Atomic spectroscopy

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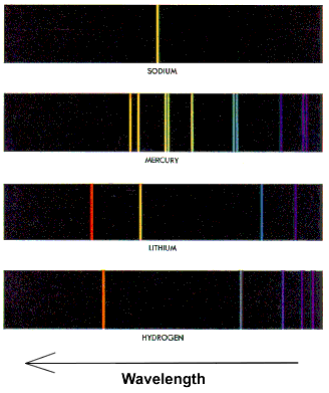
Atomic spectroscopy
Principle of operation

*In **atomic spectroscopy***, generally we study the electronic transitions in atoms, therefore these spectroscopic methods provide ***analytical information about the elemental composition of a sample***. With the exception of a few special methods (see later), ***the electronic transitions of valence shell electrons in free atoms are studied*.**

Emission, absorption and fluorescence spectra of free atoms are line spectra, which means they consist of very narrow peaks (FWHM is on the order of 0.01 nm or less). A line spectrum is produced, because electronic energy levels in atoms are well defined, quantized.

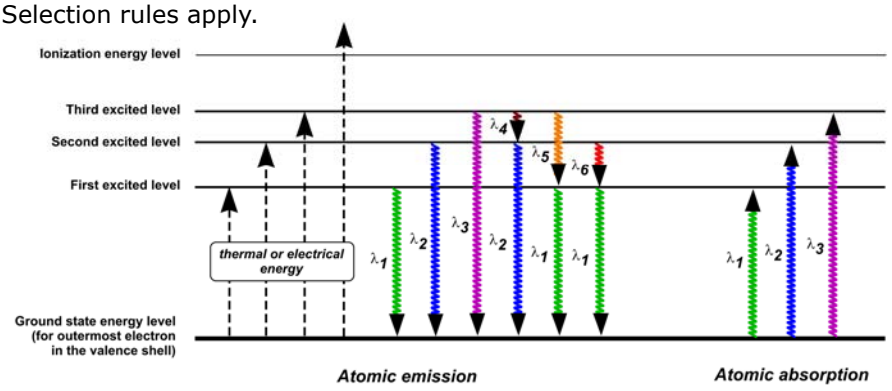


Atomic spectroscopy
Principle of operation

By the analogy of similar molecular spectroscopies, the transitions involved in an atomic emission, atomic absorption (and atomic fluorescence, not seen in the figure) spectrum can be easily imagined. Selection rules apply.

Effect of energy difference and temperature on population of excited states

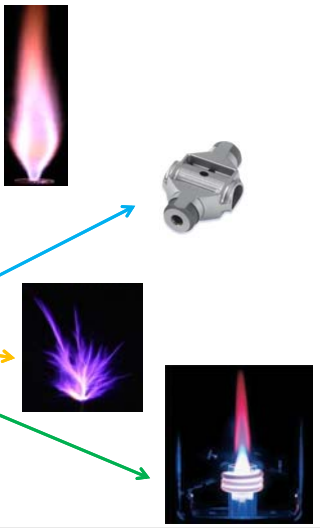
Wavelength difference of states (nm)	Energy difference of states (J/atom)	Excited-state fraction (N^*/N_0)*	
		2 500 K	6 000 K
250	7.95×10^{-19}	1.0×10^{-10}	6.8×10^{-4}
500	3.97×10^{-19}	1.0×10^{-5}	8.3×10^{-3}
750	2.65×10^{-19}	4.6×10^{-4}	4.1×10^{-2}



Atomic spectroscopy
Atomization

No matter what measurement mode we use, the first step in atomic spectroscopy is to break down the sample to produce free atoms. This is done in the ***atomizer*** of an atomic spectrometer, which is a source of high temperature (several thousand of Kelvins, locally). This can be, for example, realized in the form of:

- flames
- furnaces
- electric arcs or sparks
- plasmas

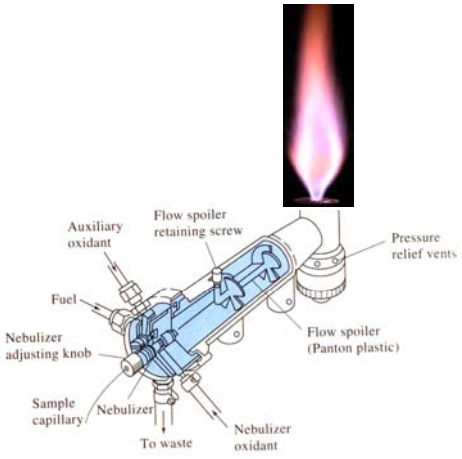


Atomic spectroscopy
Atomization

In atomic absorption spectroscopy (AAS), the atomizer is only needed to atomize the sample, but electronic excitation is done by an external line light source (hollow cathode lamp, laser, etc.). Consequently, a too high temperature of the atomizer (above ca. 3000 K) is inadvantageous, because ionization of many of the sample atoms (for example alkalis) would also occur. Remember, that AAS typically based on line absorption of ground state atoms, therefore the AAS signal is proportional to the population of the ground level.

In atomic emission spectroscopy (AES), the high temperature source is also responsible for the thermal (collisional) excitation of atoms. The efficiency of collisional excitation increases with the temperature. Also, the emission signal is proportional to the population of the excited levels, so in AES, an as high as possible temperature of the atomizer is required (min. ca. 5000K). Ionization therefore is common, and AES often measures emission from elemental ions too.

Atomic spectroscopy
Flame atomizers



Various combinations of fuel and oxidant gases can be used to produce a flame atomizer. The most populars are acetylene/air, acetylene/N_2O and propane-butane/air. The sample is introduced into the flame in the form of an aerosol, mixed into the oxidant gas flow.

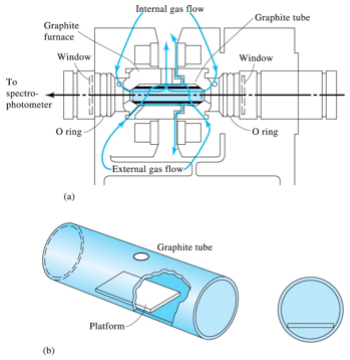
TABLE 26-2
Flames Used in Atomic Spectroscopy

Fuel and Oxidant	Temperature, °C
Gas/Air	1700–1900
Gas/O_2	2700–2800
H_2/Air	2000–2100
H_2/O_2	2550–2700
*C_2H_2/Air	2100–2400
*C_2H_2/O_2	3050–3150
*C_2H_2/N_2O	2600–2800

*Acetylene

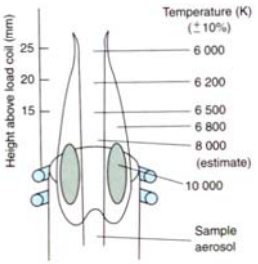
Atomic spectroscopy
Graphite furnace atomizers

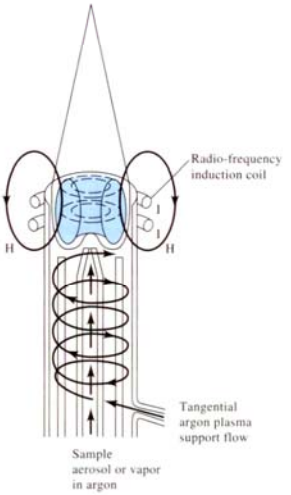
Graphite tube furnaces are heated by electric current (up to a couple of thousands A) in a controlled way, up to about 3000 K. The graphite tube is surrounded by an inert gas to prevent oxidation/burn of the graphite. The sample introduction is done usually by micropipette; a droplet of liquid is placed onto a graphite platform in the tube.



Atomic spectroscopy
Plasma atomizer (ICP)

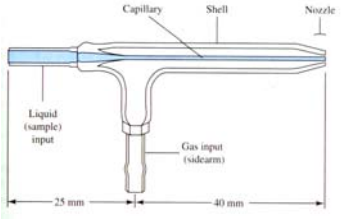
Inductively coupled plasma (ICP) atomizers are popular, very high temperature atom sources that operate on 7000-10000 K temperature work, employing an inert gas environment (typically Ar). Sample introduction is done in the form of an aerosol, mixed with the argon gas.





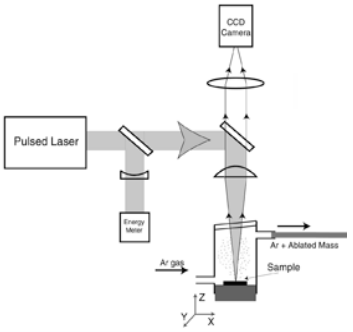
Atomic spectroscopy
Liquid sample introduction by nebulizers

As was alluded to before, many atomizers require the sample to be introduced in the form of an aerosol (usually wet aerosol, or mist). The most popular devices that produce aerosols from liquids by the action of a pressurized gas are called ***pneumatic nebulizers***. The picture below show a common concentric type pneumatic nebulizer.

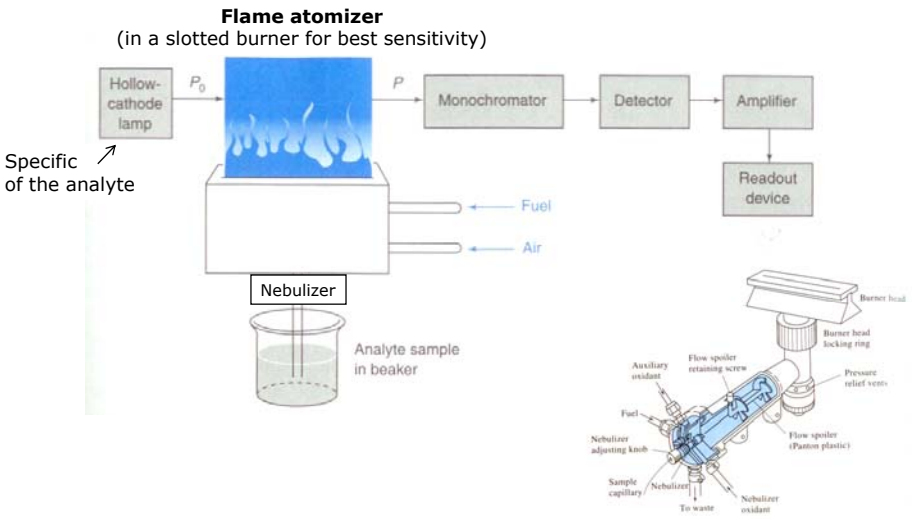


Atomic spectroscopy
Solid sample introduction by laser ablation

Laser ablation is a modern way of solid sample introduction into atomic spectrometers. An intense, pulsed laser light is focused onto the surface of the sample, which causes the sample to ablate (break down, evaporate, fragment) in the focal spot. The resulting fine, dry aerosol is the n swept into the spectrometer with the aid of an inert gas flow (e.g. Ar)



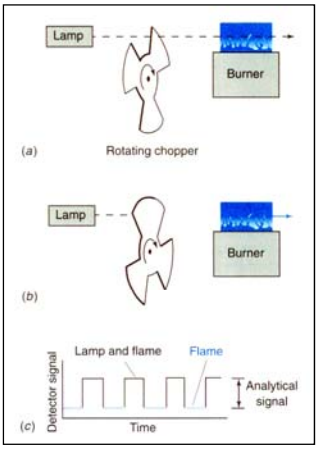
Flame atomic absorption spectrometry (FAAS)
Instrument schematic



Flame atomic absorption spectrometry (FAAS)
Instrument schematic – optical system

AAS instruments incorporate a complex optical system. This optical system helps to free the transmitted intensity of many background radiation (e.g. thermal atomic and flame emission, fluorescence, non-specific absorption, etc.).

Several types of such systems are in use (Deuterium lamp, Zeeman, Smith-Hieftje); below the operation of the simplest, essential system (rotating chopper) is shown.



Flame atomic absorption spectrometer (FAAS)
Analytical performance

Pros

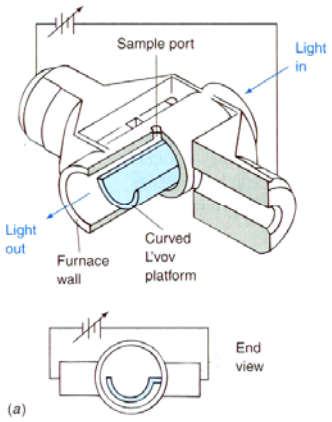
- Low efficiency of sample introduction (low signal)
- Short residence time in the light pathway (low signal)
- Reasonably low detection limits (ppm-ppb range)
- Relative ease of use
- Medium range costs of operation

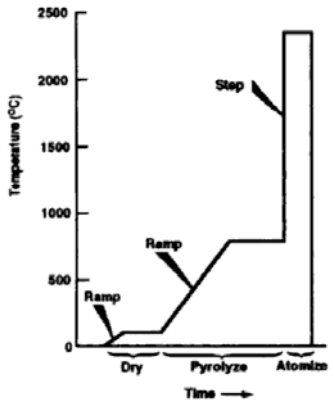
Cons

- Narrow linear dynamic range (ca. 2 orders of magnitude)
- Monoelemental method (small sample throughput)
- Reasonably high sample volume requirement (2-5 mL)
- Inability to measure non-metals
- For each analyte we need a different hollow cathode lamp
- Chemical intereference effects

Graphite furnace AAS (GFAAS)
The instrument

In GFAAS, the graphite furnace replaces the flame atomizer, and there is no need for a nebulizer to introduce the sample.





Graphite furnace AAS (GFAAS)
Analytical performance

Pros

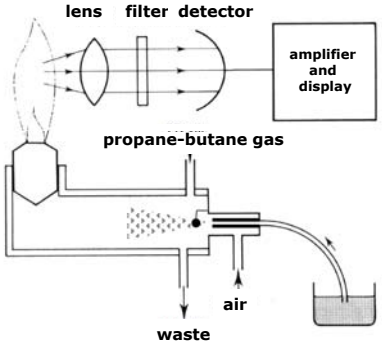
- High efficiency of sample introduction (high signal)
- Long residence time in the light pathway (high signal)
- Possibility for thermal pretreatment of the sample
- Principal ability to handle liquid and solid samples as well
- Small sample volume requirement (10-20 µL)
- Low detection limits (ppt-ppb range)

Cons

- Narrow linear dynamic range (2-3 orders of magnitude)
- Monoelemental method (small sample throughput)
- Poor repeatability (5-10%)
- Increased memory effects
- Inability to measure non-metals
- For each analyte we need a different hollow cathode lamp
- High operating and maintenance costs

Flame atomic emission spectroscopy (FAES)
The instrument

The flame photometer, or flame atomic emission spectrometer (FAES) is the simplest atomic emission spectrometer. The atomizer is a small, circular propane-butane/air flame, and instead of a monochromator, it uses color (interference) filters for wavelength selection. The sample is introduced by a nebulizer. This construction is optimized for cost and the measurement of alkalis.



Flame atomic emission spectrometer (FAES)
Analytical performance

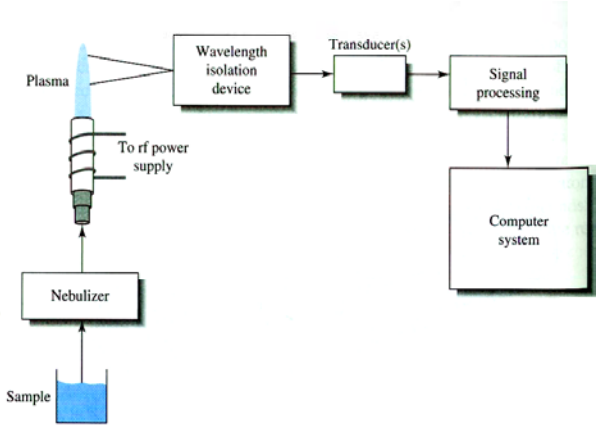
Pros

- Low efficiency of sample introduction (low signal)
- Short residence time in the light pathway (low signal)
- Reasonably low detection limits (ppm-ppb range)
- Relative ease of use
- In principle, it can be run in a simultaneous mode
- Low costs of operation

Cons

- Narrow linear dynamic range (ca. 2-3 orders of magnitude)
- Reasonably high sample volume requirement (2-5 mL)
- Strong ionization intereference effects
- Only a small number of analytes can be measured

ICP atomic emission spectrometer (ICP-AES)
Instrument schematic

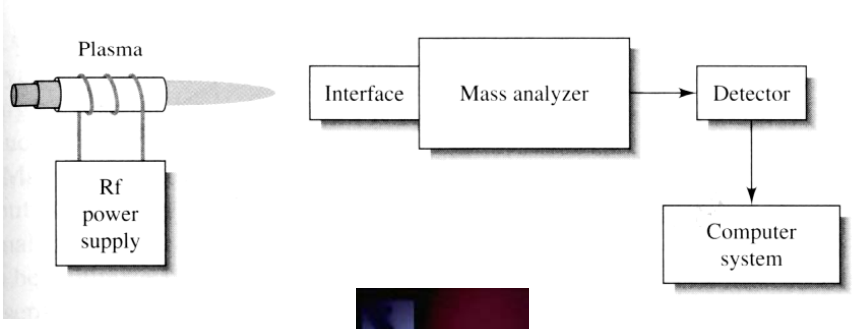


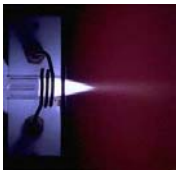
ICP atomic emission spectrometer (ICP-AES)
Analytical performance

Pros
- High efficiency atomization/excitation
- Robust and reliable
- Principal ability to handle liquid and solid samples as well
- Low detection limits (ppb range)
- Very wide linear dynamic range (5-6 orders of magnitude)
- No or very limited chemical intereferences
- Multielemental, simultaneous method (sample throughput is high)
- Ability to measure 80+ elements of the periodic table

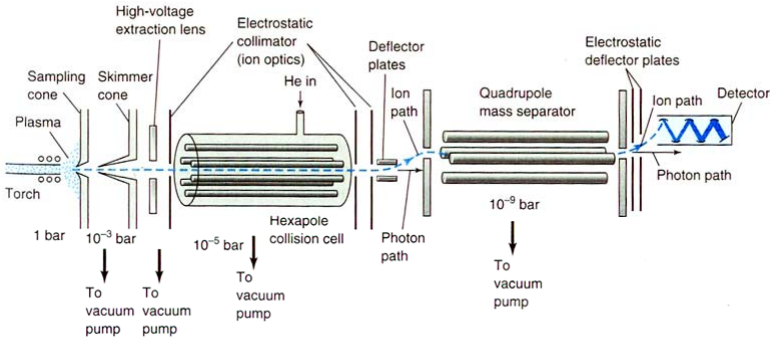
Cons
- Moderately high sample volume requirement (2-5 mL)
- Moderately high purchase and maintenance costs

ICP mass spectrometry (ICP-MS)
Principle of operation

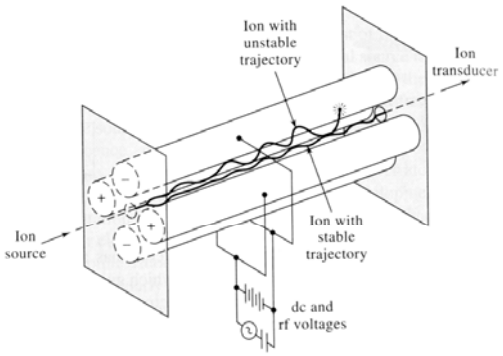


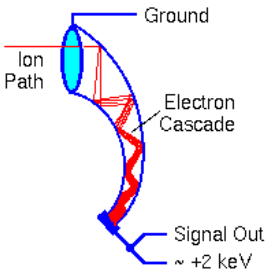


ICP mass spectrometry (ICP-MS)
Schematic of the instrument

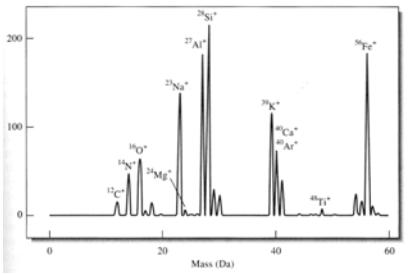


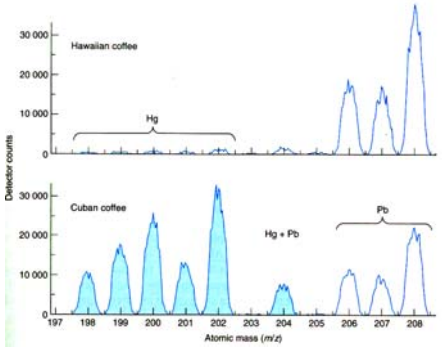
ICP mass spectrometry (ICP-MS)
Quadrupole mass analyser and detector





ICP mass spectrometry (ICP-MS)
Example spectra





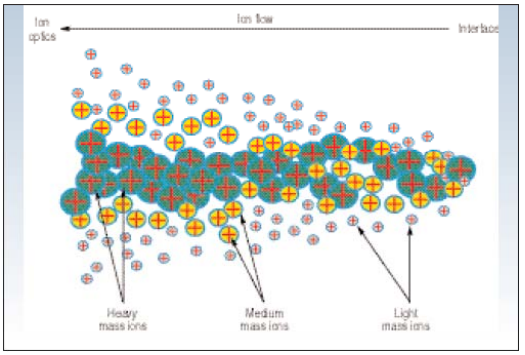
ICP mass spectrometry (ICP-MS)
Analytical properties

Pros
- High efficiency atomization and ionization
- Robust and reliable
- Handling ability of liquids and solids
- Very low detection limits (parts per trillion, ppt)
- Very wide linear dynamic range (8-9 orders of magnitude)
- Only a few interference effects
- Multielemental method (high sample througput)
- Most elements in the periodic table can be measured (80+)
- Isotopic information

Cons
- Relatively high sample volume (2-5 mL)
- High investment and maintenance costs
- Some isobaric intereference

ICP mass spectrometry (ICP-MS)
Interferences – space charge effect

Ions with high inertia (high mass) will be slightly over-represented, because these will repel lighter ions – thus the focusing of the latter will be poorer. This effect can be largely eliminated by using an internal standard.



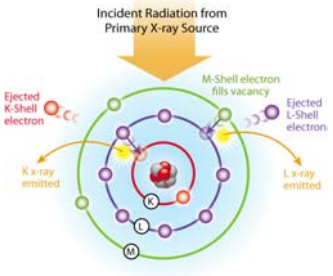
ICP mass spectrometry (ICP-MS)
Interferences – isobar effect

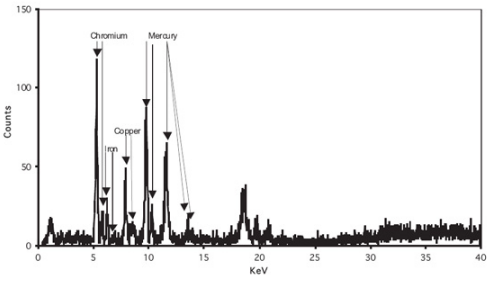
m/z	Polyatomic ion (interferent)	Analyte
28	$^{14}N_2^+$	$^{28}Si^+$
29	$^{14}N_2{}^1H^+$	$^{29}Si^+$
30	$^{14}N^{16}O$	$^{30}Si^+$
31	$^{14}N^{16}O^1H^+$	$^{31}P^+$
32	$^{16}O_2^+$	$^{32}S^+$
33	$^{16}O_2{}^1H^+$	$^{33}S^+$
34	$^{16}O^{18}O^+$	$^{34}S^+$
35	$^{16}O^{18}O^1H^+$	$^{35}Cl^+$
36	$^{36}Ar^+$	$^{36}S^+$
37	$^{36}Ar^1H^+$	$^{37}Cl^+$
38	$^{38}Ar^+$	-
39	$^{38}Ar^1H^+$	$^{39}K^+$
40	$^{40}Ar^+$	$^{40}Ca^+$
41	$^{40}Ar^1H^+$	$^{41}K^+$
42	$^{40}Ar^2H^+$	$^{42}Ca^+$
52	$^{40}Ar^{12}C^+$	$^{52}Cr^+$
54	$^{40}Ar^{14}N^+$	$^{54}Fe^+$
56	$^{40}Ar^{16}O^+$	$^{56}Fe^+$
76	$^{36}Ar^{40}Ar^+$	$^{76}Se^+$
78	$^{38}Ar^{40}Ar^+$	$^{78}Se^+$
79	$^{38}Ar^{40}Ar^1H^+$	$^{79}Br^+$
80	$^{40}Ar^{40}Ar^+$	$^{80}Se^+$
81	$^{40}Ar^{40}Ar^1H^+$	$^{81}Br^+$

m/z	Analyte	Polyatomic ion (interferent)
155	Gd	$^{138}Ba^{16}O^1H$, $^{139}La^{16}O$
156	Gd, Dy	$^{140}Ce^{16}O$
157	Gd	$^{141}Pr^{16}O$
158	Gd, Dy	$^{142}Ce^{16}O$, $^{142}Nd^{16}O$
159	Tb	$^{143}Nd^{16}O$
160	Gd, Dy	$^{144}Nd^{16}O$, $^{144}Sm^{16}O$
161	Dy	$^{145}Nd^{16}O$
162	Dy, Er	$^{146}Nd^{16}O$
163	Dy	$^{147}Sm^{16}O$
164	Dy, Er	$^{148}Nd^{16}O$, $^{148}Sm^{16}O$
165	Ho	$^{149}Sm^{16}O$
166	Er	$^{150}Nd^{16}O$, $^{150}Sm^{16}O$
167	Er	$^{151}Eu^{16}O$
168	Er, Yb	$^{152}Sm^{16}O$, $^{152}Gd^{16}O$
169	Tm	$^{153}Eu^{16}O$
170	Er, Yb	$^{154}Sm^{16}O$, $^{154}Gd^{16}O$
171	Yb	$^{155}Gd^{16}O$
172	Yb	$^{156}Gd^{16}O$, $^{156}Dy^{16}O$
173	Yb	$^{157}Gd^{16}O$
174	Yb, Hf	$^{158}Gd^{16}O$, $^{158}Dy^{16}O$
175	Lu	$^{159}Tb^{16}O$
176	Yb, Hf, Lu	$^{160}Gd^{16}O$, $^{160}Dy^{16}O$

X-ray fluorescence spectroscopy (XRF)
Principle of operation

In this method, the sample is subjected to continuum X-ray radiation (Bremsstrahlung from an X-ray tube or synchrotron). This radiation, if energetic enough, will eject an electron from a closed electronic shell – this vacancy will be filled in by one of the electrons in the atom with a lower bond energy (outer orbital). Energy difference between the two levels will then be emitted as X-ray radiation. This process, of course, takes place in the sample for all atoms and in a cascade-style manner. Emitted radiation is characteristic of the elemental composition.





X-ray fluorescence spectroscopy (XRF)
Energy and wavelength dispersive systems

XRF spectrometers come in two flavours: ***energy dispersive (ED-XRF)*** and ***wavelength dispersive (WD-XRF)***. The performance of these two types of instruments is different, as can be seen in the next slide.

Common (major) properties of all XRF instruments include:

- solid samples can be best measured
- samples have to be flat-like
- chemical information is only obtained from the surface layer (top ca. 1-2 μm)
- analysis is practically non-destructive
- light elements (below Na) can be poorly detected

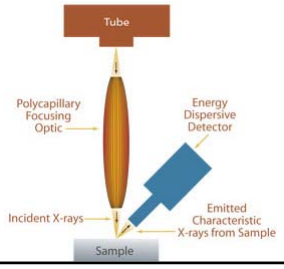
ED-XRF instruments are more compact, they can be made fully portable.

X-ray fluorescence spectroscopy (XRF)

ED-XRF vs. WD-XRF, a comparison

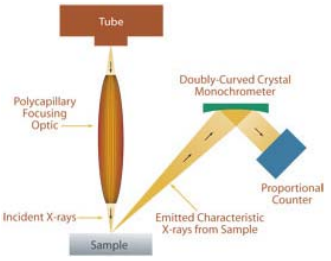
ED-XRF

- energy-based detection
- more sensitive (LODs: 1-10 ppm), as the detector collects radiation from a wider solid angle
- fast recording of the whole spectrum
- poorer spectral resolution
- operation is easy
- less costly



WD-XRF

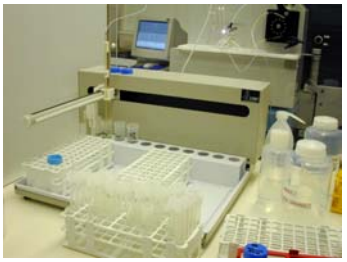
- wavelength-based detection (X-ray monochromator is applied)
- less sensitive (LODs: 10-100 ppm)
- better spectral resolution
- slower measurement
- operation is more complicated
- more costly



Automatic analyzers

Automatic analyzers
Introduction

Today, when a large number of samples have to analyzed day-by-day, it common that automatic sample changers are used with practically any instrument. These devices are practically robotic devices, which are capable of a programmed dosibng (injection) of liquid samples, mixing, reagent addition, etc.



an x-y positionable, table-based autosampler

rotary autosampler

Automatic analyzers
Introduction

Usually however, it takes more to fully automate the analytical process. Sample preparation also has to be (fully) automated, as this is the step in the analytical process which takes the most time and chemicals. At the same time, effort is made to make the sample preparation (and detection) to work with as small samples as possible, because it conserves chemicals and increases the sample throughput.

There are two distinct concepts, along which automatic analyzers are constructed.

Discrete analyzers handle samples in parallel; all samples have their assigned analytical channel (cartridge/flow channel, etc.)

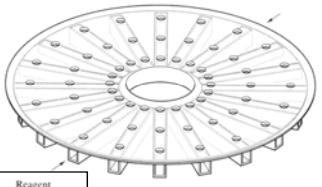
Flow analyzers work more in a serial fashion; samples are sequentially injected in a carrier flow (together with reagents), and then this will flow through devices (coils, reactors, separators, etc.) which help the mixing, reaction, separation, etc. of components. At the end of the tube there is a detector, which analyzes each sample zone one-by-one. As this concept is based on the operation of pumps and valves, it is sometimes also called „***Lab-on-a-valve***" (LOV).

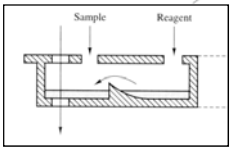
Discrete automatic analyzers

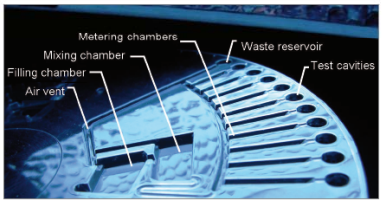
Example: centrifugal (rotary) analyzers

In centrifugal analyzers, each liquid sample has its own radial channel in a disk for sample preparation and detection. Driving of the liquid flow is achieved by the centrifugal force induced when the disk is spinned. Detection of the prepared samples is performed in the outer section of the disk (channels), in a similar manner as CDs/DVDs are read.

Diskman







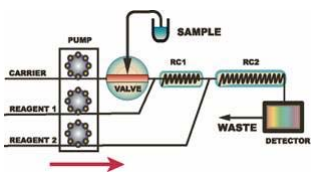
Bio-Disk with microfluidics

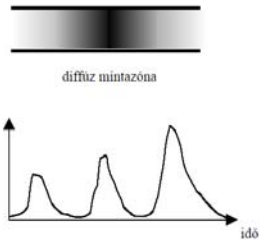
http://www.imtek.de/anwendungen/index_en.php

Flow analyzers

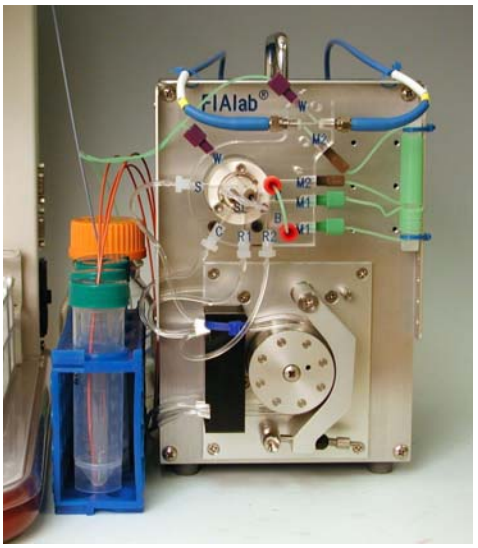
Example: flow injection analyzers (FIA)

The FIA concept was introduced in the 1970's by *Jaromir Ruzička and Elo Hansen*. In this concept, the samples are injected in the carrier flow and pumped forward with a multi-channel peristaltic pump. Using T or Y-pieces, reagent portions are added to this flow and then typically a reaction coil helps the reaction to complete. During propagation, sample zones will suffer dispersion, hence detector signals (measured by the detector placed at the end of the tube) will be peaks, which decrease in height and widen with the time/length spent in the tube. Detection of the sample zones will have to be therefore done with a tight control of time. Advantage of this system is that the sample throughput is high and it has a great flexibility.

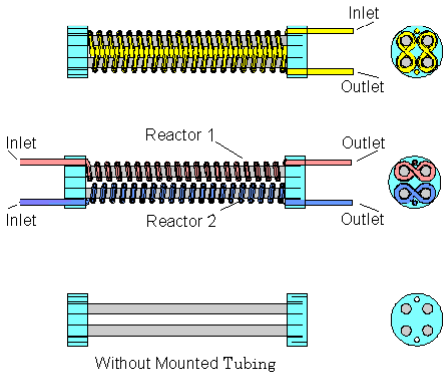


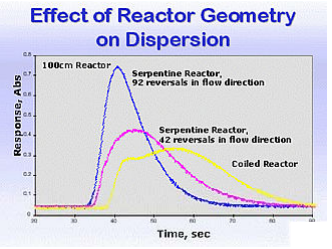


Flow injection analyzers
The look of it



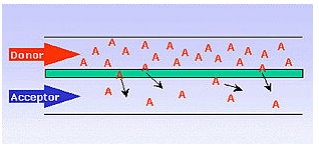
Flow injection analyzers
The reaction coil

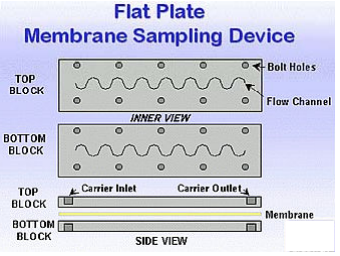


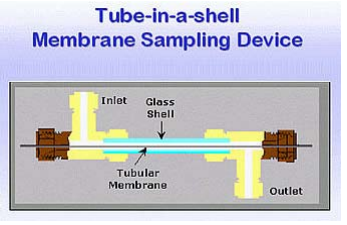


Flow injection analyzers
The use of membranes

Membranes can be used for:
- gas/liquid separation
- dilution
- liquid/liquid extraction
- filtering, etc.







Flow injection analyzers
Dilution and calibration

Dilution/calibration can be done in several ways:

1.) „electronically" (by changing the detection time or the length of tubing)
2.) zone sampling
3.) membrane transport

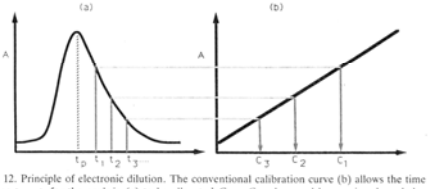
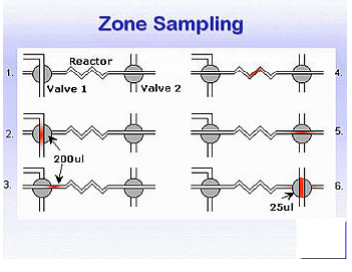


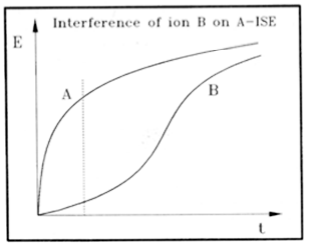
Fig. 12. Principle of electronic dilution. The conventional calibration curve (b) allows the time values $t_0 \ldots t_n$ for the peak in (a) to be allocated $C_1 \ldots C_n$ values and hence via a knowledge of the injected concentration a set of dilution factors may be calculated.



Flow injection analyzers
The use of kinetic discrimination

Kinetics is an important part of the operation of electrochemical detectors. This is strongly related to the flow rate in FIA. Thus, by changing/optimizing the flow rate, one can e.g.:

- maximize the net analytical signal (when interferents are present)
- make the calibration curves to be more linear



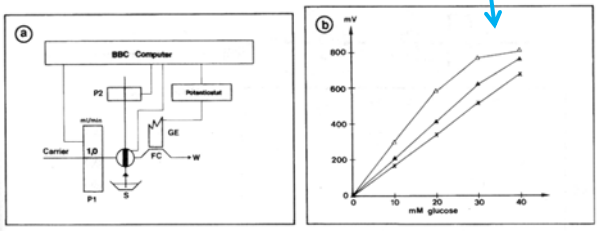


Fig. 7.4-5. a) FIA manifold for the detection of glucose with an amperometric sensor to detect enzymatically generated hydrogen peroxide; b) Calibration graphs for glucose in the concentration range 0–40 mmol/L at three different flow rates: (△) 0.50, (▲) 0.75, and (×) 1.00 mL/min
From [7.4-5] courtesy Elsevier Science Publishers

Flow injection analyzers
Other operations

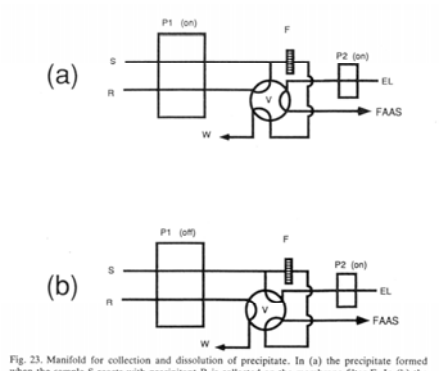


Fig. 23. Manifold for collection and dissolution of precipitate. In (a) the precipitate formed when the sample S reacts with precipitant R is collected on the membrane filter F. In (b) the acid eluent EL dissolves the precipitate.

Precipitation forming

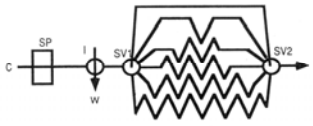


Fig. 8. Variable tube dimensions manifold. SP, syringe pump; I, injection valve; SV1 and SV2, 6-way switching valves. The same standard is injected 6 times and switched down each of the 6 lines of different dimensions in turn.

Calibration by change of tubing dimensions

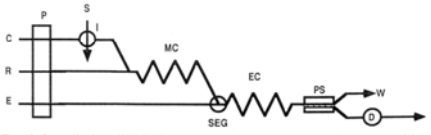


Fig. 15. Generalized manifold for FI liquid-liquid extraction. The sample is injected at I into a carrier stream C which is merged with a reagent stream R. The extractant, E, is merged at SEG, the segmentor where the carrier and extractant streams form interlocking segments. Mass transfer occurs in the extraction coil, EC, and the phases are separated at the phase separator, PS. The extractant containing the analyte flows through the detector, D, while the original solvent flows to waste, W.

Liquid/liquid extraction

Flow injection analyzers

Applications: determination of rodanide ions

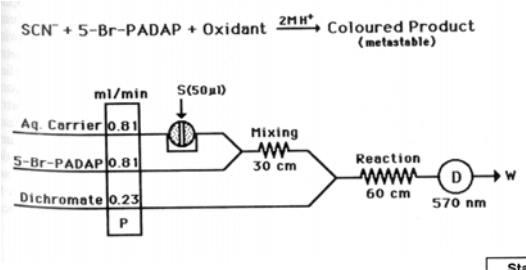
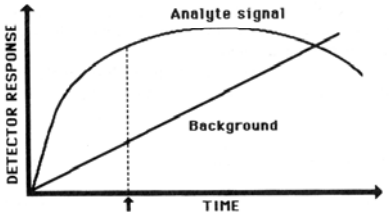
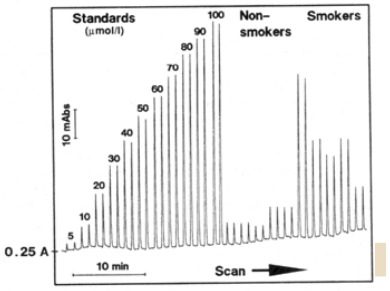


Fig. 7.4-7. Reaction scheme for thiocyanate with 5-Br-PADAP which in the presence of an oxidant (e.g., dichromate) in acidic media results in the generation of a metastable product, which has analytically interesting characteristics. FIA manifold for determination of the metastable reaction product
From [7.4-7] courtesy Royal Society of Chemistry





Flow injection analyzers

Applications: discrete sample introduction in FAAS

Advantage: lower sample consumption, higher tolerance towards viscous/concentrated samples.

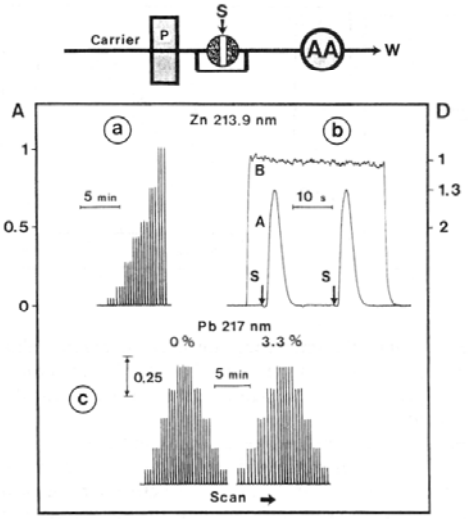


Fig. 7.4-6. Single-line FIA manifold for determination of metal ions by flame atomic absorption spectrometry (AA). Recordings obtained at a flow rate of 4.9 mL/min and an injected sample volume of 150 µL.
a) Calibration run for zinc as obtained by injection of standards in the range 0.10–2.0 ppm; b) Recorder response for the 1.5 ppm standard as obtained by (A) injection via the FIA system and (B) continuous aspiration in the conventional mode (also at 4.9 mL/min). *D* represents the dispersion coefficient value, which in (B) is equal to 1; c) Calibration runs for a series of lead standards (2–20 ppm) recorded without (0%) and with (3.3%) sodium chloride added to the standards
After [7.4-3] courtesy John Wiley & Sons