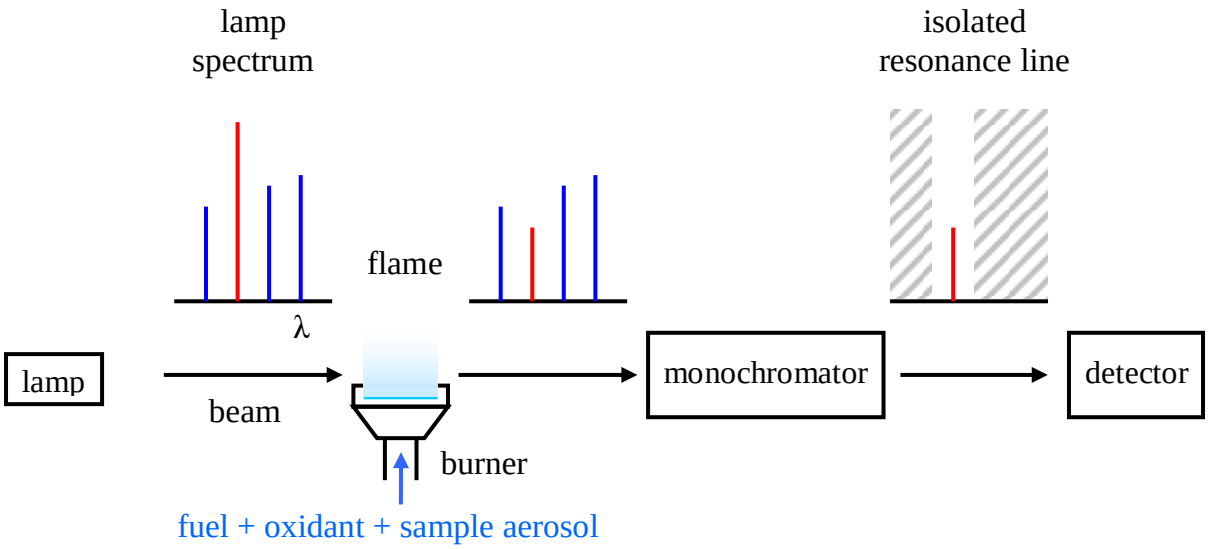
Atomic spectrometry

Atomic absorption spectrometry (AAS)

Principle of the method

absorption of resonance spectral line radiation by ground-state free atoms of the element.



Applicability of AAS

- determination of almost all metals, metalloids and some non-metals (B, Si, P)
- samples:
  - solutions in diluted mineral acids (HNO_3, H_2SO_4, HCl)
    resulting from the decomposition or hydrolysis of a solid sample
  - diluted biological fluids (plasma, blood, urine, milk etc.)
  - suspensions of solid samples (slurries)
  - (solid powdered samples).

Techniques of AAS

- **flame AAS** (**F AAS**) – intended for determination of higher concentrations (tenths to tens μg/ml)

- **electrothermal AAS** (**ET AAS**) or **graphite furnace AAS** (**GF AAS**) – for determination of trace and ultratrace concentrations (tens pg/ml to tens ng/ml)
- **vapour generation techniques** (VG AAS)
  - **hydride generation AAS** (**HG AAS**) – trace conc. of As, Se, Sb, Te, Sn...
  - **cold vapour AAS** (**CV AAS**) – trace conc. of Hg.

Parts of conventional AA spectrometer

- source of emission line of the element (e.g. hollow cathode lamp – HCL)
- continuum radiation source – D_2 lamp
- atomizer (flame, graphite furnace or quartz tube)
- background corrector
- monochromator
- detector (e.g. photo-multiplier)
- control unit or computer.

Analytical features of AAS

Sensitivity – a slope of calibration line; sensitivity in F AAS is indirectly expressed as *characteristicconcentration* (i.e. such concentration [μg/ml] of the element that gives the absorbance of 0.0044); *characteristic mass* [pg] is used to characterize analytical sensitivity in GF AAS.
Detection limits – in F AAS approx. 2 to 5 times lower than characteristic concentration.
Working range – approx. 2 to 3 orders of magnitude (a narrower range in GF AAS).
Repeatability – in F AAS under optimum conditions RSD 0.5-1.5 %; RSD in GF AAS ranges approx. from 1 to 5 %.
Accuracy, trueness – especially in GF AAS accuracy can be affected by the sample matrix (e.g via analyte transport, formation of thermally stable compounds, non-atomic absorption).

Measures to assure quality of analytical results in AAS

- appropriate calibration

- optimization of fuel-oxidant gas composition (in F AAS)
- optimization of all steps of the atomizer temperature programme (in GF AAS)
- selection of suitable matrix modifier for electrothermal atomization
- optimization of burner height (in F AAS)
- addition of suitable reagents (releasing or deionizing) to the samples in necessary cases (in F AAS).

Flame AAS

- the liquid sample is aspirated into a nebulizer (4-7 ml/min) and the formed aerosol is introduced into flame, where aerosol desolvation, evaporation and analyte atomization occur
- a steady-state absorbance signal is measured

Flames

- **air-acetylene flame** (*t* 2000-2300°C): for readily atomizable metals (alkali metals, Mg, Ca in the absence of interferents, Zn, Cu, Cd, Pb, Mn, Fe, casually Cr)
- **nitrous oxide- acetylene flame** (*t* 2800-3000 °C): for hardly atomizable elements (Sr, Ba, V, Cr, Mo, Al, Si, B etc.); it is also applied for determination of other elements (Ca, Mg, Ni, Fe) in difficult matrices (those containing phosphates, silicates…)

Factors influencing the sensitivity of F AAS analysis

- selection of analytical line
  e.g. the most sensitive line for Cu detn. is 324.7 nm (characteristic conc. approx. 0.025 μg/ml), while the least sensitive one is 244.2 nm (characteristic conc. 9 μg/ml)
- current of the lamp
- efficiency of sample aerosol formation (the nebulizer setting up, the viscosity and surface tension of the sample solution)
- length of atomization zone (the air-C_2H_2 burner has 10 cm slot, the N_2O-C_2H_2 one only 5-6 cm slot)
- height of observation (given by vertical position of the burner)

- atomization efficiency (effect of temperature).
- ionization of the analyte (ions formed from atoms by loss of electrons do not absorb the line radiation; temperature affects the rate of analyte ionization)

Some problems (difficulties) of F AAS application

1. partial **ionization of some elements** (alkali metals, alkali earth metals) in the flame and non-uniform deionizing effect of the matrix
   consequence: some loss of sensitivity, convex distortion of calibration curve, inaccurate results in the presence unknown amounts of other easily ionizable elements
   solution: addition of a compound of an easily ionizable element (CsCl or KCl) in a large excess (CsCl 1-5 mg/ml)
2. **chemical interferences** induced by the sample matrix resulting in **the incomplete atomization of the analyte** (e.g. that of Ca in the presence of Al, Ti, phosphates, silicates etc.)
   consequence: e.g. negative bias of the results of Ca determination in phosphorus-containing samples (all biological materials)
   solution: addition of releasing agent ($LaCl_3$, La conc. up to 10 mg/ml) to the samples and standards (in air-C_2H_2 flame) or measurement
   in hot N_2O-C_2H_2 flame (addition deionizing agent is needed).

Advantages of F AAS

- fast analysis (10-15 s per sample per element)
- very good precision (repeatability)
- no or moderate interferences that can be easily corrected
- easy automation of the measurement
- low cost

Electrothermal AAS

Synonyms: ***AAS with electrothermal atomization*** (ET AAS); the most common atomizer is a graphite tube; therefore the method is also known as ***graphite furnace AAS*** (GF AAS)

- the volume of a sample (10-50 µl) is injected into the atomizer
- the sample is thermally treated and atomized
  (duration of measuring cycle is 1-3 min)
- absorbance of the element is measured during the atomization step
  (total absorbance peak and peak of the background signal is recorded)
- the method is by 2-3 orders of magnitude more sensitive than F AAS

Atomizer

is usually a **graphite tube** (diameter 3-4 mm, length 20-25 mm) with a sampling hole (injection port);
the tube is electrically heated, cooled by water and rinsed by a flow of inert gas (Ar or N_2);
a graphite **platform** can be inserted into the tube.

Types of graphite tubes

- made of porous graphite (normal tubes) or pyrolytically coated tubes
  (non-porous glassy surface)
- with or without a platform or a probe
- heated longitudinally or transversally

Steps of the measuring cycle in GF AAS

1. **injection** of the sample (and the modifier) on the wall or on the platform of the tube
2. **drying** – evaporation of solvent at a temperature slightly above the boiling point (solutions in diluted HNO3 are dried at 120 °C); the solution must not boil; duration of drying depends on the sample volume (1-2 s/µl); inert gas flows through the tube

3. **pyrolysis** – thermal decomposition at higher temperatures (300-1200 °C) →
   → decomposition of sample matrix to gaseous products removed by the flow of inert gas
   e.g decomposition of nitrates:
   $2\ M(NO_3)_2 \rightarrow 2\ MO + 4\ NO_2 + O_2$
   other processes: reaction between the analyte and the modifier, between matrix components and the modifier
   duration of pyrolysis: tens seconds
4. **atomization** – fast heating to high temperature (1400-2700 °C) → evaporation of the analyte, splitting molecules to atoms:
   $MO \rightarrow M + O$
   total absorbance and background signal are recorded (duration: 3-5 s)
   just before atomization the flow of inert gas is stopped
   two possibilities: atomization of the wall, or of the platform
5. **cleaning** – heating to very high temperature (2400-2700 °C) for approx. 3 s; inert gas flow removes all evaporated compounds off the atomizer
6. **cooling** of atomizer to laboratory temperature.

Matrix modifiers in GF AAS

Matrix modifiers are compounds added to the sample before injection or injected to the atomizer together with the sample. Modifiers affect the thermal processes taking place in the atomizer to minimize losses of analyte during pyrolysis and to enable more effective matrix components removal.
Some modifiers change the sample matrix to evaporate the matrix components at lower temperature; other type of modifiers work as an analyte stabilizer.

Modifiers – types and examples

- compounds (e.g. NH_4NO_3) converting a non-volatile matrix (NaCl) to a volatile compound:

$NaCl$	+	NH_4NO_3	→	$NaNO_3$	+	NH_4Cl
b.p. 1418 °C		decomposes at 210 °C		decomposes at 380 °C		sublimes at 345 °C

- compounds converting an analyte halogenide (volatile species) to a less volatile salt (e.g. sulphate or phosphate) – e.g. H_2SO_4 for detn. of Tl , $NH_4H_2PO_4$ for most metals (Cd, Pb, Ni, Mn…):
  $MX_2 + NH_4H_2PO_4 \rightarrow M_2P_2O_7 \rightarrow MO + P_2O_5$;
  the analyte can be thermally stabilized also by the formation of intermetallic compound: e.g. compounds of platinum group metals (Pd, Ir) are applied for stabilization of volatile analytes (Pb, Cd…) – mixture of $Pd(NO_3)_2$+$Mg(NO_3)_2$ or Pd^{2+} salt + reducing agent (ascorbic acid); Ni^{2+} and Cu^{2+} salts are used to stabilize Se, As or Te

Non-specific absorption in AAS (absorption background)

is an attenuation of the analytical line radiation, which is not caused by absorption by free atoms of the element. If the non-specific absorption is not corrected it induces a positive bias. It is much more serious for GF AAS as compared to F AAS, especially in the region of 180-350 nm.

Non-specific absorption is caused by

- **light scattering** on solid particles of dry aerosol or particles of carbon resulting from the incomplete burning of acetylene in reducing flame;
  in GF AAS the non-volatile components of the sample matrix cause this effect in the step of atomization if they were not removed in the step of pyrolysis;
- **absorption of the radiation by molecules and molecular fragments** – it is manifested by broad absorption bands in the region of 200-400 nm (alkali halogenides) or fine structure rotational and vibrational transitions of radicals, molecules or molecular ions and fragments

Correction of absorption background

- **using continuum source of radiation**
  i.e. D_2 lamp (most effective up to 350 nm) or halogen bulb with tungsten filament (in the region of visible light)
  two signals are measured:

– total absorption – measured with line source (e.g. HCL)

– non-specific absorption – measured with the continuum source

- **using Zeeman effect**

  – based on splitting of en energy levels of the atom (spectral lines) in magnetic field

Temperature programme of the graphite tube atomizer

is chosen according to:

- physico-chemical properties of the analyte and its compounds
- contents of matrix components
- way of sample preparation
- type of atomizer (with or without a platform etc.)
- kind of matrix modifier

Optimization of temperature programme:

- **test of drying temperature** and the duration of drying
- **pyrolysis and atomization temperature plot**
  - analyte alone
  - analyte + modifier
  - analyte + matrix
  - analyte + matrix + modifier

  optimum pyrolysis temperature is the maximum temperature, at which any losses of the analyte do not occur yet and maximum analyte absorbance and minimum background is achieved during atomization;

  optimum atomization temperature is minimum temperature , at which a complete and fast evaporation of the analyte is achieved and a reproducible signal (in terms of height and shape of the peak) is recorded.

Possible GF AAS applications

- trace analysis and microanalysis (from very small samples)
- analysis of liquid samples even when organic matrix is present (beverages, milk, blood, plasma etc.)
- analysis of liquid samples with permanent inorganic matrix (urine, sea water etc.) – rather difficult task
- analysis of powdered solids or suspensions of solid samples

Disadvantages of GF AAS

- a lot of interferences – a thorough optimization of analysis conditions is necessary
- limited concentration working range (especially with Zeeman's instruments)
- slow analysis
- expensive equipment

Hydride generation AAS

- HG AAS is applied namely for determination of trace amounts of As, Se (Te, Sb, Ge, Sn, Pb...)
- the gaseous hydride of the analyte (e.g. AsH_3 or H_2Se) is formed from the corresponding compound of the analyte (H_3AsO_3 or H_2SeO_3) by reducing reaction with $NaBH_4$ ("sodium borohydride"); the reaction takes place in a hydride generator, gaseous products are delivered to the atomizer (usually a heated quartz tube)
- the technique is by 2-3 orders of magnitude more sensitive than F AAS
- as a consequence of analyte transfer into gaseous phase most of interferences are eliminated (namely those manifested on analytical lines of As and Se that are located in the region of wavelength < 200 nm).

Conditions of the hydride-forming reaction

- the reaction takes place in an acidic solution – the acidic solution (HCl or H_2SO_4) of a sample is mixed with an alkaline solution of sodium borohydride (0.5- 10 % $NaBH_4$ in 0.1-1 M NaOH); the reaction of BH_4^- and H^+ generates hydrogen atoms
  $BH_4^- + H^+ + 3\ H_2O \rightarrow H_3BO_3 + 8\ H$
  that reduce the analyte compounds into the form of hydride
  $H_3AsO_3 + 6\ H \rightarrow AsH_3 + 3\ H_2O$
  $H_2SeO_3 + 6\ H \rightarrow H_2Se + 3\ H_2O$
- it is advisable to assure that the analyte is present in one oxidation state only (As^{III} or As^{V}, Sb^{III} or Sb^{V}, Se^{IV} or Se^{VI}); as the lower valency is more advantageous the analyte compounds of the higher valency are mostly reduced before the hydride-forming reaction; heating of a sample with potassium iodide in acidic medium and with hydrochloric acid alone is used for reduction of As^{V} and Se^{VI}, respectively:
  $H_3AsO_4 + 2\ I^- + 2\ H^+ \rightarrow H_3AsO_3 + I_2 + H_2O$
  $H_2SeO_4 + 2\ Cl^- + 2\ H^+ \rightarrow H_2SeO_3 + Cl_2 + H_2O$

Arrangement of the hydride-generation system

hydride generator (reactor) → gas-liquid separator → atomizer
or
hydride generator (reactor) → gas-liquid separator → collector → atomizer

Hydride generator

consists of

- a pump for a sample solution and reagents
- a reactor (a container or a capillary)
- a gas-liquid separator

Types of hydride generators

1. **continual generators** – the sample solution, the sodium borohydride solution (and diluted hydrochloric acid) are aspirated by the peristaltic pump; the flows are joined and mixed in a PTFE capillary; small bubbles of gaseous products (hydrogen + hydride) are formed; the flow of liquid and gas enters the gas-liquid separator and the gaseous phase is transferred with carrier gas (N_2 or Ar containing traces of oxygen) to the atomizer, where the hydride is atomized and a steady-state absorbance is recorded
2. **batch generators** – use a container (flask) as a reactor; to the sample dose in the reactor the borohydride reagent is injected and the gaseous products are delivered by the carrier gas flow to the atomizer; the peak of absorbance is recorded
3. **flow injection generators** – a certain volume of the sample is injected into the flow of carrier liquid (HCl solution), the flow is mixed with the flow of the borohydride solution; after the reaction, gas separation and atomization an absorbance peak is recorded.

Atomizer for HG AAS

is most often an **externally heated quartz T-shaped tube** positioned above the air-acetylene burner (heated by flame) or in a heating block (electrically heated to approx. 900 °C); trace amount of oxygen is necessary for splitting of the hydride molecules into atoms.

Advantages of HG AAS

- low detection limits (0.1-0.3 ng/ml of As or Se using conventional systems)
- quite fast measurement (30-50 s per sample)
- most of interferences disappear when the analyte is transferred to a gaseous state

Disadvantages (problems) of HG AAS

- the specific chemical form of the analyte (certain valenncy) is required – some ways of sample decomposition (e.g. procedures usin HNO_3 only or HNO_3 + H_2O_2 without H_2SO_4) are not suitable as oxidising agents mostly interfere with hydride generation
- high concentrations of Cu, Ni, platinum group metals and other transition metals cause serious interferences
- a large excess of the hydride-forming element makes determination of traces of the other one impossible (e.g. a lot of Se and traces of As or *vice versa*).

Atomic emission spectrometry

Principle of the method

elements contained in a sample are atomized and partially ionized in a suitable excitation source; the atoms and the ions change their energy state to a higher level; when they return from the higher state to the lower or even the ground state they emit a spectrum consisting of characteristic spectral lines; the intensity of the spectral line is proportional to the element content.

Some excitation sources used for AES

- flame
- spark discharge
- electric arc discharge
- plasma discharge
  - direct current plasma (DCP)
  - microwave induced plasma (MIP)
  - inductively coupled plasma (ICP)

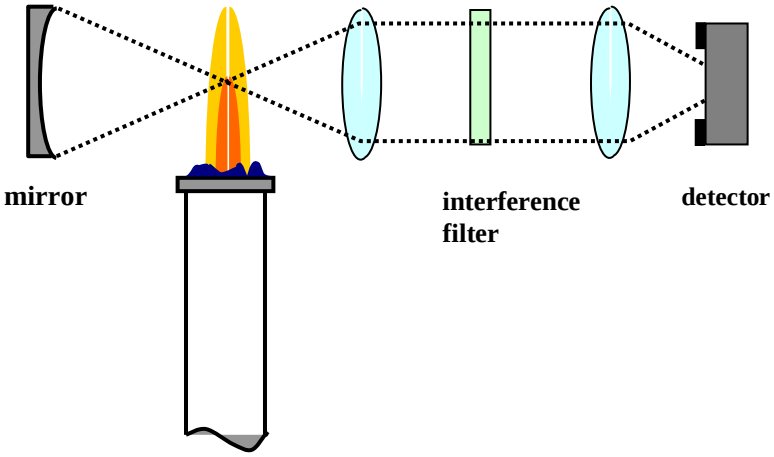
Flame photometry

Synonymous name: ***flame (atomic) emission spectrometry*** (F AES or FES)

Flames and burners

- air-acetylene or nitrous oxide acetylene
- an aerosol of a sample is delivered to the burner
- the burner (in contrast with burners for AAS instruments) is a single vertical tube (but each flame AA spectrometer can operate in the emission mode)

Scheme of flame photometer



Applications of flame photometry: namely determination of alkali and alkali-earth metals.

Advantages: wider dynamic range than that in F AAS, simple and cheap instruments.

Disadvantages: the method is limited only to easily excited and easily ionized elements.

Inductively coupled plasma atomic emission spectrometry

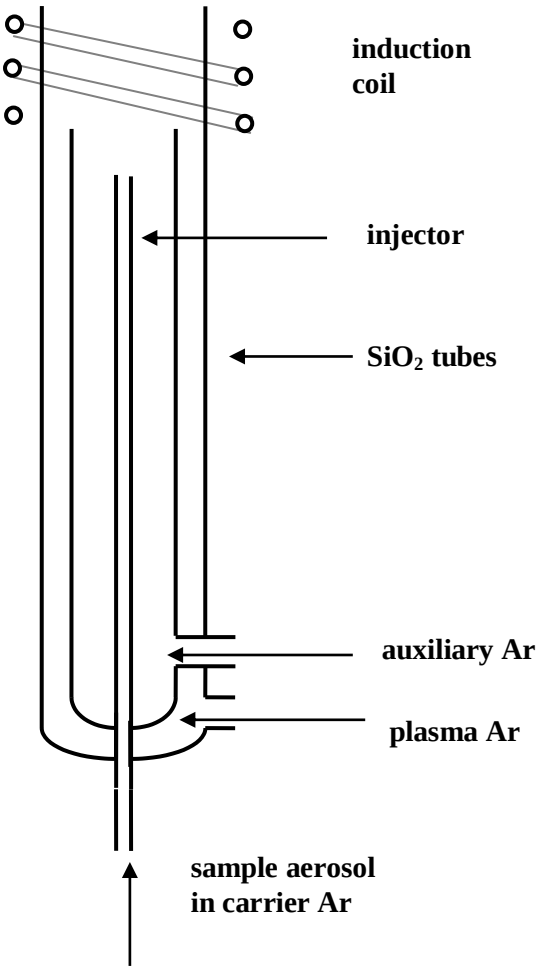
Synonymous name: ***inductively coupled plasma optical emission spectrometry***
Abbreviations: ICP-AES, ICP-OES

- an aerosol of the liquid sample is introduced into ICP, the elements are atomized and ionized at a very temperature (approx. 6000 K) and the intensities of emitted lines are measured
- the method allows fast multi-element analysis (including all metals and some non-metals such as P, S)
- detection limits are lower than those of flame AAS
- concentration working range is much wider than that in AAS; linear calibration within the range of 5 or more orders of magnitude are usually possible
- needs a spectrometer of high quality and high spectral resolution (expensive instruments)
- quite high operating costs (large argon consumption)

ICP discharge

- is created in the flow of excited argon at the outlet of plasma torch
- it is initialized by spark discharge and maintained by high-frequency energy from an induction coil (power input 1-1.8 kW)
- temperatue of the plasma discharge is 3500-10000 K

Inductively coupled plasma torch



The torch consists of three concentric quartz tubes (the injector tube is made of quartz or corundum or sapphire) positioned co-axially in an induction coil (made of copper). Argon flows through the individual tubes.

Flows of argon:

– **plasma** (outer plasma): 12-20 l/min
creates the discharge
– **auxiliary** (intermediate): 0-1 l/min
stabilizes the discharge
– **carrier** (central): 0.5-1.5 l/min
introduces the sample aerosol
and creates an analytical channel

ICP spectrometer

consists of

- a peristaltic pump for sample aspiration
- a nebulizer and a spray chamber
- a high-frequency generator operated at 27.12 or 40.68 MHz
- a torch
- a wavelength selector (monochromator or polychromator)
- a detector
- a control unit or a computer

The emitted lines can be viewed in radial direction (torch in a vertical position) or axial direction (torch in a horizontal position). Some instruments enable a dual view of the plasma.

Measurement of spectral line intensity

- scanning of the line profile
- measurement at the top of the line

A subtraction of background signal in the proximity of the line is necessary.

Problems of ICP spectrometry

- spectral interferences (spectral lines overlap, spectral background)
- non-spectral interferences
  - e.g. a drop of analyte intensity caused by less efficient excitation and ionization of the analyte in the presence of excess of an easily ionisable element, such as K
  - can be compensated using an internal standard element