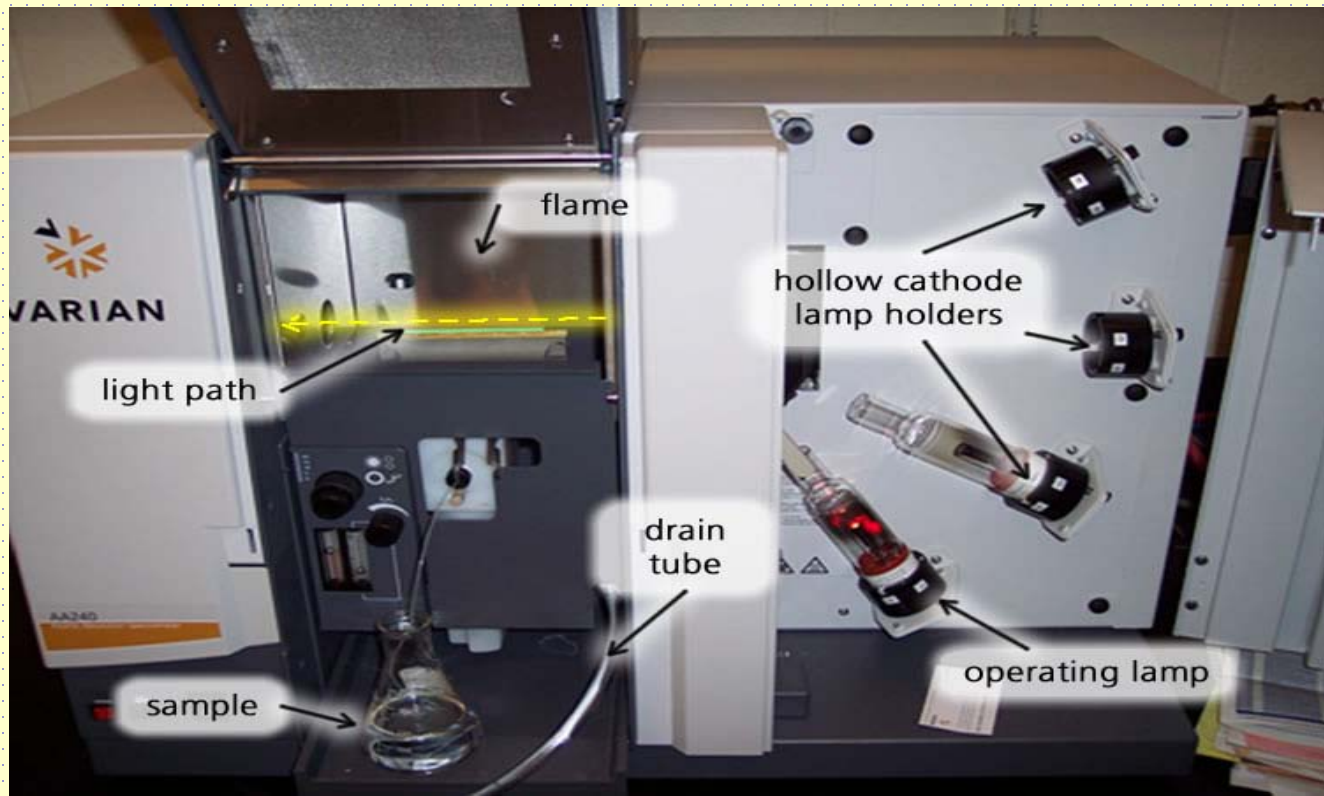
AAS is based on the absorption of the light of the specific wavelengths by the atoms of the elements of interest, while OES method is based on the emission of light with characteristic wavelengths by excited atoms.

Atomic
Absorption
Spectroscopy



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Flame atomic absorption spectrometry is specially favored on account of its selectivity and fairly low operational cost.



**However, it is inadequately sensitive
for the extremely low concentration of
heavy elements residues present in
some matrices such as food.**



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Graphite furnace atomic absorption spectrometry (GFAAS) is an effective choice and a powerful analytical tool for the determination of trace elements in environmental and food samples, because of ...



...its high sensitivity and low detection limit,
using small sample size;
thus, **GFAAS** is established as one of the most
common methods to determine trace elements
in food.



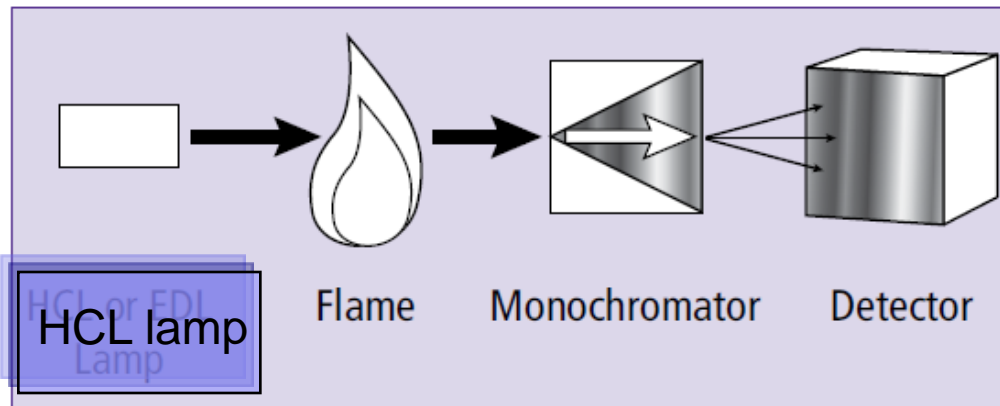
However, this technique has some disadvantages such as :

- ✓ expensive apparatus,
- ✓ complicated operation,
- ✓ high cost of maintenance,
- ✓ and requiring well-controlled experimental conditions.

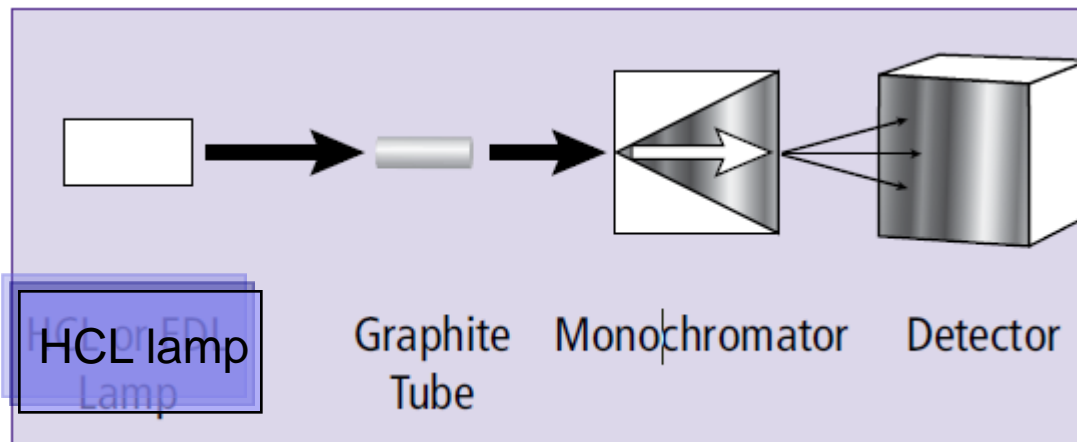


Principles behind GFAAS

AAS with GF uses flameless source for transferring the elements forms present in the sample solution into the atoms capable to absorb light of characteristic wavelengths.



Simplified scheme of a flame AAS

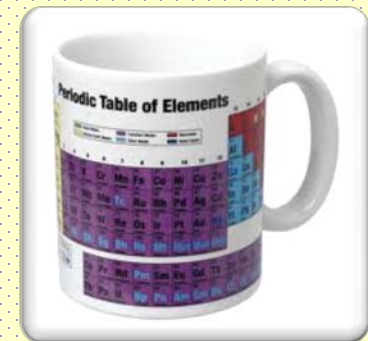


Simplified scheme of a graphite AAS

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Furnace atomization is not applicable to all 67 elements which can be analyzed by flame atomization, and this inability is not related to any temperature limitation.

Namely, dissociation and atomization of certain metals in graphite furnace is not possible, since it does not contain reactive radicals (e.g. C, C₂, CH, H, O, etc.) like flame, which strongly enhances the dissociation of metal compounds.



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Light source emitting the beam of wavelength specific for the analyte used in GFAAS is hollow cathode lamp (HCL) for particular element.



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The following processes occur during the heating of the graphite furnace after the introduction of the sample solution:

- ✱ **DRYING** stage during which the solvent is removed from the samples in the furnace,
- ▣ **ASHING** stage which removes organic molecules or inorganic material,
- ◆ **ATOMIZATION** stage in which free atoms are generated within a confined zone. The absorption signal produced in the atomization stage is in a form of the sharp peak, which height (or area) can be related to the amount of analyte present.

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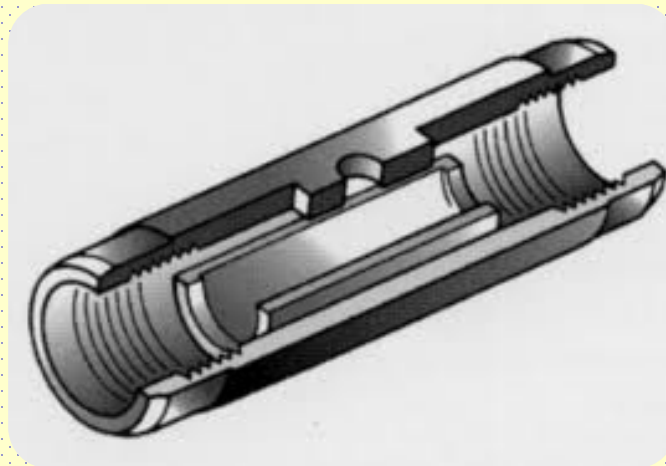


Two types of graphite tubes are available.

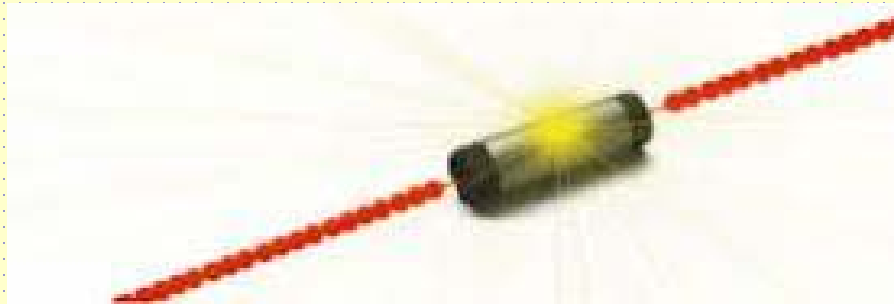
The pyrolytic coated partitioned tube is the one which is normally used for analytical work which does not require the pyrolytic platform. It is especially suitable for high concentrations of acids.

The other type of tube is the pyrolytic coated plateau tube and it is not normally recommended for use alone.

The effect of the platform is to delay the vaporization of the sample until the graphite tube has reached a stable (high) temperature.



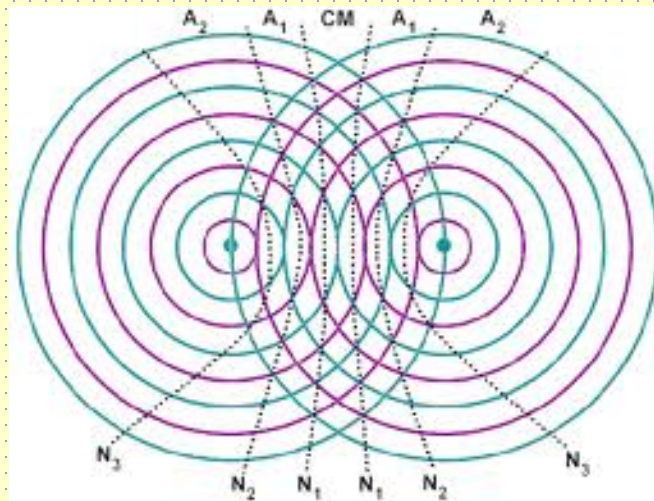
For elements that require a high atomization temperature (around 2700 °C), the lifetime of the graphite components may be relatively short (about 500 firings).



Moreover, the lifetime of graphite tube would be severely reduced if the sample contains high concentrations of certain compounds such as strongly oxidizing acids.

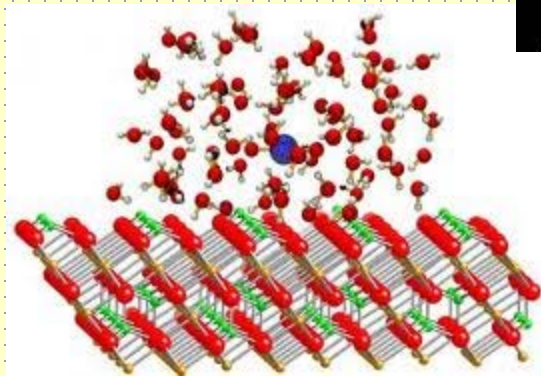
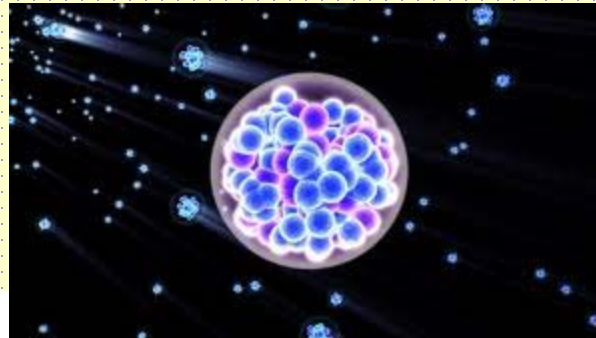
Interferences in graphite tube atomizers may be:

- chemical,
- physical or
- spectral in nature.



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Chemical interferences occurring when the ground-state population of atoms generated within the atomizer is altered as a result of interference by matrix components.



Physical interferences may result from different behaviour in the atomizer during the dry stage of samples of differing surface tension, viscosity or volume.



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Absorption of the incident hollow cathode radiation due to light scattering or to molecular absorption in the graphite tube can cause a false analytical signal unless it is corrected.

Such absorption is typically called background absorption or non-atomic absorption.

In our lab, we used deuterium lamp background correction.



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The chemical modifier is often used in heavy elements analysis which when is added to the sample either to reduce interference or to isolate the analyte in specific form that allows separation between background and analyte atomic absorption signals.



The main purpose of using a modifier or modifier mixture is to stabilize volatile elements in order to use higher pyrolysis temperatures and reduce interferences with the analyte in the atomization step.

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Chemical modifiers for specific elements in GFAAS

Analyte	Modifier	Effect
As	Ni (50 µg/ml) Pd or Pt (100 µg/ml to 2 mg/l)	Permits a higher ashing temperature and enhances the signal
Cd	H ₃ PO ₄ or NH ₄ H ₂ PO ₄ (1000 µg/ml)	Conversion to less volatile phosphate which atomizes at a higher temperature
Hg	Pd (0.1 % solution) (NH ₄) ₂ S in excess	Permits a higher ashing temperature and enhances the signal Stabilizes the signal
Pb	H ₃ PO ₄ or NH ₄ H ₂ PO ₄ (5000 µg/ml) EDTA, citrate, oxalate (0.5%-1% v/v)	Permits a higher ashing temperature and stabilizes the signal Stabilizes lead which atomizes at a lower temperature than does a nitrate or chloride matrix

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