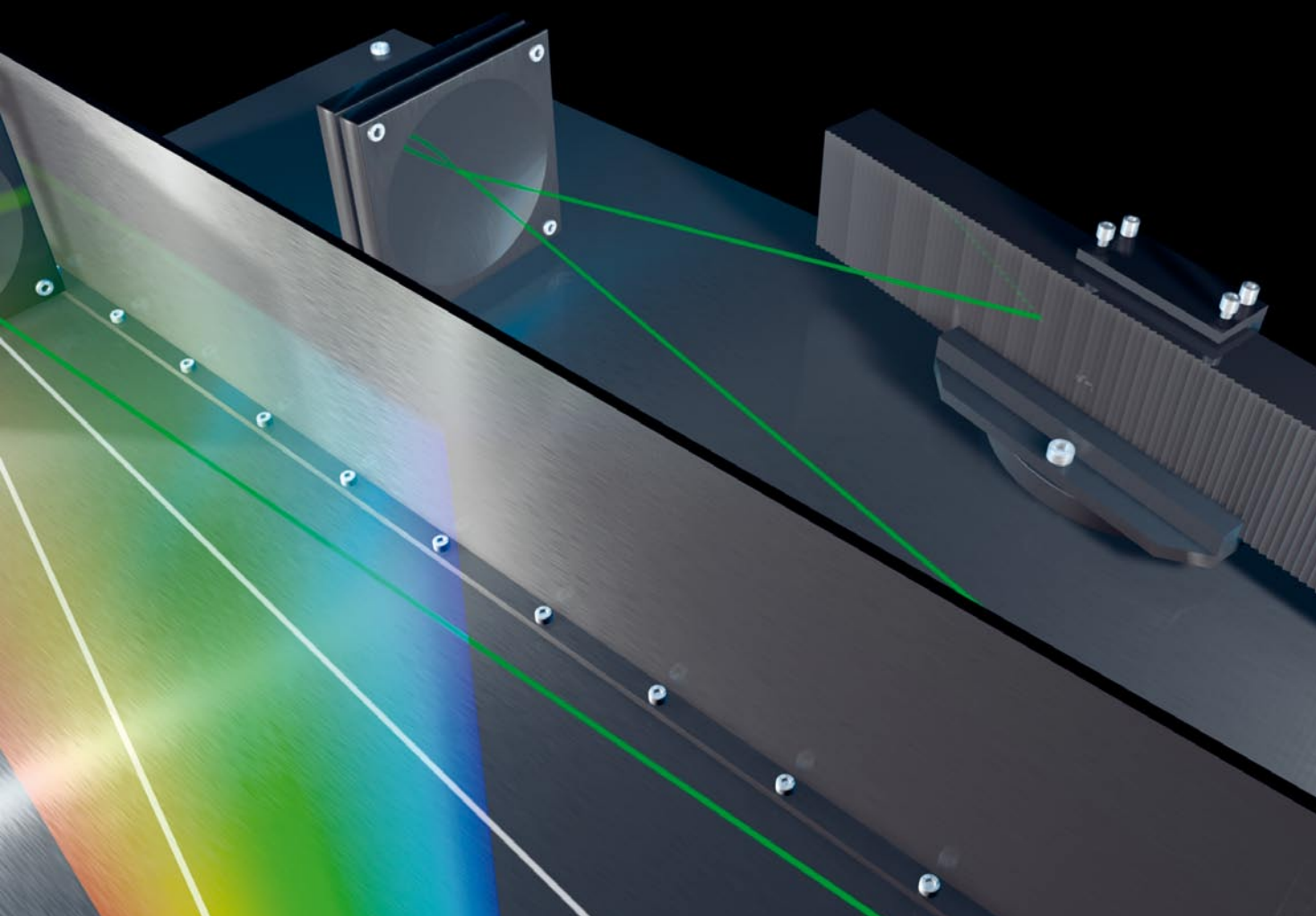# Fundamentals

Instrumentation and Techniques of
Atomic Absorption Spectrometry

Content

1 Fundamentals and definitions

1.1 Atomic structure

Many physical phenomena can only be explained satisfactorily with a basic knowledge about the structure of matter. The chemical elements are substances that cannot be divided into further material components. The smallest particles of the elements that still exhibit their properties, and that cannot be further sub-divided chemically are the atoms

Rutherford and Bohr found out that atoms consist of a positively charged nucleus and negatively charged electrons that are circling around the nucleus in defined orbits.

According to Bohr, an atom can pick up or release energy only in defined steps. In case an atom collides with another particle or a photon of appropriate energy, it can take over this energy and become excited. This excitation, be it of electrical, thermal or optical origin, expresses itself in a transition of an electron from an inner to a (more energetic) outer 'shell' (orbit). The absorption of photons by atoms is the basis of *Atomic Absorption Spectrometry* (AAS). After a few nanoseconds the electron usually returns to its original orbit and the atom into the ground state. If the energy released in this process is emitted in the form of radiation, we are talking about (Optical) *Atomic Emission Spectrometry* (OES)*. The energy released in the various possible transitions can be depicted in the form of a line spectrum. Each element has its own individual line spectrum that is characteristic for this element.

Excited atoms are often chemically more reactive than atoms in the ground state and can participate in chemical processes in which they are not involved under normal circumstances.
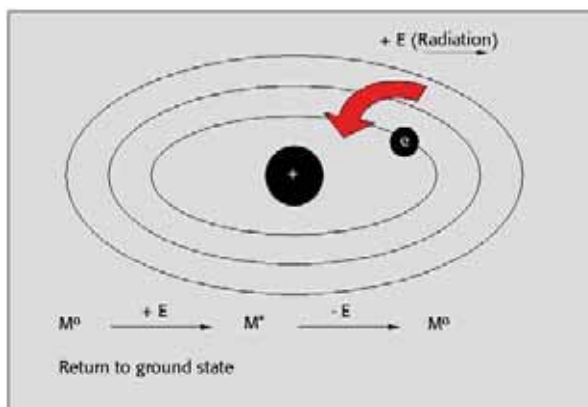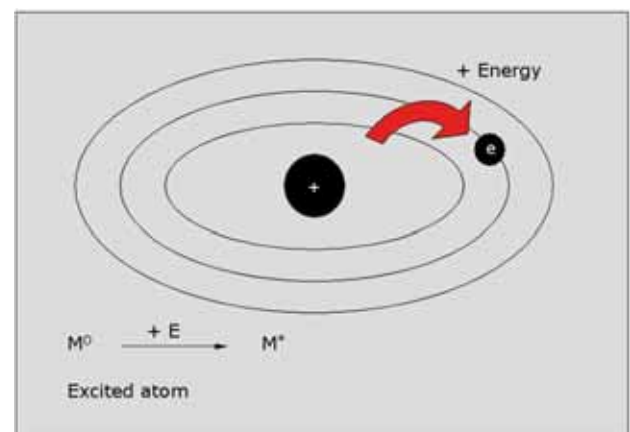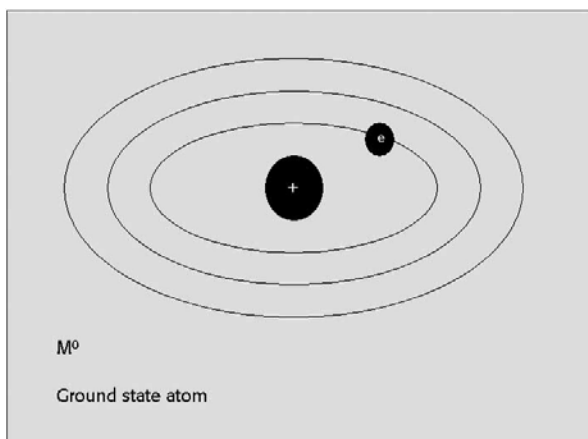
Fig. 1-1: Atom in the ground state
Fig. 1-2: Excited atom
Fig. 1-3: Return to the ground state

If the energy that has been picked up by absorption of a photon is again released as a photon, we talk about *Atomic Fluorescence Spectrometry* (AFS)*.

In case the energy supplied to an atom exceeds the binding energy of an electron, the latter will be removed from the field of electric attraction of the nucleus, i.e., it will be separated from the atom. This process is termed *Ionization.* The outermost electron of an atom is bound most weakly, and can hence be separated most easily.

1.2   *Atomic spectroscopy*

Atomic spectroscopy is the sub-division of spectroscopy that investigates the line spectra that are observed upon interaction of electromagnetic radiation with free atoms. As free atoms can absorb as well as emit electromagnetic radiation of the same energy (wavelength), atomic spectra can be observed as absorption spectra, emission spectra and fluorescence spectra, a combination of the former two.
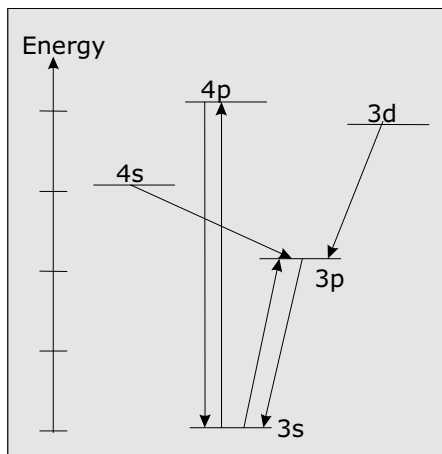
Fig. 1-4: Energetic arrangement of the electron shells. The arrows indicate transitions, which the electrons can undergo. Downward arrows indicate emission; upward arrows indicate absorption, i.e. excitation.

As the spectra are closely related to the structure and the properties of atoms, from which they are absorbed or emitted, they are specific for the atom under consideration and can be used for its detection. When different atomic spectra are considered it becomes obvious that the arrangement of the spectral lines depends on the position of the atom in the periodic table. Elements with only one valence electron (e.g. alkaline metals) exhibit spectra with relatively few lines; elements with a greater number of valence electrons (e.g. transition metals) exhibit spectra with a significantly larger number of lines.
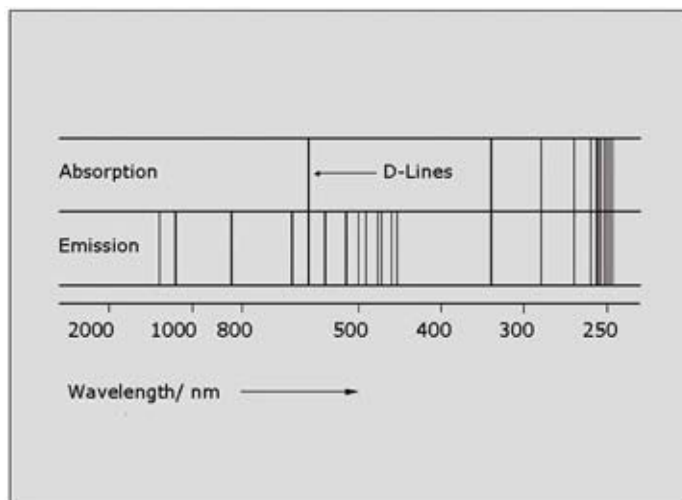
Fig. 1-5: Absorption and emission spectra of sodium (schematic)

1.2.1 Emission, Absorption, Fluorescence

Emission

The principle of atomic emission consists in transferring the element of interest into a higher energy state with the help of an excitation source (flame, electric arc or spark, plasma). Upon its return to the ground state the atom emits radiation, the energy of which is corresponding exactly to the difference in energy between the ground state and the excited state. These energies, and hence the wavelength of the lines, are specific for each element.

The emitted radiation is focused onto the entrance slit of a monochromator or polychromator, spectrally dispersed, and detected sequentially or simultaneously. The determination of the position of the lines (wavelength) makes possible a qualitative analysis of a sample. A quantitative determination can be carried out by correlating the intensity of the lines with the concentration or mass of the element.

The temperatures used in atomic emission spectrometry are usually significantly higher than those used for atomic absorption spectrometry, so that the most different excitation states can be reached, including excited ions. For this reason atomic emission spectra are characterized by a much greater number of lines compared to atomic absorption spectra.
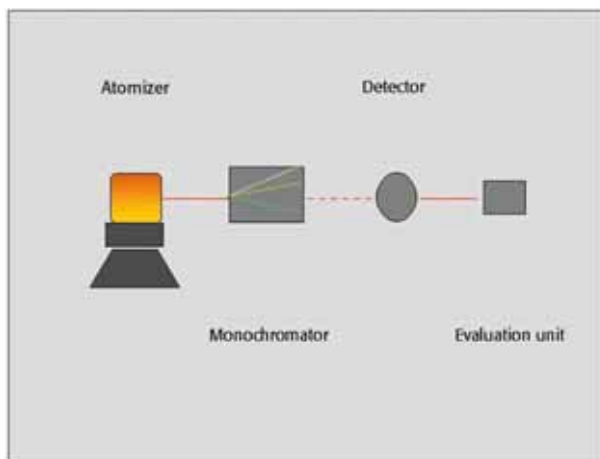
Fig. 1-6: Atomic emission
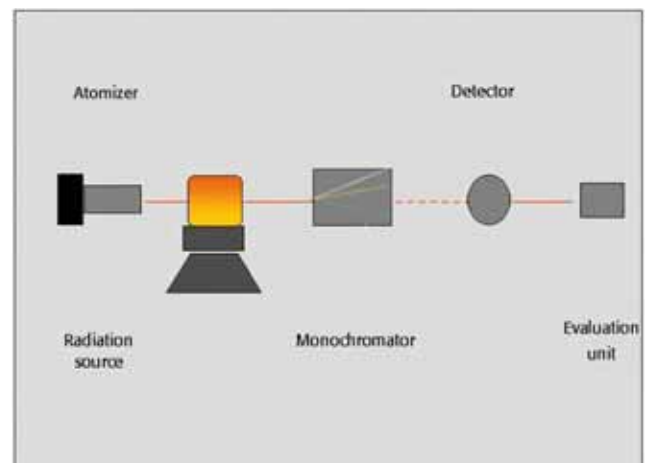
Fig. 1-7: Atomic absorption
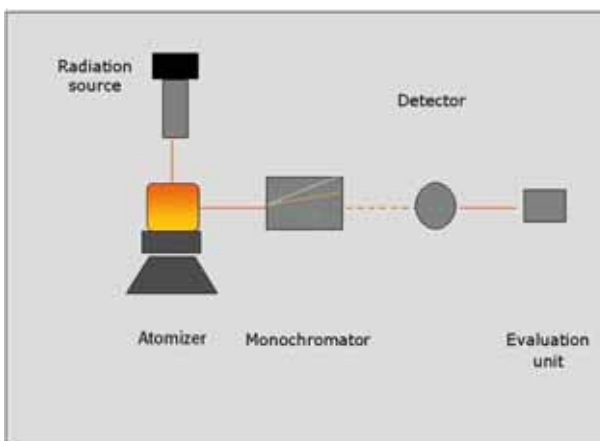
Fig. 1-8: Atomic fluorescence

Absorption

Free atoms in the gas phase can be transferred into higher energy states by the supply of energy in the form of electromagnetic radiation. Electrons are transferred from the outer shell to higher energy levels and the atom into an excited state. Only radiation of well defined wavelengths can be absorbed, as an atom in the ground state can take up only given values of energy. The reduction in the radiation intensity of a selected line is correlated via the Absorbance *A* with the number of absorbing atoms in the absorption volume, and hence with the concentration of the element in the sample. This process is the basis for a quantitative determination of an element in a sample to be investigated.

Fluorescence

Intense monochromatic radiation, as it is emitted by discharge lamps (e.g. Hg low pressure lamps) is focused onto an atomic cloud, which is produced in a low-background flame or electrothermally, similar to atomic absorption spectrometry. Because of the relatively low temperatures used in this technique the atoms are essentially all present in their ground state. By absorption of the radiation the atoms are transferred to an excited state. After a residence time of a few nanoseconds they return to the baseline or to a lower excited state, emitting the absorbed energy, or part of it, in the form of fluorescence radiation. The fluorescence radiation is focused onto the entrance slit of a monochromator – usually at right angle to the exciting radiation in order to prevent its entrance into the monochromator – spectrally dispersed, and its intensity measured by a suitable detector. In case of negligible background radiation it is possible to dispense with a monochromator for the measurement of the fluorescence radiation.

1.2.2 Quantitative analysis in AAS

Basis for the quantitative evaluation of absorption spectra is the law of LAMBERT and BEER, which says that the absorbance *A* is proportional to the thickness *d* of the absorbing layer and the concentration *c* of the absorbing matter. The molar absorbance coefficient ε is specific for the absorbing matter and, under stable external conditions, a concentration-independent constant that can be used to characterise the absorbing species.

$$A_\lambda = \log \frac{I_0}{I_d} = \varepsilon_\lambda \cdot c \cdot d$$

I_0	Incident radiation intensity
I_d	Transmitted radiation intensity
ε_λ	Molar absorbance coefficient
c	Molar concentration
d	Thickness of the absorbing layer
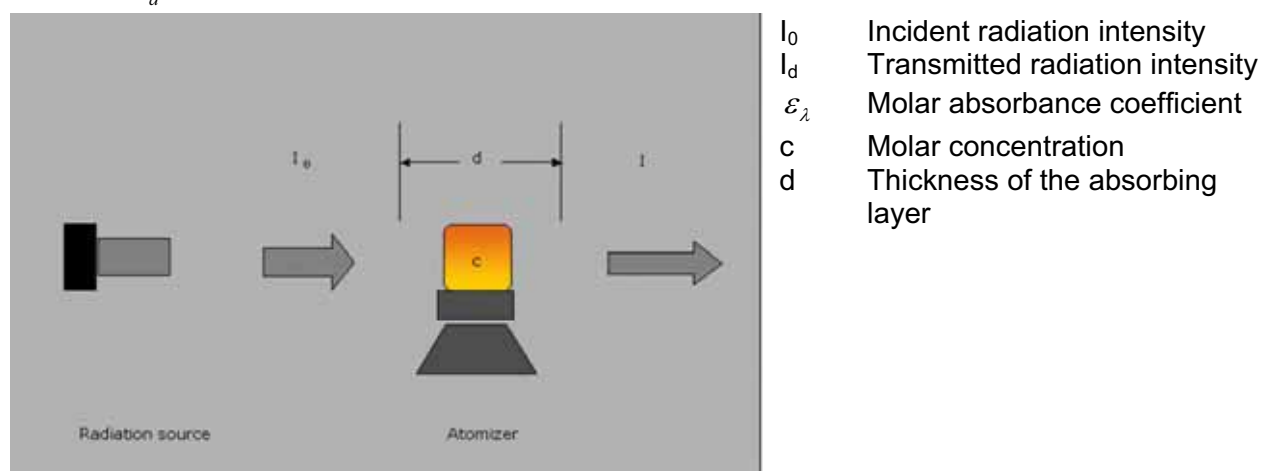
Fig. 1 1-9: The Lambert-Beer Law

The Lambert-Beer Law can be strictly applied only for monochromatic radiation and ideally diluted solutions. In non-ideal solutions ε_λ is no longer independent of the concentration, as the properties

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of the absorbing matter might be influenced by interactions between molecules, such as dissociation or complex formation.

Transferring this generally valid formula to AAS, we arrive at:

$$A_\lambda = \log \frac{I_0}{I_d} = k_\lambda \cdot N_0 \cdot l$$

k_λ Absorption coefficient
N_0 Number of atoms in the absorption volume
l Length of the absorbing layer

If the atomic vapor of a sample is irradiated by emission lines of the element of interest (using a line source), we observe resonance absorption. This results in an attenuation of the incident radiation energy, which can be measured as absorbance, and which is proportional to the concentration of the analyte in the atomizer.

The free atoms in the gas phase, required for the resonance absorption, are produced thermally, e.g. in a flame. This way equilibrium is established between the number of excited atoms N_j and the atoms in the ground state N_0.

$$\frac{N_j}{N_0} = \frac{P_j}{P_0} \cdot e^{-\frac{\Delta E}{k_B \cdot T}}$$

P   Statistic weights
k_B Boltzmann constant
T   Absolute temperature
ΔE Excitation energy
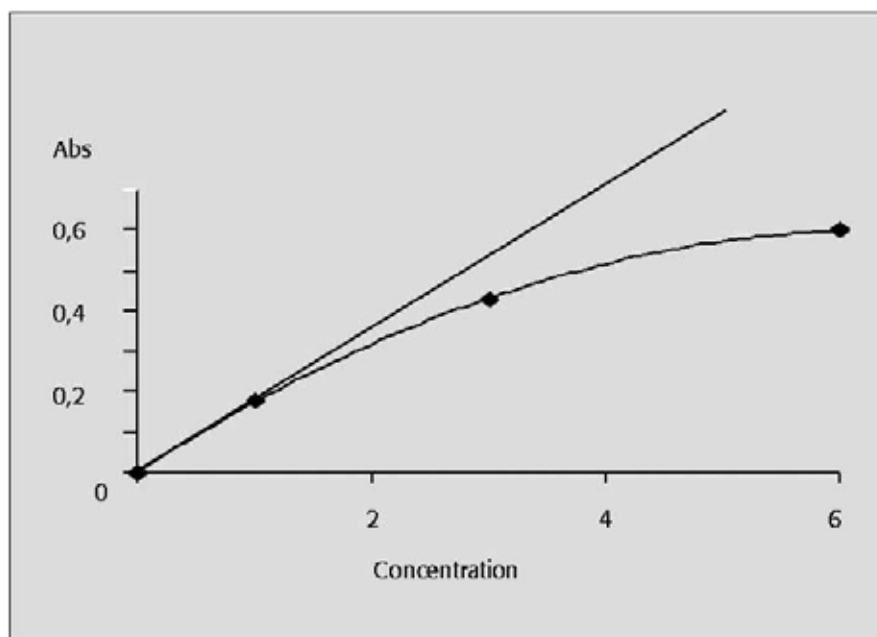
Fig 1-10: Correlation between concentration and absorbance of standards

At temperatures of less than 3000 K, as they are typical for AAS, this equilibrium is essentially completely on the side of atoms in the ground state. Even for the alkali metals, which are excited most easily, the number of excited atoms never exceeds 1%. In a first approximation we can therefore assume that in AAS all atoms are in the ground state.

The linearity of the relation between absorbance and concentration that can be derived from the Lambert-Beer Law is only a first approximation that can be applied for low concentrations. With increasing concentration of the analyte a deviation of the calibration function from linearity

becomes apparent. In some application areas of AAS (e.g. pharmaceutical industry) it is therefore essential to work exclusively in the linear range.

If the AAS method is based on a calibration function the analyte content in an unknown sample can be determined quickly and reliably using modern instrumental techniques. This is equally valid for concentrations that are outside of the linear range.

1.2.3   Characteristic concentration and mass

The characteristics on an analytical method are defined by several figures of merit, which can be determined experimentally. Such data may be used to compare different analytical methods or techniques or to judge analytical results. They also give information if a method is suitable for a given analytical task or not.

One of these figures is, e.g. in the case of flame atomization, the characteristic concentration c_0, the analyte concentration that corresponds to an absorbance $A = 0.0044$ (1% absorption).

$$C_0 = \frac{(0.0044 \cdot \text{concentration of the standard})}{\text{Absorbance of the standard}}$$

The characteristic concentration is often considered as a criterion for the sensitivity of an analytical instrument. It should be within 20% of the value specified by the instrument manufacturer (if available). Almost all manufacturers of AAS instruments provide such tables that make possible to control the performance of the equipment.

All instrumental parameters should be checked and the method be optimized in case the characteristic concentration is significantly higher. A significantly lower characteristic concentration, however, is frequently an indication for a contamination problem.

In the case of electrothermal atomization in a graphite furnace we use the characteristic mass m_0 instead of the characteristic concentration c_0 and integrated absorbance A_{int} (peak area) instead of absorbance A.

1.2.4   Limit of detection

The limit of detection (LOD) is another important figure of merit for an analytical technique or a method. It is a measure for the analyte content or mass, above which the presence of the analyte in a solution for measurement can be detected with a certain statistical probability compared to a blank test solution. As the measured signal has to be distinguished with a certain probability from that of a blank test solution, it is closely related with the precision obtained for the blank test solution.

In case of an instable or noisy signal it is difficult or almost impossible to decide if a small increase in absorbance is due to a change in analyte concentration or to an increasing baseline noise.

The LOD is defined (IUPAC) as the analyte concentration or mass that gives a signal corresponding to three times the baseline noise of the blank test solution (3σ-criterion).
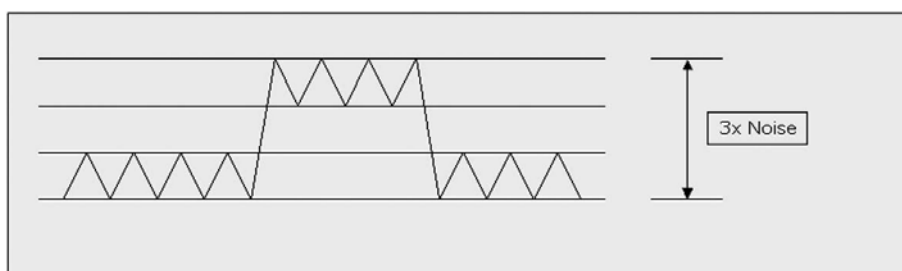
Before purchasing an instrument it is quite common that the user compares limits of detection. However, it has to be pointed out that in routine analytical application concentrations are usually well above the instrumental LOD, not only because of the increased standard deviation within a series of measurements.

1.2.5 Limit of quantification

At the limit of quantification (LOQ) the presence of the analyte is taken for granted. It is the lowest analyte concentration or mass that can be determined quantitatively with a certain precision. In the concentration or mass range between the LOD and the LOQ the analyte may be detected, but no quantitative evaluation is permissible.
The LOQ corresponds roughly a value three times the LOD or ten times the standard deviation of the blank test solution.

LOD and LOQ have to be determined separately for each sample type (matrix) and must not only be determined for calibration solutions.
When the LOD and LOQ of different laboratories or instrument manufacturers are compared, it is important to know how these figures of merit have been determined, and for which matrix.

2 Design of an AA Spectrometer

Basically all elements can be determined by AAS, as the atoms of all elements can be excited, and are hence capable of absorbing radiation. The usable wavelength range of an AA spectrometer depends on the radiation source, the optical components of the light path and the detector. In practice this range usually extends from 852.1 nm, the most sensitive resonance line of cesium to the most frequently used analytical line of arsenic at 193.7 nm in the beginning vacuum UV.

2.1 Components of a conventional AA Spectrometer

The basic design of an AA spectrometer is shown in Fig. 2-1. The high resolution that is required for the measurement of atomic absorption is in this case provided by the line source, so that it is possible to use monochromators of relatively low resolution.
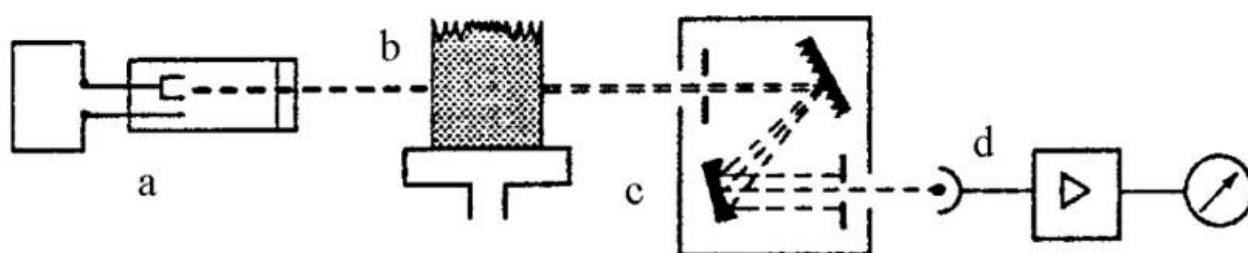
Fig. 2-1: Schematic design of a conventional AA spectrometer

A hollow cathode lamp (HCL) is typically used as the radiation source (a), whereby the cathode is made of the element to be determined. The atomization unit (b) has to produce analyte atoms in the ground state. The radiation emitted by the radiation source is attenuated upon passing through the atomization unit and conducted into the monochromator (c). The latter consists of an entrance slit, a dispersive element (diffraction grating), usually several mirrors and an exit slit. The grating spectrally disperses the radiation that is passing the atomizer. The exit slit separates the analytical line from the total spectrum, blocking off the other lines emitted by the radiation source. The detector (d) converts the photon current (radiation flux) into an electric signal and registers the attenuation of the analytical line.

2.1.1 The radiation source

Hollow cathode lamps (HCL) and Superlamps (S-HCL) are the radiation sources typically used in commercially available line source AA spectrometers. The requirements regarding line width of the radiation sources are particularly high when medium- or low-resolution monochromators are used, as the half widths of absorption lines are very small (a few picometers).

Hollow cathode lamps (HCL)
Hollow cathode lamps basically consist of a glass cylinder that contains a cathode and an anode. The glass cylinder itself is filled with neon or argon with a pressure of a few millibars. The cathode has the shape of a hollow cylinder and either consists of, or is filled with the element of interest. Applying a voltage of several hundred volts, a glow discharge develops between the electrodes. A flow of positive gas ions (Ne^+ or Ar^+) impacts on the cathode, sputtering atoms from its surface, which are excited and emit the spectrum of the cathode material. Because of the lower pressure and lower temperature in a HCL, compared to that in the atomizer, the width of the lines emitted by the radiation source is significantly smaller than that of the absorption lines. Depending on the wavelength of the main analytical line the exit window of the lamp is made of silica or glass. The fill gas is selected in a way that no spectral interferences are encountered between the spectrum of

the fill gas and the analytical line, and to achieve the highest possible emission intensity of the analyte spectrum.
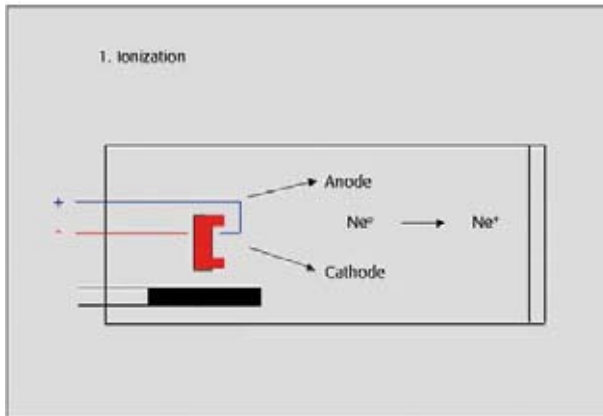
Fig. 2-2: Ionization of gas atoms
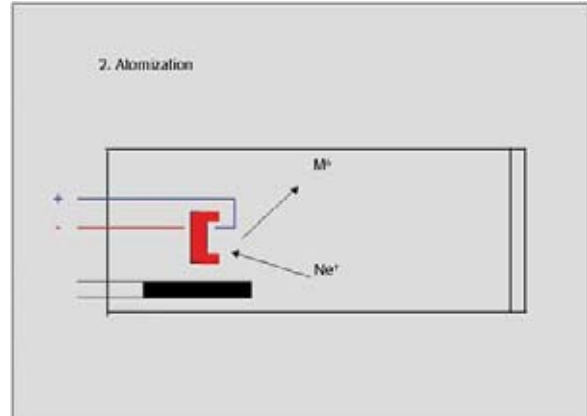
Fig. 2-3: Sputtering of metal atoms
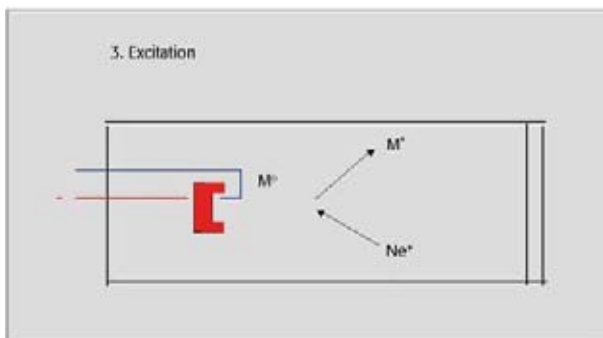
Fig. 2-4: Excitation of metal atoms
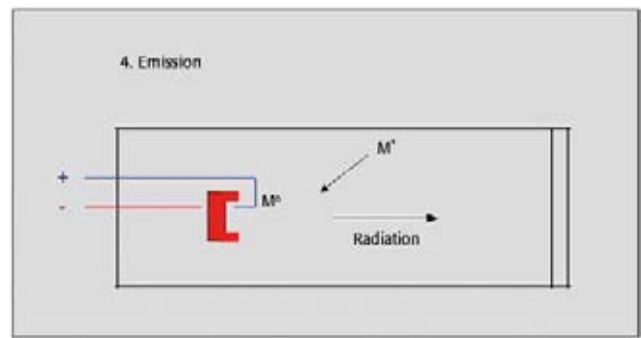
Fig. 2-5: Emission of radiation

Hollow cathode lamps have a limited life time. Firstly, sputtered atoms are deposited in part on colder parts of the lamp, e.g. the glass cylinder, forming a metal film; secondly, the fill gas is absorbed slowly by the metal film and the glass.

Hollow cathode lamps can be manufactured for a wide variety of elements. For certain combinations of elements it is also possible to make so-called multi-element lamps, which contain an alloy or a mixture of several metals. These lamps have the advantage of being more economic than single element lamps. In addition they shorten the change-over time if more than one element has to be determined. Their disadvantage is the lower intensity of the lines emitted for each element, and the associated deterioration of the signal-to-noise ratio, which equally affects precision and LOD.

Superlamps (S-HCL)
Superlamps are recommended for the determination of elements, which have their main analytical lines in the far UV range, such as arsenic and selenium. In addition, superlamps can be used successfully for the determination of the lowest concentrations, as the baseline noise and the line width (narrow) are better for some elements than those of conventional HCL. This results in an improved signal-to-noise ratio and better LOD.
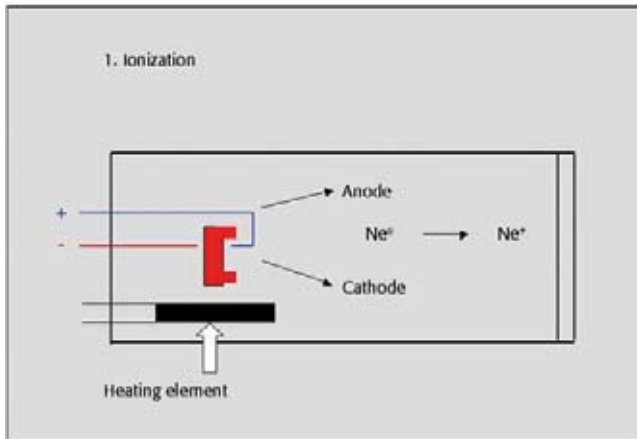
Fig. 2-6: Ionization of gas atoms
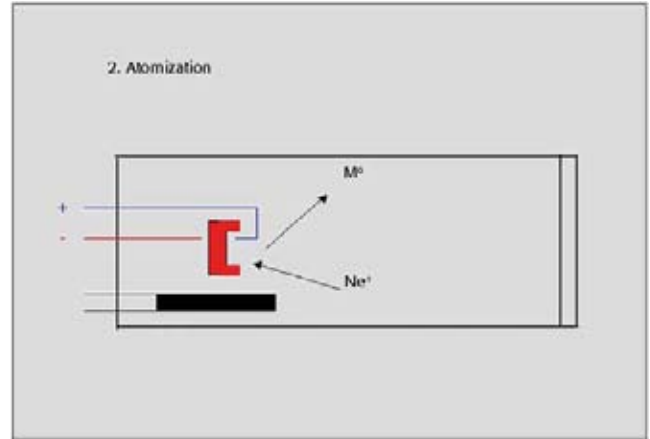
Fig. 2-7: Sputtering of metal atoms
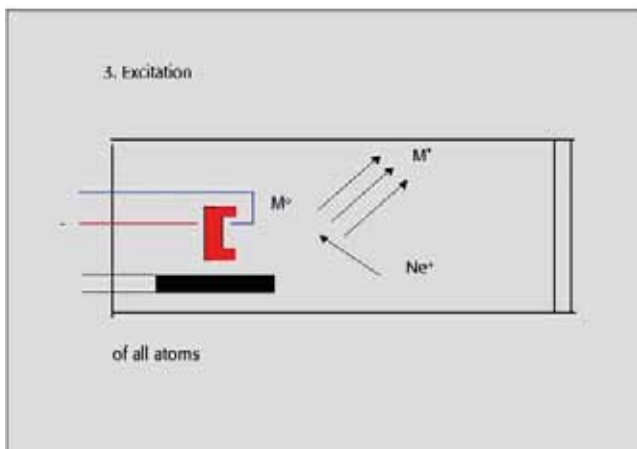
Fig. 2-8: Excitation of all metal atoms
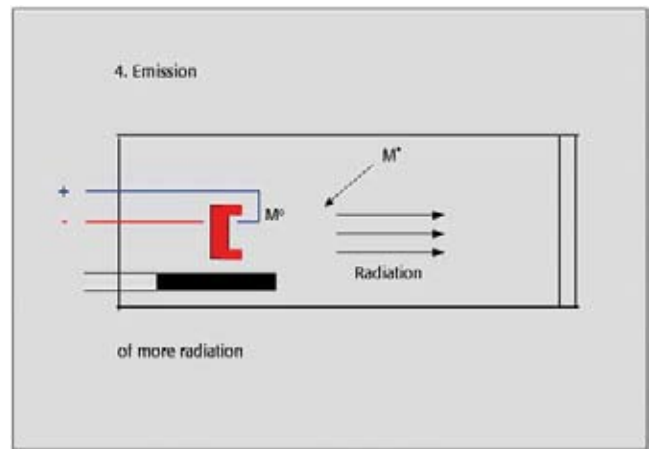
Fig. 2-9: Emission of radiation (high intensity)

Superlamps, in contrast to regular HCL, are equipped with an additional heating device, so that they need a socket with four instead of two electric cables. The heating device is supplied by the so-called boost current, which intensifies the electric current to the cathode. This way a lot more sputtered metal atoms can be excited than in conventional HCL, and the risk that a cloud of metal atoms in the ground state is forming in front of the cathode is significantly reduced. In normal HCL those atoms absorb part of the emission from the cathode. This phenomenon is known as self absorption and self reversal of the line, and is observed particularly with high lamp currents. With superlamps it is practically not observed. The additional currents above the cathode also provide a relatively low space charge density of the excited metal atoms. This results in a smaller width of the emission line and a better sensitivity compared to regular HCL.

For the same chemical element the superlamp requires the same current for the discharge between anode and cathode as a HCL. However, a higher cathode current may be chosen because of the higher efficiency of the excitation in the S-HCL. The boost current has an optimum, where the S-HCL intensity reaches a maximum. The position of the optimum depends on the element, and is additionally influenced by the electrical properties of the AAS and the selected cathode current. The user may find this optimum easily by manually adjusting the boost current. The life time of S-HCL is comparable with that of conventional HCL. However, life time is reduced according to the amount of sputtered cathode material if the S-HCL is frequently operated with high cathode current.

The technical effort and the running cost are significantly higher for S-HCL, so that the user has to decide if it is meaningful to invest in these lamps.

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2.1.2 The atomizer

The following atomization techniques are nowadays used in AAS:
- Flame technique
- Graphite furnace technique
- Hydride and Cold Vapor techniques
- HydrEA technique (combination of Hydride and Graphite furnace technique)
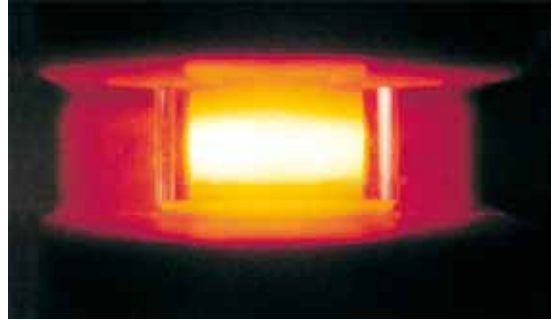
Fig. 2-10: Flame   Fig. 2-11: Graphite furnace   Fig. 2-12: Hydride technique

Atomization in a flame
The sample is transferred into liquid form, e.g. by dissolution. The nebulizer aspirates the solution and transfers it into a fine aerosol. This is directed onto an impact bead for post-nebulization in order to create an even finer aerosol. Large droplets are separated in the mixing chamber, and the aerosol is mixed with the fuel gas and additional oxidant. The aerosol-fuel gas –oxidant mixture is ignited above the burner head.
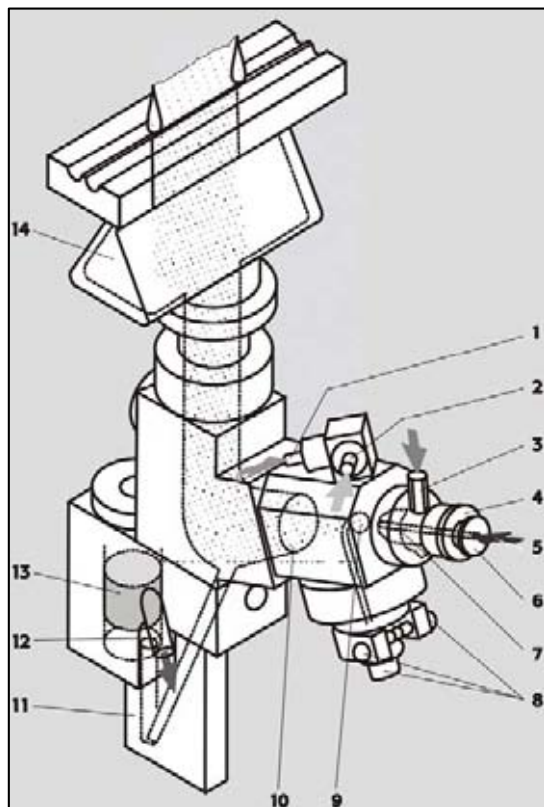
1	Additional oxidant supply
2	Fuel supply
3	Oxidant supply
4	Adjustment screw
5	Supply of solution for measurement
6	Lock nut
7	Nebulizer
8	Impact bead adjustment
9	Impact bead (silica; teflon coated)
10	Mixing chamber
11	Siphon trap
12	Siphon drain
13	Float
14	Burner head (50mm, 100mm)

Fig. 2-13: Schematic design of the nebulizer-burner system

In the flame the solvent of the solution evaporates; solid particles melt, evaporate and dissociate to free atoms. The flame gases are supplied by the gas control system with constant pressure, guaranteeing well defined flow rates of fuel gas and oxidant. Flame atomization if fast, economic and generates reproducible measurement results in the mg/L and % range.

Atomization in a graphite furnace
With this technique the sample to be investigated may be liquid or solid, and is introduced directly into a graphite tube. A controlled voltage is applied at the ends of the graphite tube, which is heated rapidly to high temperatures (up to 2600°C) due to its resistance. Using time-controlled stepwise heating of the graphite tube the sample solution is first dried, and then the matrix can be destroyed or removed, until finally the element of interest is atomized.
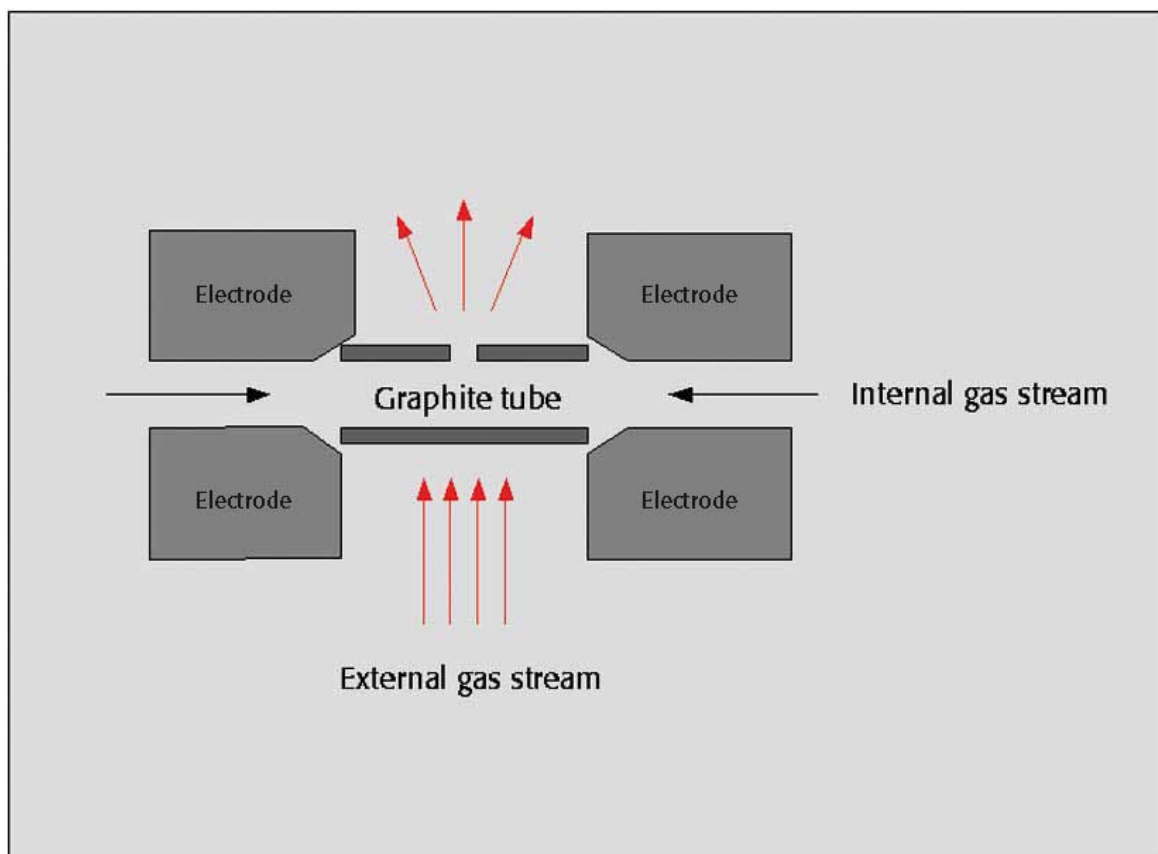
Fig. 2-14: Schematic design of a graphite tube furnace

The graphite tube is permanently flushed with argon while it is in operation. The protective gas flow efficiently prevents entrance of air, and hence guarantees long lifetime of the graphite tube and an undisturbed determination. Integrated water cooling provides rapid cooling of the graphite tube after the operating voltage has been switched off to provide high sampling frequency. Graphite tube atomization results in LOD that are up to a factor of 1000 better than those obtained with flame atomization On occasions sophisticated temperature programs are required to control matrix effects.

Atomization using the Hydride und Cold Vapor systems
Mercury and the elements that are forming volatile hydrides (e.g. As, Se, Sb, Te, Sn, Bi) may be determined using the cold vapor (Hg) or the hydride technique. The solution for measurement is mixed with sodium borohydride solution in a suitable apparatus. The generated hydrides are purged out of the solution using a carrier gas flow. Doing so, the analyte can frequently be separated completely from the matrix. Atomization may be carried out in a heated quartz tube

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placed in the beam of the spectrometer. Because of the relatively low temperature of the quartz tube atomization cannot be due to thermal dissociation, but proceeds via free hydrogen radicals formed in the entrance part of the quartz tube (for details see: B. Welz, M. Sperling, Atomic Absorption Spectrometry).

Reaction mechanism for As with NaBH$_4$ as reducing agent

$BH_4^- + 3\,H_2O + H^+$ $\longrightarrow$ $H_3BO_3 + 8\,H$

$2As^{3+} + 12\,H$ $\longrightarrow$ $2AsH_3 + 6\,H^+$

$2AsH_3$ $\longrightarrow$ $2As + 3H_2$
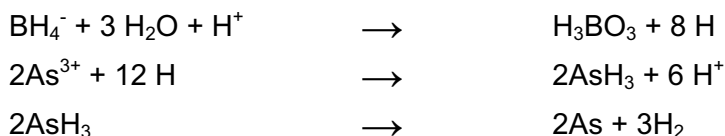
Mercury is the only metallic element that exhibits a significant vapor pressure already at room temperature. It can easily be reduced to the elemental state (using $SnCl_2$ or $NaBH_4$), stripped from solution, and determined by AAS directly without an additional atomization step.

Reaction mechanism for Hg using $SnCl_2$

$Hg^{2+} + Sn^{2+}$ $\longrightarrow$ $Sn^{4+} + Hg^0$

Reaction mechanism for Hg using $NaBH_4$

$BH_4^- + 3\,H_2O + H^+$ $\longrightarrow$ $H_3BO_3 + 8\,H$

$Hg^{2+} + 2\,H$ $\longrightarrow$ $Hg^0 + 2\,H^+$
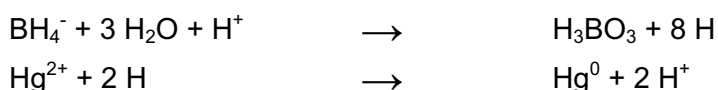
With the hydride technique LOD may be attained that are comparable to or better than those of the graphite furnace technique, depending on the applied sample volume.
A clear advantage compared to the graphite furnace technique is the relative absence of matrix effects due to the separation of the analyte by chemical reaction. It has to be mentioned, however, that in the presence of several transition metals at high concentration in solution, these metals may be reduced as well, precipitate in a finely dispersed form and react with the generated hydrides. These hydrides are obviously lost for the absorption process unless proper action is taken. It has therefore to be decided in each case, which technique should be applied.

Atomization using the HydrEA technique
The HydrEA technique is a combination of the graphite furnace and the hydride technique. It is used to obtain even lower LOD for the hydride-forming elements. For this purpose the hydride is not introduced into a heated quartz tube, but into a graphite tube, treated with iridium, where it is pre-concentrated. The graphite tube is subject to a temperature program as usual; the analyte is atomized and measured by AAS.

2.1.3 The optical system

The optical components that are required for an AA spectrometer may be combined into two major groups:
▪ The monochromator, which has the duty of dispersing the incoming radiation spectrally, and to prevent that any radiation, except for the analytical line, reaches the detector.
▪ Lenses and mirrors, which focus the radiation of the HCL, first in the atomization zone (flame, graphite tube, quartz tube), then on the entrance slit of the monochromator, and finally on the detector.
In order to separate the analytical line it is of advantage to use a small spectral bandwidth. In order to obtain a stable measurement signal with a favorable signal-to-noise ratio it is of advantage that as much radiation energy as possible enters the monochromator. This requires a large (geometric)

slit width. These two apparently contradictory conditions can be mastered using a monochromator with high dispersive power. In practice a spectral bandwidth in the range of 0.2 nm....1.2 nm is typically used.

The imaging optics is designed in a way that, depending on the atomization zone, the radiation of the HCL is conducted through the differing cross-sections in an optimum manner. The size of an AA spectrometer is in part also determined by these components. Intelligent selection and design can contribute to a reduction of the overall dimensions of equipment. Mirrors (spherical and toroidal) are preferred over lenses in order to minimize imaging errors.

2.1.4   The detector

The detection of radiation in conventional AA spectrometers is typically accomplished by a photomultiplier tube (PMT). A PMT is an electronic tube that is capable of converting a photon current into an electrical signal and of amplifying this signal. A PMT consists of a photo cathode and a secondary electron multiplier.
The photons impact on the photo cathode and sputter electrons from its surface. These electrons are accelerated in an electrical field and impact on other electrodes, so-called dynodes, from the surface of which each impacting electron sputters several secondary electrons. This cascade effect results in a significant increase in the number of electrons. In order to function this way, the dynodes have to be on an increasingly positive potential. At the end the electrons impact on an anode and flow off to the mass. The resulting current is measured.
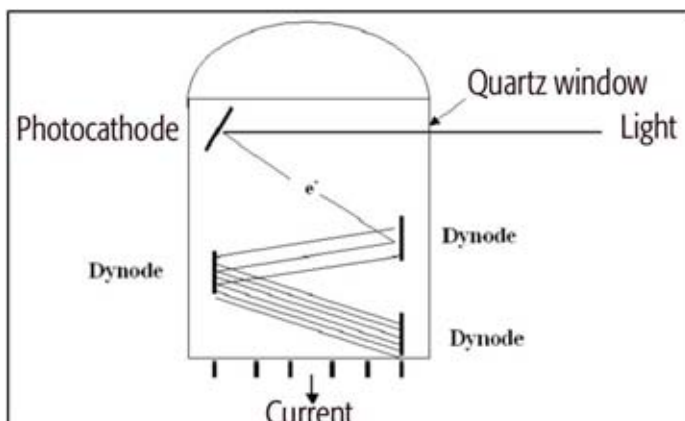
Fig. 2-15: Operation principle of a photomultiplier

The amplification factor increases exponentially with the number of dynodes. Typical PMT have some 10 dynodes, which corresponds to an amplification factor of about 10^7.

2.2   Components of a High-Resolution Continuum Source AAS (HR-CS AAS)

The basic design of a High-Resolution Continuum Source Atomic Absorption Spectrometer is depicted in Fig. 2-16.
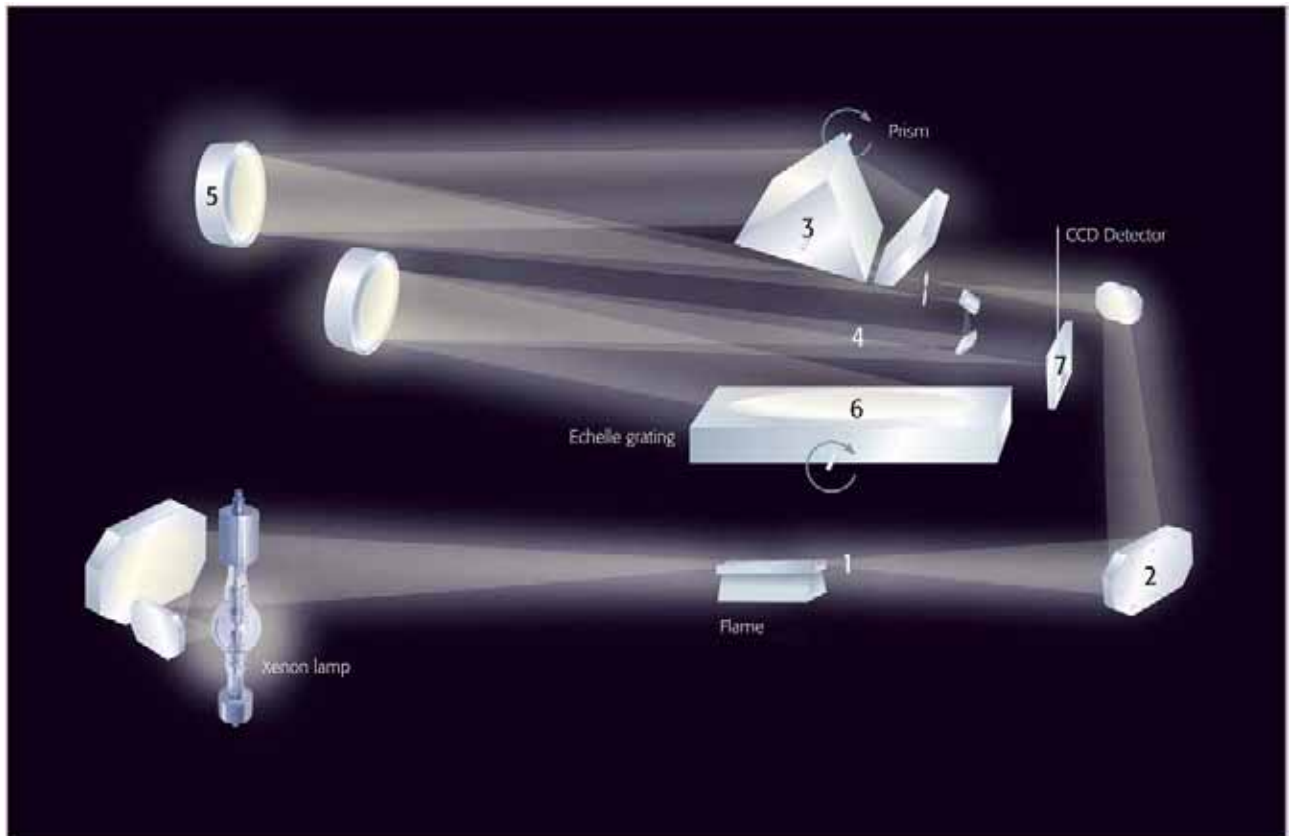
Fig. 2-16: Schematic design of an HR-CS AA-Spectrometer

A specially designed xenon short-arc lamp is used as the radiation source. The atomization unit produces analyte atoms in the ground state as in conventional AAS. The radiation emitted by the continuum radiation source, after its attenuation in the atomization unit, is conducted to the double monochromator which consists of an entrance slit, a prism pre-monochromator, an intermediate slit and an echelle grating monochromator. The intermediate slit has to separate the part of the spectrum that contains the analytical line. That part enters the second monochromator, where it is highly resolved. The second monochromator does not have an exit slit, so that the entire part of the spectrum transmitted by the intermediate slit reaches the detector, a linear CCD array that not only detects the analytical line, but also its spectral environment at high resolution.

Based on patented ISAS Technology

ISAS
Institute for Analytical Sciences

2.2.1 The radiation source in HR-CS AAS

In HR-CS AAS one single radiation source is used for all elements and wavelengths, a xenon short-arc lamp. This type of lamp is used nowadays to a great extent, e.g. for the illumination of stadiums, in projectors and even for cars. However, these commercially lamps don't have enough energy in the far UV range, where most of the analytical lines of AAS are located. It was therefore necessary to re-design this lamp type for use in AAS.

Fig. 2-17: Xenon short-arc lamp for HR-CS AAS

The lamp shown in Fig. 2-17 has a modified electrode configuration and works under high pressure. Under these conditions a hot spot is forming that reaches a temperature of about 10 000 K. The emission intensity of this lamp is at least a factor of 10 higher than that of conventional xenon short-arc lamps, and more tan a factor of 100 higher in the far UV range. And, what might be even more important for AAS, the emission intensity of this lamp is in average a factor of 100 higher than that of conventional HCL over the entire spectral range.
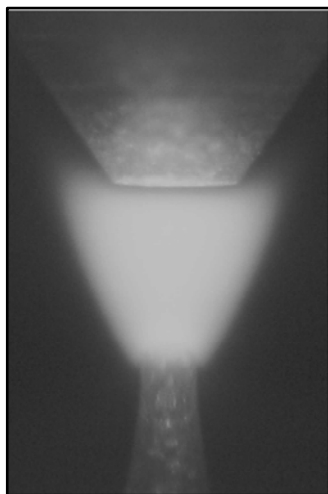
(a)   (b)

Fig. 2-18: Arc discharge of (a) a commercial and (b) of the xenon short-arc lamp developed for HR-CS AAS

One of the big advantages of HR-CS AAS is for sure that only a single radiation source is required for all elements and all wavelengths over the entire spectral range from 190 – 900 nm. Another advantage results from the significantly higher emission intensity of this lamp. Although the radiation intensity has no influence on sensitivity in AAS, it has an influence on the signal-to-noise ratio. As a result of this, detection limits are in average about a factor of 5 better in HR-CS AAS, compared to line source AAS.

2.2.2 The atomizer in HR-CS AAS

In HR-CS AAS the same atomizers are used as in classical line source AAS, so that we can refer in full to Section 2.1.2. It might be worthwhile to mention briefly that method development and optimization is greatly facilitated and simplified in HR-CS AAS due to the visibility of the spectral environment of the analytical line at high resolution.

2.2.3 The optical system in HR-CS AAS

The optical system in HR-CS AAS is fundamentally different from that in AAS, although similar components are used. The use of a continuum radiation source inevitably requires a high-resolution monochromator. Classical monochromators of this type, as they were used in optical emission require a lot of space and have a tendency to exhibit wavelength drift. Both of these characteristics are unacceptable in HR-CS AAS. This problem was solved with the design of a compact double monochromator with active wavelength stabilization, which is shown in Fig. 2-19. Both monochromators are in Littrow mounting with focal lengths of 30 and 40 cm, respectively.

Visible in figure 2-16 the radiation of the continuum source enters the monochromator through the entrance slit (1); the first parabolic mirror (2) reflects the radiation onto the prism (3), which has a mirror on the other side. This way the radiation passes the prism twice before it is reflected back onto the parabolic mirror, now spectrally dispersed. This mirror conducts the radiation via a second mirror onto the intermediate slit (4). The prism is rotated in a way that the radiation in the environment of the analytical line passes through the slit and enters the second monochromator. The second parabolic mirror (5) conducts the radiation onto the Echelle grating (6), where the selected spectral range is highly resolved. The entire section of the highly resolved spectrum that contains the analytical line and its environment is reflected onto the detector (7) via the parabolic mirror (5).

The resolution of the double monochromator is in the range of 140 000, which corresponds to a spectral bandpass of 1.6 pm at 200 nm – a value that is about a factor of 100 better than the resolution of classical AAS monochromators.

2.2.4　The detector in HR-CS AAS

In HR-CS AAS a linear CCD array with typically 512 pixels (picture elements) is used as the detector, 200 of which are used for analytical purposes. Each individual pixel is evaluated independently, so that the equipment basically works with 200 independent detectors. All the 200 pixels are illuminated simultaneously (for 1-10 ms) and read out simultaneously. The next illumination is already being carried out during signal evaluation, making possible a very rapid measurement frequency. Fig. 2-20 is an example of typical detector readout, where the measured value for each pixel in the environment of the analytical line for sodium at 330.237 nm is shown. The absorption line is essentially covered by three pixels, while the other pixels only exhibit the statistical variation of the baseline, i.e. the noise.
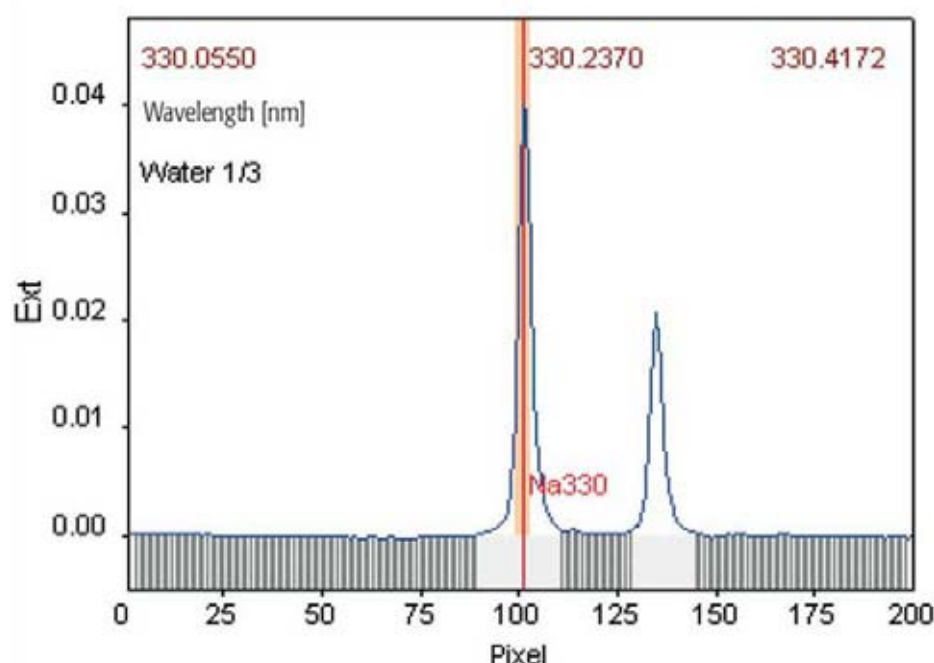
Fig. 2-20: Readout of the integrated absorbance measured by each individual pixel in the environment of the analytical line of Na 330.237 nm

As only three pixels are used in most cases to measure atomic absorption, the others may be used for correction purposes. As all pixels are illuminated and read out simultaneously, any variation of the intensity that is independent on wavelength, such as variations in lamp emission, can be detected and eliminated through the use of correction pixels. This results in an extremely stable system with low noise level and significantly improved signal-to-noise ratios. The same correction system also eliminates any continuous (over wavelength) background absorption, as will be discussed in a later section.

Another decisive advantage of this measurement principle with 200 detectors is that the entire environment of the analytical line becomes 'visible' at high resolution. This way it is possible for example to recognize and avoid spectral interferences much more easily.

2.3 Automation in AAS

Mankind has always tried to mechanize and automate processes in order to simplify life. This is not a bit different in instrumental analysis. Besides simplifying certain duties, automation can also contribute to reduce cost (time and personnel) and improve precision, e.g. by using an automatic sampler. Obviously, automation is in no way limited to injecting the solution for measurement, it comprises all aspects of sample preparation, the course of an analysis up to data evaluation and handling. The latter aspect is nowadays primarily handled by computers (PC). In addition to presenting the measured data in an appropriate format, the computer is also used to control certain functions of the spectrometer. The communication between computer and user software is of particular importance.

In the following we will discuss the various possibilities of automation that help to facilitate work in the laboratory, and are the basis of a multi-element routine measurement.

2.3.1 Autosamplers

Automatic sample changers (autosamplers) have been found useful for routine work in all AAS techniques as they facilitate daily routine and contribute to improve precision. Particularly in graphite furnace analysis where micro-amounts have to be handled, they have become indispensable as they also reduce considerably the risk of contamination.

Fig. 2-21: Autosampler for graphite furnace AAS

Fig. 2-22: Autosampler for flame AAS

Frequently special positions in the autosampler can be selected for calibration, blank, modifier and/or buffer solutions. The sequence of measurements and the number of replicates can usually be programmed without limitation. The adjustment of the autosampler arm is usually controlled via the user software.

Autosamplers can not only be used for the automatic introduction of the solutions for measurement, they are also capable of establishing calibration curves from a single calibration solution. Two options are available for that purpose in the software of graphite furnace AAS. In case of dilution in the graphite tube the injection volume is kept constant by completing the standard solution with blank solution. Alternately, different volumes of the standard solution are injected into the graphite tube without the addition of blank solution. In any case, whether used for graphite furnace or flame AAS, the software automatically calculates the slope of the calibration curve, the intercept with the y axis, the characteristic concentration or mass, and the correlation coefficient.

The properties of samples regarding surface tension and viscosity might be quite different, considering for example the difference between an aqueous solution and a concentrated acid. These properties have significant influence on the repeatability of depositing a sample in the graphite tube or on the aspiration rate of the nebulizer. A good autosampler should provide means to cope with those problems.

In practical work we are often facing the duty to analyze samples of quite different analyte concentration in the measurement cycle. As the linear working range in AAS is limited, and may be extended only to a certain extent with the use of non-linear evaluation functions, dilution of the sample solution often becomes a necessity. This should be done automatically and with high precision by the autosampler in order to minimize or avoid time-consuming manual dilution and re-evaluation of individual samples. The software automatically calculates the dilution factor from the measured absorbance and the stored calibration curve. The dilution factor is documented in the measurement report and may be reproduced at any time.

2.3.2 Automatic control and optimization functions

Basically all parameters and functions of an AA spectrometer can be adjusted, controlled and changed automatically. The optimization routines that are available in the equipment and through the user software are of great importance as they facilitate making the proper decisions.

In computer-controlled spectrometers certain parameters, such as analytical line and spectral bandwidth are usually adjusted automatically according to stored programs. The respective lamp (HCL) is moved into the measurement beam and its position is optimized automatically. All critical parameters, such as gas supply and optical parts are controlled and re-adjusted if necessary.

Adjustment and optimization possibilities in flame AAS
In flame AAS the flame is automatically ignited and extinguished; gas flow and pressure are controlled by sensors and supplied to the system free of fluctuations. Highest safety of operation is guaranteed at any time. Error messages and the non-ignition or automatic extinguishing of the flame in case the wrong burner head is installed, the level of the liquid in the drain is too low or in case of a power failure are part of this safety routine. An automatic optimization routine evaluates of the optimum gas flow and burner height.
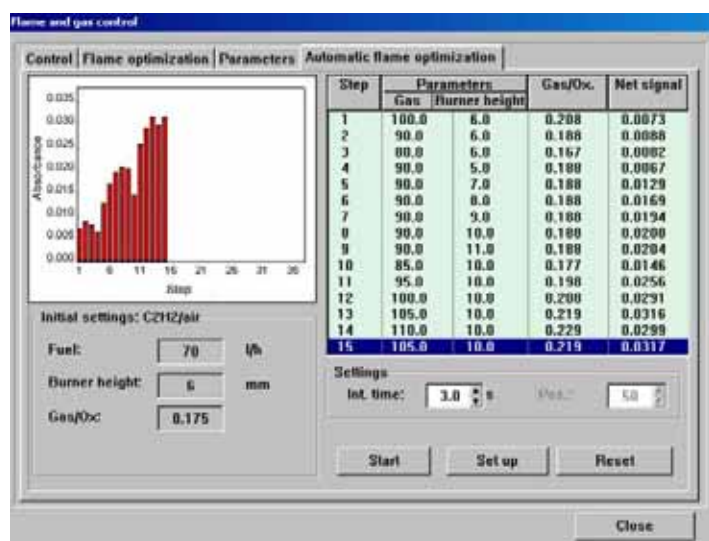
Fig. 2-23: Automatic optimization routine in flame operation

Starting point for this routine are the stored 'cookbook conditions' that are available for each element. Fuel gas and burner height are modified mutually, using a method-specific standard to guarantee maximum sensitivity and flame stability. If these parameters are excluding each other, it

is also possible to optimize for minimum interference. These adjustments are part of a method and can be stored once they have been optimized.

Options for settings and optimization in the graphite furnace technique
In the graphite furnace technique, as in the flame technique, all gases (purge, protective and alternate gas) are controlled by sensors. Turning on and off of these gases is fixed in a program. Certain measurement conditions are controlled automatically and might interact with the analytical cycle. Among these is the control of the tube quality and of the cooling water.
The actual electrothermal atomization is carried out according to a temperature program that has to be optimized in advance by the user, based on an element-specific cookbook procedure. The goal of method development is to remove the matrix as much as possible without volatilizing the analyte.
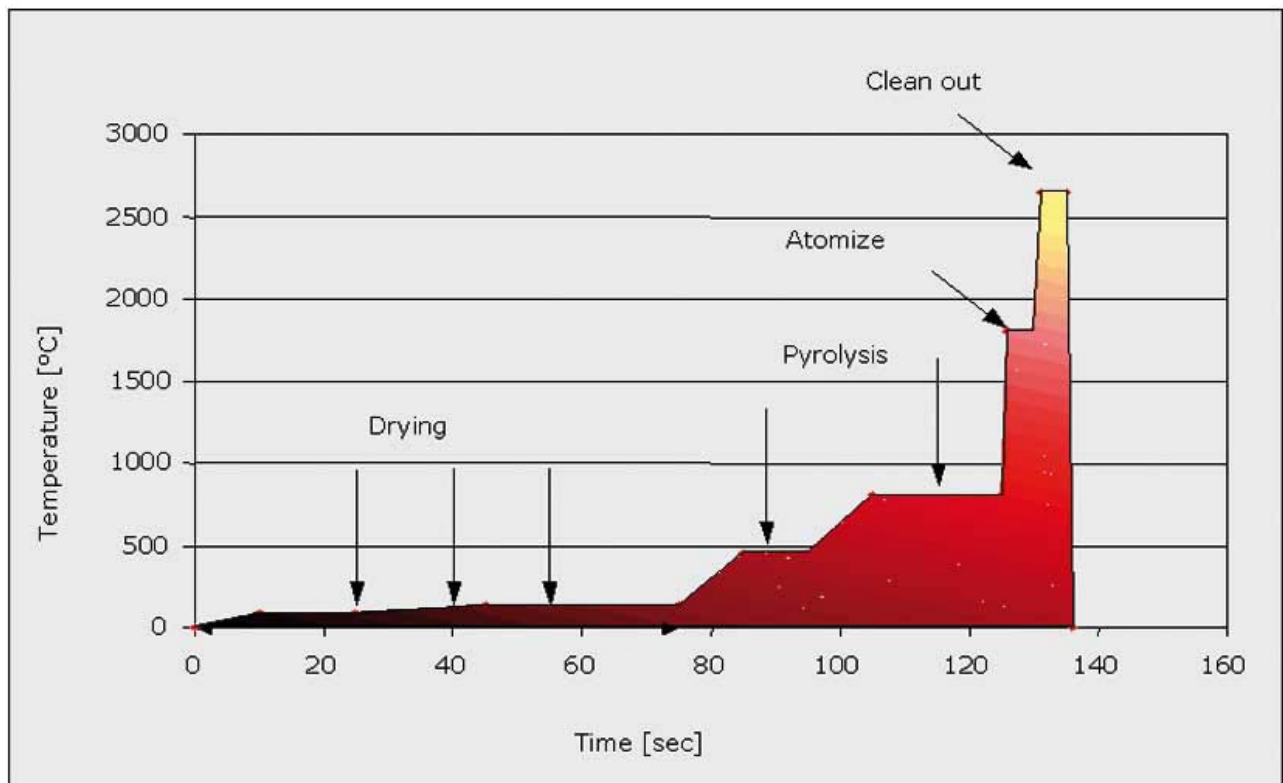
Fig. 2-24: Temperature program in the graphite furnace technique

Options for settings and optimization in the hydride-generation technique.
In the hydride-generation technique optimization is mostly regarding dosing of the solutions for measurement, control of the inert gas, and pre-concentration of mercury. Continuous flow systems offer a higher degree of automation than batch systems.

2.3.3   Further accessories

Injection switch SFS (Segmented Flow Star)
The injection switch has been developed in order to further extend the applicability of the flame technique. The SFS helps to reduce transport and vaporization interferences and to maintain stable burner conditions, particularly when only a small sample volume is available or when samples with high acid or salt content have to be analyzed The module switches automatically between sample and blank solution and provides efficient cleaning of the entire nebulizer-burner system.

Fig. 2-25: Injection switch SFS

Fig. 2-26: Scraper

Scraper
Besides the cooler air-acetylene flame, the hotter nitrous oxide-acetylene flame is frequently used for elements that are difficult to atomize because they are forming stable oxides, such as aluminum, silicon, molybdenum or tungsten. Besides the optimum chemical and thermal conditions that this flame is providing it has to be pointed to the increased fuel content, which can result in clogging of the burner slot by carbon deposits, and hence in irreproducible results. This process is further favored by organic samples that do anyway have higher carbon content. In cases like these the scraper is particularly useful. Once activated by the software it cleans the burner slot automatically during the burn-in phase, so that no manual interaction is necessary. The scraper allowes continuous and reproducible measurement, as the burner surface is cleaned automatically before sample and recalibration measurements. The scraper hence becomes a fixed accessory of a routine analysis when the nitrous oxide-acetylene flame is involved.

3 Flame AAS

Ideal conditions for flame AAS are given if:
- the total salt content in the solution to be analyzed is below 1%,
- only one element is present in solution,
- the physical properties (viscosity) of the solution are identical to those of an aqueous solution,
- the concentration of the analyte corresponds to an absorbance of A = 0.2...0.4, as the relative error of A is smallest in this case,
- the flame temperature is sufficient to dissociate all analyte compounds without causing ionization,
- stoichiometric or fuel-lean flames can be used to avoid carbon deposits at the burner slot,
- the main analytical wavelength can be used for measurement, as the slope of the calibration curve is optimum in this case,
- the radiation intensity of the HCL is high enough so that low lamp currents can be used. This increases lamp lifetime and results for most elements in a gain of sensitivity
- low multiplier voltage and gain can be used as this results in good signal-to-noise ratio, a pre-condition for low detection limits,
- high-purity reagents are used for digestion and dilution.

In practical analysis the upper mentioned ideal conditions will almost never be fulfilled completely. Some points might be realized, but the majority will deviate from the optimum. It is the analyst's task to evaluate carefully during method development which compromises are necessary in the selection of instrumental parameters, in sample preparation and in the analytical procedure in order to obtain optimum conditions for a given task.

Instrumental parameters that have to be selected and optimized include:
- analytical wavelength
- slit width
- HCL current
- gain
- multiplier voltage
- type of flame
- fuel/oxidant ratio
- burner adjustment

All parameters, except for gain and multiplier voltage, have an influence on the sensitivity. Gain and multiplier voltage, however, are important for the LOD.

3.1 Choice of the analytical wavelength

The recommended main analytical wavelength either gives the best sensitivity or the best signal-to-noise ratio. For this reason it is selected to measure samples with low analyte concentration. To measure high analyte concentrations the use of a less sensitive line is a way to reduce the absorbance into the range A < 0.6, which is more favorable for flame AAS.

3.2 Choice of the slit width

The amount of radiation that enters the monochromator is determined by the slit width. A large slit width means that a lot of radiation reaches the monochromator and detector, i.e., we can work with low gain and multiplier voltage. This results in a low noise level compared to the signal.
An optimization of the slit width is recommended – unless it is given in the cookbook – in order to separate the analytical line from other lines that are emitted as well by the HCL. The slit width

Fundamentals , Instrumentation and Techniques of Atomic Absorption Spectrometry   27/ 65

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should be chosen as wide as possible (in order to enable as much radiation as possible to enter the monochromator), and as narrow as necessary (in order to exclude other lines). The most important criteria are the signal-to-noise ratio and the linearity of the calibration function.

3.3 Choice of HCL power

In general HCL are operated under the optimum conditions given in the cookbook. For difficult tasks, or for lamps provided by a different supplier, it might however be necessary to alter the current.

Advantages of a lower lamp current:
- Increased lifetime of the HCL (2000-5000 mAh) Note: Hollow cathode lamps are ageing even when they are not used.
- For most elements the sensitivity is improving.
- The risk of line reversal is minimal.

Advantages of a high lamp current:
- The fact that certain energy has to be emitted by the lamp in order to obtain an acceptable signal-to-noise ratio.

3.4 Choice of gain and multiplier voltage

Gain and multiplier voltage are set automatically by the software after all other parameters have been optimized and the energy adjusted.
The range of the photomultiplier voltage is typically 250 V-450 V. It has to be noticed that the signal-to-noise ratio deteriorates for higher multiplier voltages. The absolute limit is 600 V, which means that essentially no more energy is reaching the detector.

3.5 Choice of the fuel/oxidant ratio

Recommendations about the fuel/oxidant ratio for an element may be taken from data sheets or from the cookbook. The automatic flame optimization should be used for final optimization (see Section 2.3.2).
Optimization of the flame stoichiometry helps to reduce or eliminate interferences; this has to be considered in the decision about the fuel/oxidant ratio.

3.6 Gases in flame AAS

It has been discussed earlier that the flame has to convert the elements present in the solution into free atoms. There is an optimum flame and an optimum temperature for each analyte compound, as will be discussed in the following.

3.6.1 Conditions for the use of flames

The chemical composition of the flame can have a significant influence on the processes of vaporization and atomization, which results in certain conditions for the flame to be used:

- Fast and complete atomization of the analyte without ionization
- Low self absorption or emission in the spectral range of interest
- Possibility to use oxidizing or reducing flame conditions
- Suitable temperature range for the analyte to avoid ionization
- Low flow rate for a long residence time of the analyte atoms
- Safe and inexpensive

3.6.2   Overview of different gases

Two flames have established with time – the air-acetylene and the nitrous oxide-acetylene flame – the different temperatures and oxidizing or reducing properties of which allow determining all elements under optimum conditions. They are complementing each other quite well and come close to fulfill the above-mentioned conditions. The flame used most frequently in AAS is the air-acetylene flame. The characteristics of this and a few other, less frequently used flames are compiled in the following table.

Properties of different flames				
Oxidant	**Fuel**	**Burning velocity [cm/s]**	**Temperature [°C]**	**Remarks**
Air	Natural gas	55	1840	For easily ionized elements
Air	Methane	70	1875	For easily ionized elements
Air	Propane	80	1930	For easily ionized elements
Air	Acetylene	160	2300	Most common flame
Nitrous oxide	Acetylene	180	2750	For refractory elements

3.7   Interferences in flame AAS

Interference is defined as an influence of matrix components on the analytical result. As AAS is a relative technique, interferences are observed when the matrix causes a different behavior in sample and calibration solutions.
It is therefore important to investigate if interference is present, and if yes, how it can be eliminated, or how its influence on the measurement result can be minimized.

Interferences are classified into:
- Spectral interferences
- Non-spectral interferences
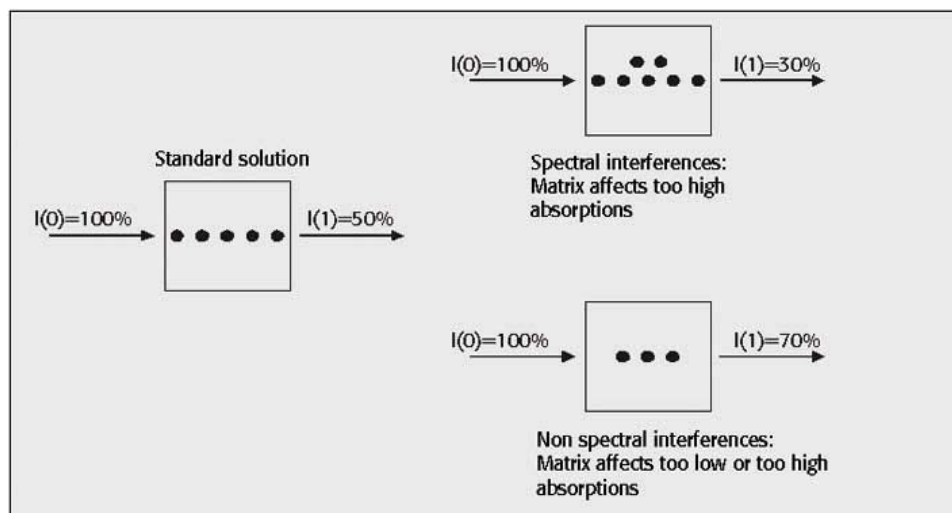
Fig. 3-1: Survey about interferences

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3.7.1 Spectral interferences in flame AAS

The most frequent spectral interference in AAS is background absorption. It is caused by radiation scattering at particles in the atomization unit or by molecular absorption, e.g. by difficult-to-dissociate oxides, hydroxides or halides.

Spectral interferences may also be caused by direct overlap of the analytical line with the absorption line of a matrix element. Although this interference is rare in AAS, it exists, and the most prominent examples are listed in the following table.

Analyte	Wavelength [nm]	Interferent	Wavelength [nm]
Cd	228.802	As	228.812
Mg	285.213	Fe	285.179
Zn	213.856	Fe	213.859
Zn	213.856	Cu	213.850

It is worth mentioning that there is no instrumental or mathematical way in classical line-source AAS to eliminate or compensate for measurement errors caused by direct line overlap. The only possibility to avoid this interference is to change to a different, undisturbed analytical line. Usually, however, these lines are less sensitive, so that this possibility is not always applicable. Particularly for cadmium and zinc the secondary lines are at least a factor of 100 less sensitive than the main line, which is usually no alternative.

3.7.2 Non-spectral interferences in flame AAS

Non-spectral interferences are generally classified into:

- Transport interferences
- Spatial distribution interferences
- Vaporization interferences
- Dissociation interferences
- Ionization interferences

Transport interferences
Transport interferences comprise all processes from the aspiration of the solution for measurement over nebulization and transport of the aerosol up to the flame. Transport interferences are caused by different physical properties of sample and calibration solutions. All factors that can influence aspiration and nebulization, such as viscosity, surface tension or specific gravity, are of importance.

Organic solvents usually have a positive effect in flame AAS, as most of them have a viscosity and specific gravity lower than that of water, and are hence more easily aspirated. The lower surface tension in addition causes finer nebulization, so that much more sample solution finally reaches the flame per unit of time. Inorganic salts, mineral acids and organic macro molecules (proteins, sugars), in contrast, reduce the aspiration rate and are forming bigger droplets that are preferentially separated in the mixing chamber. This is causing a reduction in sensitivity, as a smaller fraction of the solution is reaching the flame.

Up to a total dissolved salt content of 1 % it is usually sufficient to match the matrix in the standard solutions (e.g. same solvent). Dilution is another way to control this interference in case the analyte content is high enough. A further, generally applicable possibility to correct for transport

interferences is the application of the analyte addition technique, which will be discussed in more detail later.

Spatial distribution interferences

Spatial distribution interferences may be observed in flames if the distribution of the analyte over the width of the flame is different in the presence of concomitants than in their absence. This could result in measurement error if the absorption radiation is not covering the entire width of the flame. Spatial distribution interferences are found more frequently in the hotter nitrous oxide-acetylene flame, as this flame has a greater lateral extension than the air-acetylene flame (thermal conditions).

Spatial distribution interferences disappear when the burner head is rotated 90°, as the lateral extension does not play a role under these conditions. However, this procedure is not always applicable, as it is associated by a significant reduction of sensitivity. The interference also changes with the observation height in the flame. A further, generally applicable possibility to correct for transport interferences is the application of the analyte addition technique, which will be discussed in more detail later.

Vaporization and dissociation interferences

Vaporization interferences are caused by formation of compounds in the condensed phase between the analyte and matrix constituents that are more difficultly (more slowly) transferred to gaseous molecules than the analyte in the calibration solution. The kinetic (speed) of vaporization is of significant importance in flame AAS, as slower vaporization means that the vaporization products (gaseous molecules), and hence also the analyte atoms are only produced at greater height in the flame (above the absorption volume). This results in lower measurement values compared to matrix-free solutions.

Calcium for example is forming pyrophosphates in the presence of phosphate, which are difficult to vaporize in normal flames. Magnesium is forming mixed oxides in the presence of aluminum; alkaline earth elements are generally affected by aluminum, phosphate, sulfate and silicate.

Dissociation interferences are of the same origin and are caused by the formation of difficult-to-dissociate (gaseous) molecules of the analyte with matrix constituents. As gas phase dissociation is an equilibrium reaction, kinetics usually don't play a role. Similarly, equilibrium reactions with the participation of flame gas components (O, OH, C, H), don't play a role either, as they are affecting sample and calibration solutions equally.

In spite of the significantly different mechanisms of these two interferences they are difficult to distinguish in practice, which is actually not necessary, as both have the same source, and can be controlled using the same means.

The addition of lanthanum or strontium salts or complexing agents in excess usually removes these interferences. These so-called releasing agents form compounds with the interfering substance that is thermally more stable than the corresponding compound of the analyte. Lanthanum chloride has largely replaced the previously used strontium chloride; however it is important that the chloride is used and not the nitrate.

All alkaline earth elements show higher sensitivity in a fuel-rich (reducing) flame, vaporization interferences, however, are less pronounced in fuel-lean (oxidizing) flames. Both, vaporization and dissociation interferences are much less pronounced in the hotter and more reducing nitrous oxide-acetylene flame, so that the latter one should in general be preferred.

Ionization interferences

The temperature of the flames used in AAS is too low to cause any significant thermal ionization, even of the most easily ionized elements. The concentration of ions and radicals in the primary reaction zone of the air-acetylene, and particularly the nitrous oxide-acetylene flame, however, is high enough to cause appreciable ionization of alkali, alkaline earth and rare-earth elements by charge-transfer reactions.

The partial ionization of an analyte atom itself cannot be called interference as long as it is affecting the analyte in the sample and in the calibration solution to the same extent. However, it is most desirable to avoid ionization of an analyte, as it always reduces the sensitivity (ionized atoms are not available for absorption). The degree of ionization is in addition depending on analyte concentration (low concentrations are ionized more strongly), which results in a strongly non-linear calibration curve.

Real ionization interference is observed if the sample solution contains other easily ionized elements that are not present in the calibration solution. In this case analyte ionization is suppressed in the sample solution according to the Saha equation, and is hence different from that in the calibration solution.

Ionization und ionization interferences can generally be removed by the addition of another easily ionized element in great excess to sample and calibration solutions. Alkali elements (K, Cs), which have a very low ionization potential, are particularly suited for that purpose. These elements are influencing the ionization equilibrium in a flame in a way that analyte ionization is strongly reduced. This effect will be explained in the following using the example of barium. In a nitrous oxide-acetylene flame this element might be ionized up to 88% (depending on its concentration), i.e. the equilibrium is shifted in favor of the barium ion. The addition of ionization buffers, such as KCl or CsCl (chlorides are more efficient than nitrates or sulfates), can remove this effect. Potassium and cesium are almost completely ionized in a nitrous oxide-acetylene flame, hence producing a large excess of electrons, which shift the ionization equilibrium for barium into the desired direction (the atoms).

$$Ba \quad \underset{\longleftarrow}{\overset{\longrightarrow}{}} \quad Ba^+ + e^-$$

Addition of 0.2% Potassium as KCl

$$K \quad \underset{\longleftarrow}{\overset{\longrightarrow}{}} \quad K^+ + e^-$$

$$Ba^+ + e^- \quad \underset{\longleftarrow}{\overset{\longrightarrow}{}} \quad Ba$$
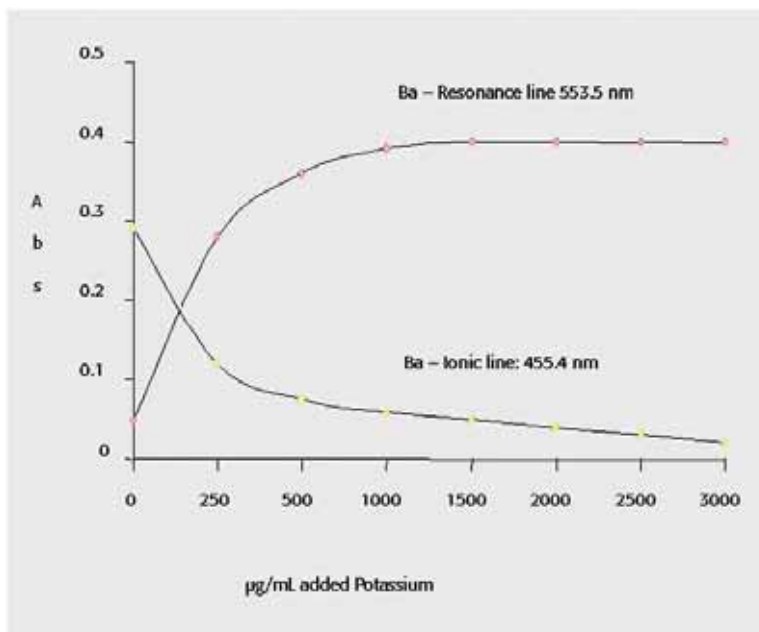
Fig. 3-4: Influence of potassium on the ionization of barium

3.7.3 The analyte addition technique

Transport and spatial distribution interferences might be eliminated to a certain extent by matrix matching. This procedure might be feasible for large series of very similar samples; however it is too laborious for individual samples of very different composition. In many cases it might not be possible to match the matrix in the standards, as it is too complex or simply unknown. In this case the analyte addition technique is the method of choice to correct for this kind of interference. The sample solution is divided into usually five aliquots with the same volume. To each of the aliquots an equal volume of calibration solution with increasing and known analyte concentration is added. The analyte content in the original sample solution is determined by extrapolation of the measurement values to absorbance zero.

The analyte addition technique is based on the assumption that the added analyte is behaving in the same way as the analyte present in the sample, which is usually the case in flame AAS. The analyte addition technique can only be used to correct for interferences that affect the slope of the calibration graph, never to correct for spectral interference or ionization.
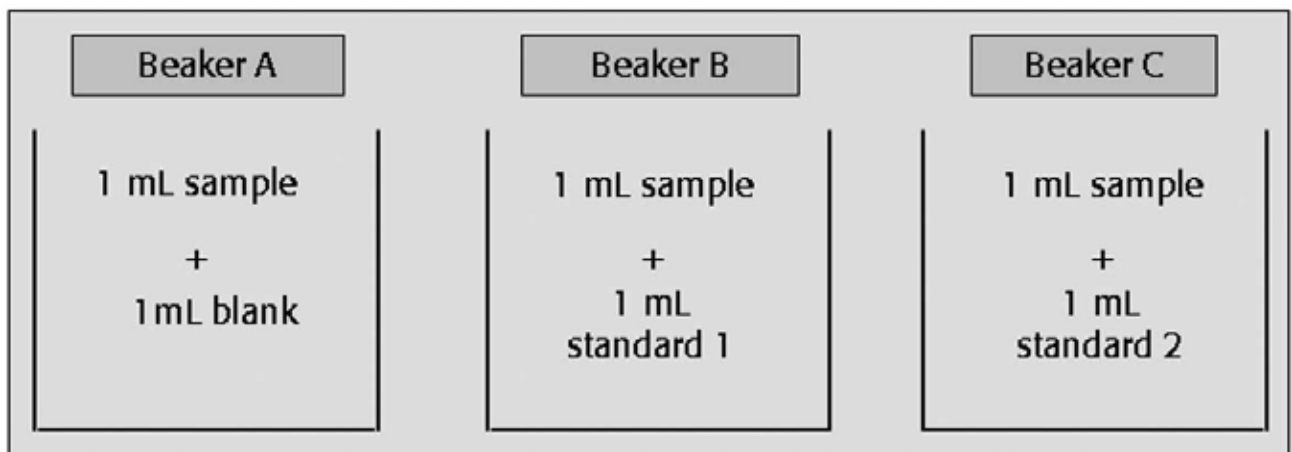
Fig. 3-5: Example for the preparation of a series of analyte additions

Example for a set of additions:

The sample solution is divided into three to five aliquots of equal volume. To each of the aliquots the same volume of a usually aqueous solution is added that contains the analyte in known and increasing concentration. One of the aliquots is only diluted to volume without adding the analyte. Plotting the absorbance obtained for the individual additions against the added concentration we obtain a calibration curve that intersects the absorbance axis at a value greater than zero. This absorbance represents the analyte content in the diluted sample aliquot. The analyte content may be obtained by extrapolation to A = 0. To obtain the analyte content in the original sample it is necessary to consider the dilution made with the additions. This is usually done automatically by the software.
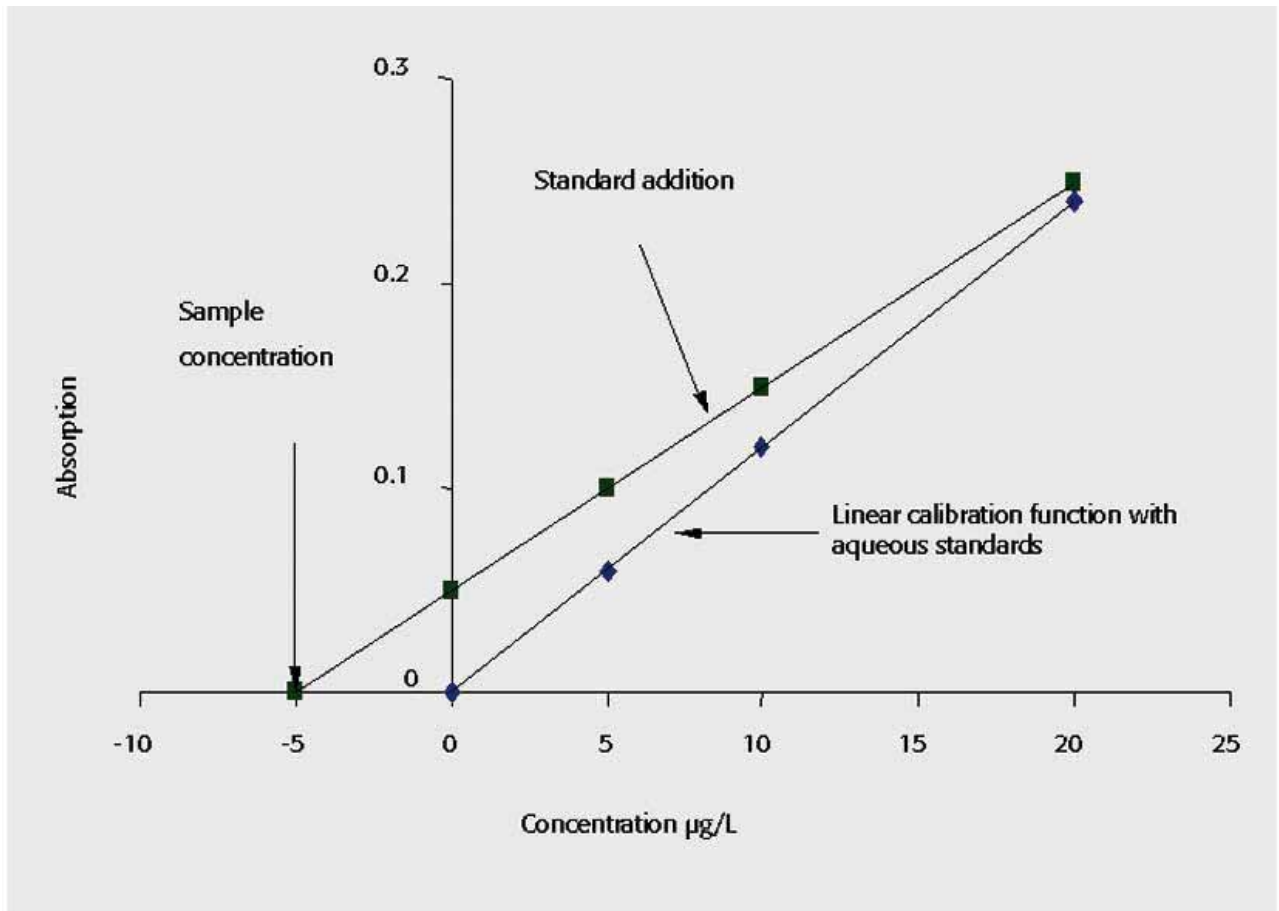
Fig. 3-6: Calibration curve using the analyte addition technique

4 Graphite furnace AAS

In graphite furnace AAS the sample is introduced into the graphite tube as a small volume of liquid or in solid form. The tube is heated due to its resistance by passing a controlled current through it. This way the sample is dried, thermally pretreated (pyrolysis) and finally atomized. The inert gas (purge gas) that is conducted through the graphite tube during drying and pyrolysis removes solvent and matrix vapors. In an ideal case only analyte atoms are produced in the atomization stage. The inert gas flow is interrupted during atomization (gas stop) to increase the residence time of analyte atoms in the absorption volume (up to ~ 1 s). This typically results in an increase in sensitivity of 2-3 orders of magnitude compared to the flame technique. As the atmosphere during atomization is essentially free of oxygen, losses of atoms in the form of oxides or hydroxides are minimized. The residence time of atoms in the graphite tube is some 1000 times longer compared to a flame, resulting in much higher atom density. The small sample consumption of typically 5....100 µL is equally important as the high freedom from interference of the graphite technique. Physical properties, such as viscosity or density have essentially no influence on the signal.

## 4.1 The temperature program

In graphite furnace AAS it is possible to separate in time processes such as drying, removal of a solvent, separation of the matrix from the analyte, and generation of atoms in the ground state. The data that are necessary for an efficient separation and atomization are combined in the so-called temperature program (TP) which has to be optimized for each analyte and each type of matrix.

A temperature program usually consists of the following stages:
- Drying (removal of the solvent)
- Pyrolysis (thermal pre-treatment in order to remove matrix components)
- Atomization (Generation of atoms in the ground state)
- Cleaning (removal of residual matrix or analyte)

For each stage of the TP it is necessary to select the heating rate and the hold time at the selected temperature.

No	Step Type	Temp °C	Ramp °C/s	Hold s	Time s	Gas Inert	Gas Add.	AZ s	Run s	Inj.	E/P
1	Drying	90	5	20	34.0	Max	Stop				
2	Drying	105	3	20	25.0	Max	Stop				
3	Drying	110	2	10	12.5	Max	Stop				
4	Pyrolysis	900	250	10	13.2	Max	Stop				
5	AZ*	900	0	6	6.0	Stop	Stop	0.0	5.7		
6	Atomize	1400	1400	4	4.4	Stop	Stop				
7	Cleanout	2000	500	4	5.2	Max	Stop				

Fig. 4-1: Typical TP for lead

4.1.1 Drying

The purpose of the drying step is to remove the solvent from the sample. The drying temperature should be chosen slightly above the boiling point of the solvent. The evaporation should be fast but not too fast to avoid spattering of the solvent, which would result in poor reproducibility. In order to optimize the drying parameters it is recommended to observe the process using a mirror. Components with a higher boiling point, such as some acids, might require a second or even a third drying step for safe removal.

The drying time depends on the temperature and the sample volume. As a rule of thumb, multiply the sample volume in µL by 2 to arrive at the necessary drying time in seconds. If drying takes much longer it might be necessary to increase the temperature.

4.1.2 Pyrolysis

The purpose of the pyrolysis step is to remove matrix components that are more volatile than the chemical compounds of the analyte in order to reduce or eliminate interference, e.g., due to non-specific absorption. While a pyrolysis time of 15 s at 300-600°C might be enough for dilute aqueous solutions, complex samples require careful optimization of all parameters.

The optimization often requires a compromise between two contradictory conditions:
- A sufficiently high temperature and a sufficiently long time have to be applied in order to remove potentially interfering sample matrix as complete as possible.
- The temperature has to be low enough and the time short enough to make sure that no analyte is lost in the pyrolysis stage.

In cases where the sample matrix is significantly more volatile than the analyte, the determination can be carried out without problems after proper selection of the parameters of the temperature program (TP). If, however, the volatility of the analyte is similar or higher than that of the matrix, it is necessary to take additional actions. These additional steps are primarily intended to eliminate potential background absorption. One possibility is the use of a background correction system, another one is the addition of a modifier to the sample in the graphite tube. This addition should help to volatilize the matrix components and/or transfer the analyte into a more stable compound. This technique is called chemical modification.

4.1.3 Atomization

The atomization temperature depends on the chemical form of the element and on the matrix, and should be optimized for each analytical task. The lifetime of graphite tubes is quickly deteriorating at temperatures above 2700°C, which should therefore not be exceeded. The atomization time should be chosen as short as possible, as it also has an influence on the lifetime of the tubes. It is important that the analyte signal returns to the baseline during the atomization cycle in order to avoid memory effects.

A high heating rate should be chosen for atomization in order to obtain maximum density of atoms in the ground state.

4.1.4 Cleaning

After the atomization it is necessary to insert a cleaning step in order to volatilize potential residues in the graphite tube. This cleaning step is of particular importance in cases where the analyte is more volatile than the matrix.

4.2 Gases in graphite furnace AAS

Argon is typically used as purge gas (to remove matrix components) and protective gas (to protect the graphite tube from ambient air). The use of helium causes loss of sensitivity due to a faster diffusion rate. Nitrogen is forming toxic nitrogen oxides above 2000°C, and also causes sensitivity losses for some elements. Both gases are therefore no real alternative for graphite furnace AAS.
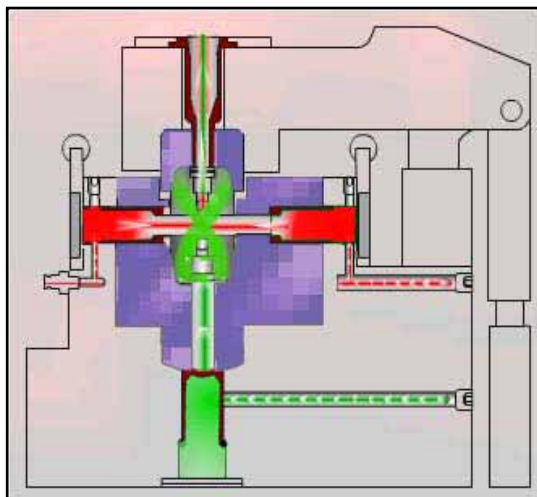

*Fig. 4-2:*red: inner (protective) gas flow

green: outer (purge) gas flow

The use of two separate gas flows is nowadays state of the art in graphite furnace AAS. The purpose of the internal gas flow (marked in red) is to remove all volatilized sample constituents through the dosing hole during the drying, pyrolysis and cleaning stages. During atomization, in contrast, a stationary situation is desirable in order to achieve maximum atom density and hence maximum sensitivity. For this reason the internal gas flow is interrupted (Gas-Stop) short before the onset of atomization. The gas flows can be optimized for the particular analytical task.
The purpose of the outer gas flow (marked in green) is to protect the graphite tube from oxidative attack, and remains on throughout the entire measurement cycle.
For organic matrices, such as blood, it might be useful to introduce an ashing stage prior to the pyrolysis in order to avoid carbon deposits in the graphite tube. Air or oxygen can be introduced as alternate gas for that purpose to convert carbon into carbon dioxide. The temperature during this ashing stage must not exceed 500 ºC in the case of oxygen and 600 ºC in the case of air in order not to affect tube lifetime. For the same reason it is essential to purge the air or oxygen from the graphite tube with argon before the temperature is further increased.

4.3 Spectral interferences in graphite furnace AAS

The reasons for spectral interferences in the graphite furnace technique are the same as in the flame technique.
Spectral interferences may be encountered when the absorption line of a concomitant element overlaps with the radiation emitted by the lamp. The results of the determination are too high in this case because of the contribution of the matrix element. This kind of interference is rare in AAS, as stated for flame AAS, but it exists.
Background absorption is another form of spectral interference that is due to non-specific absorption of radiation, resulting in an excessively high signal. The recorded signal consists of the analyte-specific absorption and the non-specific absorption of the background. There is no simple way to separate the two signals. In conventional line source AAS a deuterium lamp or the use of

the Zeeman Effect may be applied to correct for background absorption. In HR-CS AAS continuous background is corrected automatically and structured background can be eliminated using a computer program.

4.3.1 Deuterium background correction

Non-specific absorption is absorbing the same portion of the continuum radiation from the deuterium lamp as from the radiation of the line source. The element-specific absorption, however, is in first approximation only reducing the radiation of the line source, but not that of the deuterium lamp.

A The analyte HCL emits a line spectrum
The deuterium HCL emits a continuum

B The slit isolates the analytical line from the spectrum emitted by the line source and cuts a section from the continuum, corresponding to the spectral bandpass.

C The intensities of both radiations are adjusted

D Line absorption: The analyte reduces I_{HCL} according to its concentration, whereas I_{D2} is essentially not attenuated.

E Broad band background absorption is attenuating the intensities of both radiation sources to the same extent.

F Additional line absorption reduces I_{HCL} according to the analyte concentration, whereas I_{D2} is essentially not attenuated.
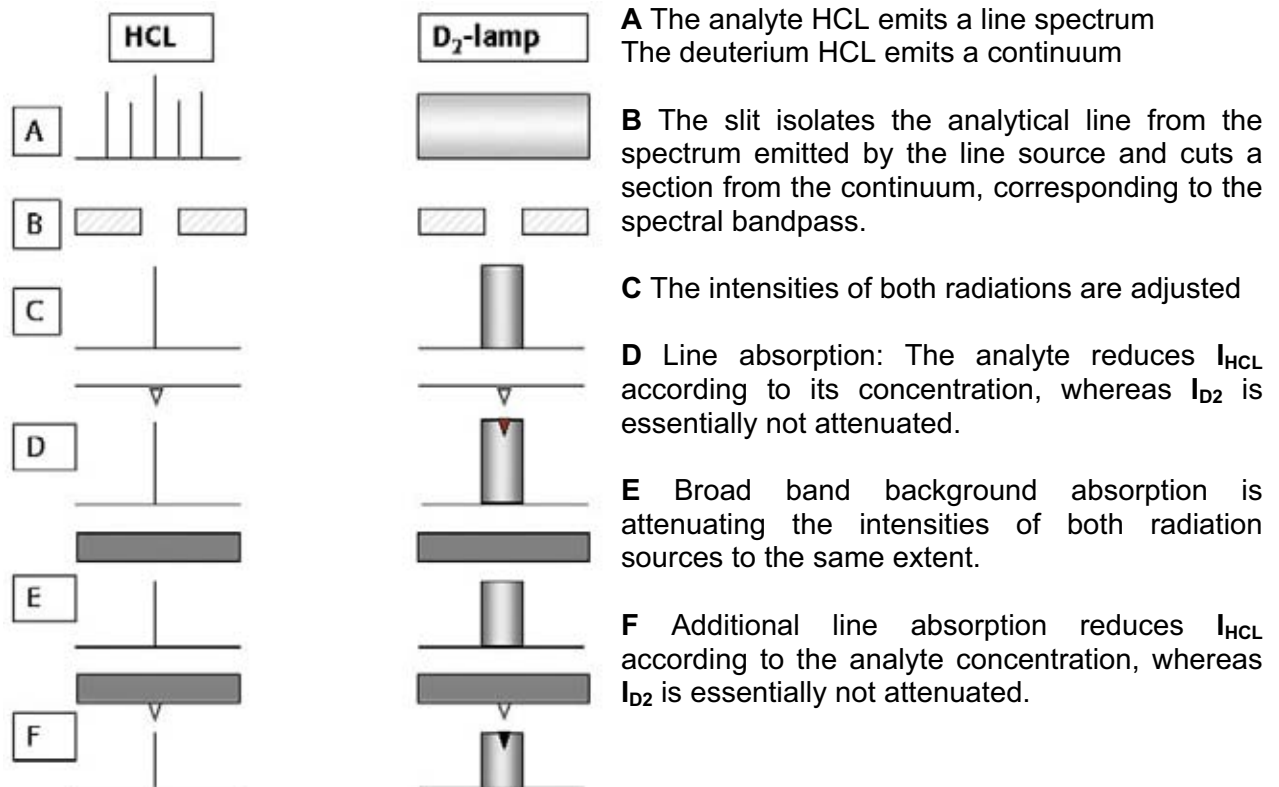
Fig. 4-3: Mode of operation of D$_2$ background correction

The radiation of the two sources is passing through the atom cloud in rapid sequence. The line source is measuring the sum of element-specific and non-specific absorption; the continuum source essentially only measures non-specific absorption. Subtracting the two values results in the element-specific absorption.
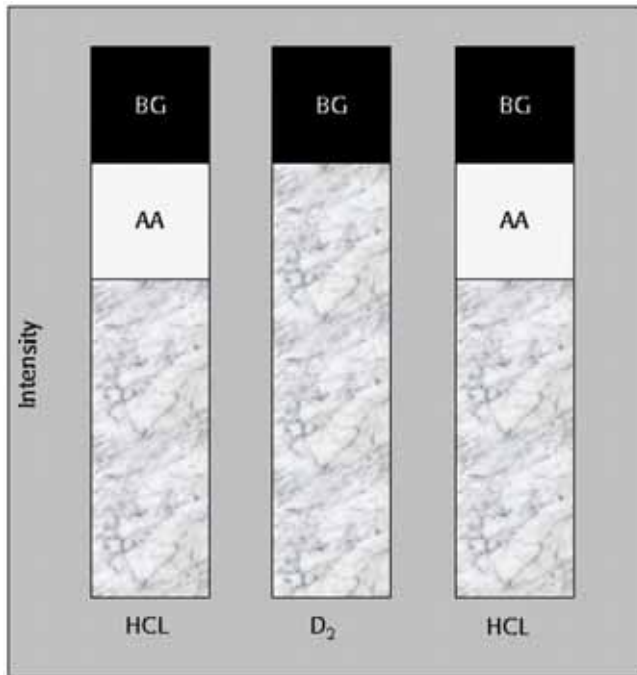
$$AA = (AA + BG) - BG$$

Advantages of D_2 background correction:
- Simple and inexpensive
- Easily retrofittable
- No loss of sensitivity
- Frequently sufficient accuracy

Disadvantages of D_2 background correction:
- Limited wavelength range
- Cannot be used to correct structured background
- Two radiation sources (requires accurate adjustment; increased noise)

4.3.2   Zeeman-Effect background correction

The Zeeman-Effect is based on the shift of energy levels of atoms and molecules in a magnetic field. If a magnetic field is generated at the atomizer (graphite furnace), the absorption lines of the analyte atoms are split into three components. Two of these components (σ-components) are shifted to slightly lower and higher wavelengths, respectively, whereas the third component (π-component) remains largely unchanged. The π-component can be removed from the spectrum using a polarizer.
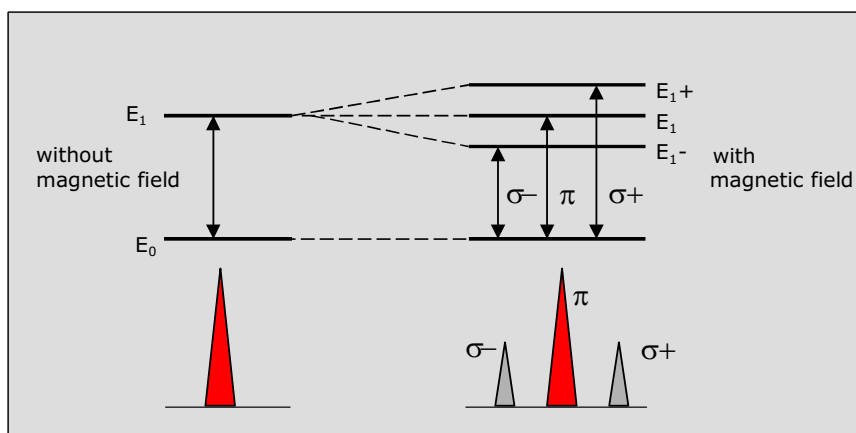

Fig. 4-4: Zeeman-Effect

For background correction using the Zeeman-Effect, a strong magnetic field is turned on and off in rapid sequence. Total absorbance (element-specific and non-specific background absorption) is measured with the magnetic field off and the background absorption with the magnetic field on. The difference of the two values gives the corrected element-specific absorption.

Advantages of the Zeeman technique:
▪ Measurement of total and background absorption on the same wavelength.
▪ Correction of rapid and structured background.
▪ No special lamps required.
▪ Correction over the entire wavelength range.
▪ Better signal-to-noise ratio

Disadvantages of the Zeeman technique:
▪ Loss of sensitivity (10-40% in the case of copper)
▪ Limited calibration range (roll-over effect)

4.3.3 Background correction in HR-CS AAS

In HR-CS AAS no additional system is required for background correction. The instrument is equipped with a CCD array with 200 pixels, and hence with 200 simultaneously and independently operating detectors. The software automatically selects a few of these detectors on both sides of the analytical line for correction purposes. Any change in the radiation intensity that appears equally on all of the correction pixels is corrected automatically. Among these changes are for example fluctuations of lamp emission intensity, but also any continuous background absorption. Discontinuous background absorption, e.g. direct line overlap with a matrix element or molecular absorption with rotational fine structure can be eliminated mathematically via reference spectra.

4.4 Non-spectral interferences in graphite furnace AAS

Non-spectral interferences are usually divided into:
▪ Transport interferences
▪ Spatial distribution interferences
▪ Vaporization interferences
▪ Dissociation interferences
▪ Ionization interferences

Transport interference
No transport interferences are observed in GF AAS, as the sample aliquot to be investigated is introduced directly into the graphite tube and vaporized completely.

Spatial distribution interference
Although the analyte atoms are not homogeneously distributed over the height of the graphite tube in the early phase of the atomization stage, no interference related to this phenomenon has been reported until now.

Vaporization interference
As in GF AAS, in contrast to flame AAS, the sample is not carried rapidly through the absorption volume, the kinetic of vaporization does not play a major role. The speed of vaporization only influences the peak shape; slower vaporization results in a lower, broader signal and on occasions in a double peak. This, however, does not result in interference as long as peak area is used for signal evaluation instead of peak height. This will be discussed in detail in Section 4.5 - STPF concept.

The interference most frequently observed in GF AAS is a premature volatilization of the analyte in the pyrolysis stage; this may happen if the analyte forms a compound with a matrix component that is volatile at lower temperatures than the analyte in the calibration solution. For this reason pyrolysis curves should be established not only with pure solutions, but also with at least one representative sample. The most efficient means to avoid such volatilization losses is the use of an appropriate chemical modifier. This will be discussed in more detail in Section 4.5 - STPF concept.

Dissociation interference
Dissociation interference is observed if the analyte is not 100% dissociated into atoms, and the degree of dissociation is influenced by concomitants in the sample. The efficiency of dissociation can generally be improved by isothermal atomization, i.e. atomization from a platform in a transversely heated tube. The influence of matrix constituents on the dissociation efficiency can be controlled most effectively by the use of an appropriate chemical modifier. This will be discussed in more detail in Section 4.5 - STPF concept.

Ionization interference
The temperatures that can be reached in a graphite tube are not high enough for thermal ionization; in the inert gas atmosphere there is also no ionization due to charge transfer. Hence there is no ionization interference possible in GF AAS.

Interference by carbide formation
Elements that tend to form stable carbides at elevated temperature (e.g. vanadium, molybdenum), usually exhibit an atomization signal that rapidly reaches a maximum, but returns to the baseline only slowly. This effect cannot be considered interference as long as it is affecting samples and calibration standards to the same extent, as it does not result in measurement errors.
Pyrolytically coated graphite tubes efficiently reduce the tailing of the atomization peaks.

4.5   STPF concept

The objective of the analyst in GF AAS is to separate the analyte as far as possible from the matrix prior to the atomization stage. In addition it has to be made sure that no analyte is lost in the pyrolysis stage. Finally, the influence of concomitants that could not be separated in the pyrolysis stage on the analyte in the gas phase has to be minimized. In order to reach this goal of interference-free analysis a set of measures, called Stabilized Temperature Platform Furnace (STPF) concept, was introduced by Walter Slavin in 1981. The concept includes the following conditions:

▪ Pyrolytically coated graphite tubes

▪ Graphite tubes with intrgrated platform

▪ Maximum heating rate for atomization

▪ Internal Gas Stop in the atomization stage

▪ Evaluation of peak area (integrated absorbance)

▪ Fast electronics

▪ Use of chemical modifiers

▪ Efficient background correction

4.5.1 Graphite material

The graphite material plays a decisive role, particularly in the atomization stage. Uncoated tubes or tubes in which the pyrolytic coating has been damaged (e.g. by aggressive reagents, such as H_2SO_4) have a porous surface into which the sample solution, the analyte and matrix components can penetrate easily. This results in increased matrix effects, tailing of the atomization signal and loss of analyte, as atoms can diffuse through the tube wall and are hence no longer available for measurement. More pronounced formation of carbides is another problem associated with these tubes. For these reasons uncoated tubes are only very rarely used nowadays.

Fig. 4-5: ESM photograph of an uncoated graphite tube: 600x magnification

Fig. 4-6: ESM photograph of a pyrocoated tube: 600x magnification

Graphite tubes coated with a layer of pyrolytic graphite offer a number of advantages. The life time as well as the sensitivity for refractory elements has improved significantly in comparison with uncoated tubes. Carry-over and memory effects have been reduced dramatically. In spite of their somewhat higher price, pyrolytically coated tubes have been generally accepted in the analytical field because of their improved atomization properties.

4.5.2 Platform effect

The use of a graphite tube with an integrated platform, instead of an atomization from the tube wall, is another condition for a GF AAS determination without or with a minimum of interferences. The connection between the platform and the tube is realized with a stud (PIN). This way the platform is only heated by thermal radiation and not by an electrical current. Because of the relatively slow transfer of thermal energy analyte atomization is delayed until a thermal equilibrium has established in the atomizer. The use of transversely heated tubes in addition also creates a spatial thermal equilibrium, as these tubes have the same temperature over their entire length.
Gas phase interferences and dissociation interferences are minimized or eliminated this way.
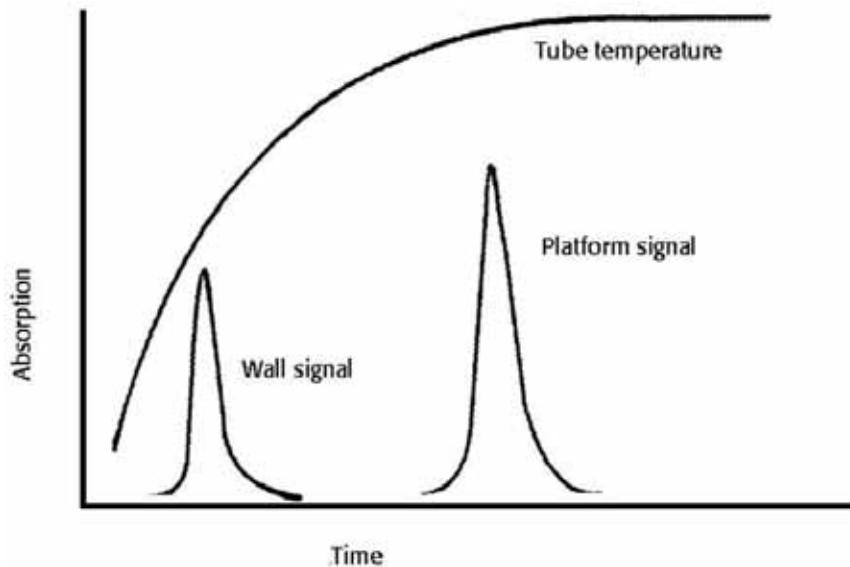
Fig. 4-7: Wall and platform atomization

With an integrated platform it is often possible to control the vaporization of analyte and matrix components via the temperature program in a way that atomization and background signal are separated in time. This allows a significant reduction of matrix effects on the analyte signal. Platform atomization might not be applicable for all analytes; some of the most refractory elements, such as molybdenum, exhibit less tailing when atomized in a tube without platform.

4.5.3   Heating rate during atomization

A very fast heating rate should be selected for atomization to obtain the maximum density of atoms in the ground state as rapidly as possible. In order to reach maximum sensitivity it is important that the process of atomization is significantly shorter than the residence time of the atoms in the absorption volume. The maximum heating rate (FP – Full Power) makes it possible to heat the graphite tube with the maximum available electrical power to the selected temperature.

Fast heating offers several advantages, such as the possibility to use lower atomization temperatures. In addition, higher sensitivity can be obtained for refractory elements and those that are difficult to volatilize. Last not least, fast heating often makes possible to separate the analyte signal from the background. It is crucial, however, to select the final temperature as low as possible and control it with a sensor, as overheating might result in loss of sensitivity due to too rapid expansion of the atomic vapor and increased diffusion out of the tube.
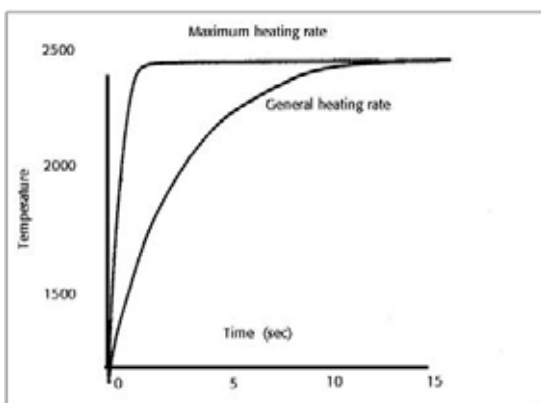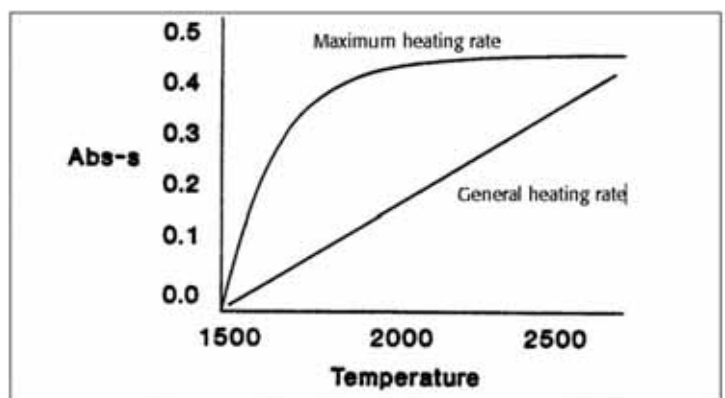

Fig. 4-8: The rapid heating rate

Fig. 4-9: Heating rate and atomization temperature

4.5.4 Gas flow during atomization

The internal purge gas flow through the graphite tube must be interrupted short before and during atomization. This avoids that the cold gas interferes with the thermal equilibrium in the graphite tube and guarantees the longest possible residence time of analyte atoms in the absorption volume. There is no risk of analyte or matrix condensation at cool parts if transversely heated tubes are used. The loss of analyte atoms in this case is only through diffusion.

4.5.5 Peak area evaluation

It is strongly recommended to use peak area (integrated absorbance) for signal evaluation and not peak height, as the optimum atomization temperature is frequently lower with the former one. The most important advantage of peak area evaluation, however, is that vaporization interferences are eliminated efficiently this way, as the peak shape is no longer of importance.

In the case of peak height evaluation we only obtain the absorbance that has been measured at the moment of greatest atom density. In the case of peak area integration all atoms are measured that are generated over time.
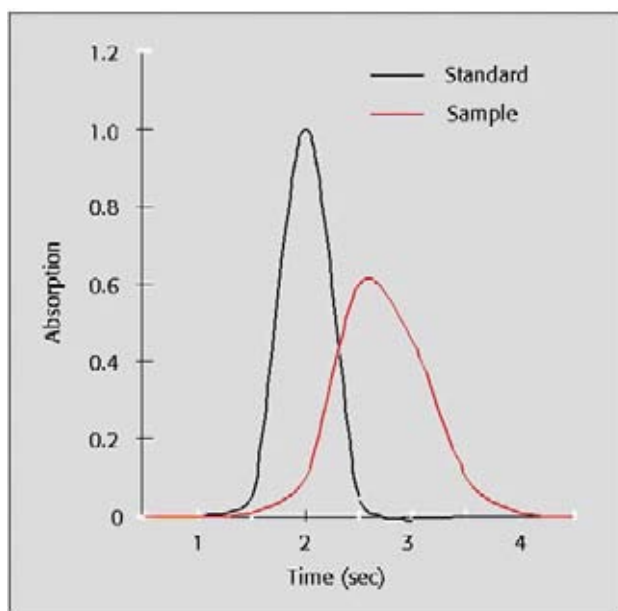
Fig. 4-10: Peak area evaluation

Peak area evaluation should be the method of choice in GF AAS, as it is known that the matrix can influence the atomization behavior of the analyte and hence the shape of the signal. Additional advantages of peak area evaluation are:
- Better repeatability and reproducibility
- Better linearity of the calibration graph
- Lower atomization temperatures, particularly for the more volatile elements.

4.5.6 Chemical modification

A temperature program should be optimized in a way that volatile matrix components are separated from the analyte in the pyrolysis stage. The analyte should be volatilized in the atomization stage only, and never during pyrolysis.

It has been recognized by Ediger as early as 1974 that the behavior of analyte and concomitants can be better controlled by chemical additives (modifiers). The task of a chemical modifier is to

stabilize the analyte thermally in the pyrolysis stage and/or to make concomitants more volatile to facilitate separation of the matrix from the analyte. In the work of Ediger, ammonium nitrate was proposed to remove sodium chloride from saline matrices by the formation of easily volatilized compounds:

$$NaCl + NH_4NO_3 \longrightarrow NaNO_3 + NH_4Cl$$
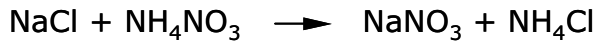
Volatility of the involved compounds

NaCl: boiling point...........1413 ºC
NaNO$_3$: decomposition…..380 ºC
NH$_4$Cl: sublimation……….335 ºC

The choice of the modifier should be made in the course of method optimization. It is important that the analyte has to be stabilized in the samples as well as in the calibration solutions.
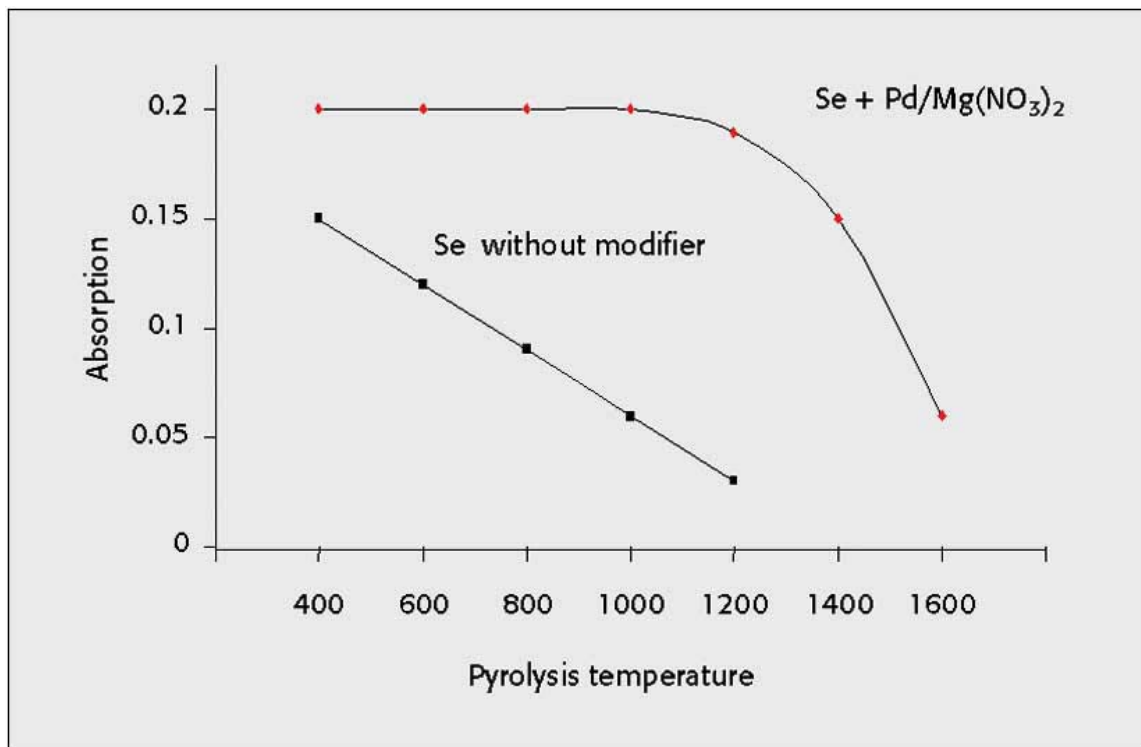

Fig. 4-11: Use of a mixture of Pd and Mg as modifier

The volatility of most elements can be controlled with a few commercially available modifier solutions; among these are:
▪ Pd/Mg modifier
▪ Mg(NO$_3$)$_2$ modifier
▪ NH$_4$H$_2$PO$_4$ modifier
▪ NH$_4$NO$_3$ modifier

4.6 Characteristics of atomization signals

The atomization signals that appear on the screen of the PC allow important conclusions to be made during method development. Under optimum conditions the atomization peaks should be relatively symmetric; irregular peaks indicate problems that might result in erroneous results. Irregularities might have the following reasons:

4.6.1 Excessively broad peaks

Relatively broad peaks are typical for elements that tend to form stable carbides (Ti, V, Mo). Pyrolytically coated tubes are mandatory for this kind of elements; they also require the maximum heating rate for atomization.

Excessively broad peaks might also be due to a too low atomization temperature, an insufficient protective (external) gas flow, or to uncorrected non-specific absorption.

4.6.2 Peaks during blank measurement

If an atomization signal appears during a furnace blank measurement (without injecting a solution), this might be due to a memory effect caused by an insufficient cleaning temperature or time of the previous measurement. If the problem cannot be solved by changing the temperature program, it might be necessary to exchange the graphite tube, and maybe other contaminated graphite parts.

4.6.3 Multiple peaks

Multiple peaks might originate from the analyte, the matrix or from memory effects caused by the previous measurement. Splashing of the sample solution during drying or pyrolysis may also result in multiple peaks, as part of the analyte might be atomized from the platform and other part from the tube wall.

Multiple peaks might also be due to insufficient or erroneous background correction. It is a clear indication that background absorption cannot be corrected properly by the system used for correction if the baseline goes below zero absorbance (overcorrection). Among the measures that can be taken are changes in the temperature program and of the modifier. In case this does not help, it might be necessary to separate the analyte from the matrix by extraction etc.

Multiple peaks may also result from the analyte itself. In this case the reason might be due to the fact that the analyte is present in more than one compound, such as an inorganic salt and an organic compound. For some elements, such as aluminum and silicon, the double peak can be explained with the atomization mechanism (double atomization). In most of these cases the addition of a chemical modifier that converts the analyte into a defined compound can solve the problem.

5 Hydride and cold vapor techniques

5.1 Principle

A number of elements, particularly antimony, arsenic, bismuth, germanium, selenium, tellurium and tin, are forming gaseous hydrides in acid solution upon the addition of sodium tetrahydroborate, $NaBH_4$ (e.g. AsH_3 or SeH_2). These hydrides can be purged from solution using an inert gas (usually argon) and transported to a heated quartz tube, where they are atomized. The tube may be heated electrically or by a flame. The advantage of the electrical heating is the lower running cost and the better temperature control. The relatively simple hydride generation technique makes possible detection limits that are comparable to or better than those of GF AAS.
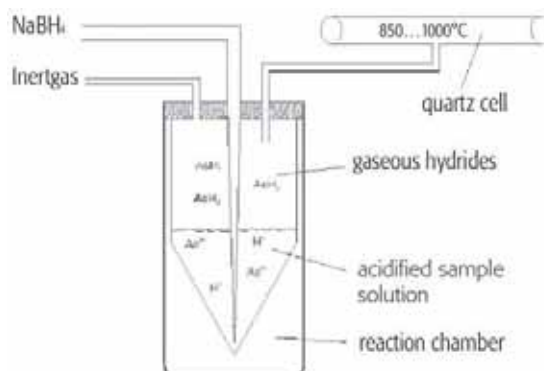

Fig. 5-1: Principle of the hydride generation technique   Fig. 5-2: Hydride forming elements

The atomization of hydrides at temperatures of 800°C-1000°C is a complex procedure that involves hydrogen radicals, which will not be discussed in detail here. This reaction is not only dependent on temperature, but also on the quartz tube surface. The quartz tube therefore has to be made of high-quality silica.

The special advantage of the hydride generation technique is its very high sensitivity combined with an efficient separation of the analyte from the matrix. In addition this technique offers the possibility of a separate determination of the various oxidation states of the analytes (speciation analysis), as they are showing significantly different reactivity.

Spectral interferences are very unlikely with this technique as only a few elements are volatilized under the conditions used here. Gas phase interferences are unlikely as well, except when other hydride-forming elements are present in the sample at high concentration. The only interference that can cause major problems is the hindrance of hydride generation and liberation from solution caused by some transition metals, such as precious metals, copper and nickel.

Mercury is reduced to the metal under the conditions used for hydride generation, and can be purged directly with an inert gas from solution as atomic vapor and measured in an unheated absorption cell by AAS. This procedure, called Cold Vapor Technique results in the best detection limits for mercury. When sodium borohydride is used as the reducing agent, the interferences are similar to those mentioned for the hydride-forming elements. Most of these interferences disappear when stannous chloride is used as the reducing agent.

For both, hydride-generation and cold vapor AAS it is important that no water vapor enters the quartz cell, as it could influence the determination.

5.2   Batch systems and flow systems

5.2.1   Batch systems

In a batch system the solution for measurement is placed into a beaker, the air is flushed out with an inert gas (argon) and the reductant is added through a valve. The gaseous analyte species is stripped from the solution and transported to a quartz tube atomizer by the inert gas. With this system a transient signal is generated, the shape of which depends largely on the liberation of the gaseous analyte from the solution. The signal is proportional to the analyte mass (not its concentration) in the solution for measurement. The volume of the solution, however has some influence on the signal and should therefore be kept constant within a measurement series.

Most reaction flasks of batch systems are designed to accept a relatively large sample volume (1-30 mL), which results in high relative sensitivity (in concentration). The biggest disadvantage of batch systems is that they are manual systems, i.e. the solutions for measurement have to be introduced into the reaction flask by the operator and the system started manually. Depending on the number of samples this might be a significant amount of work.
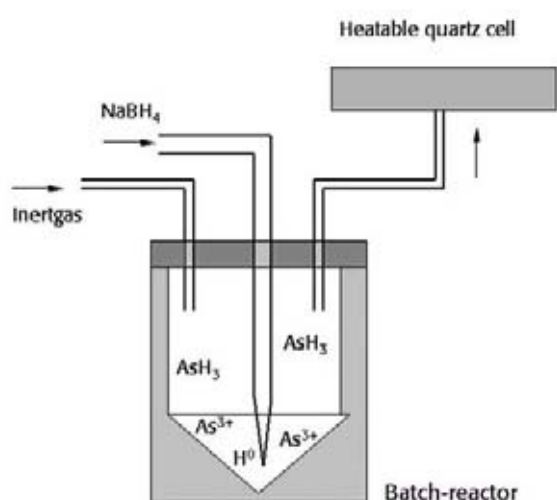
Fig. 5-3: Batch system
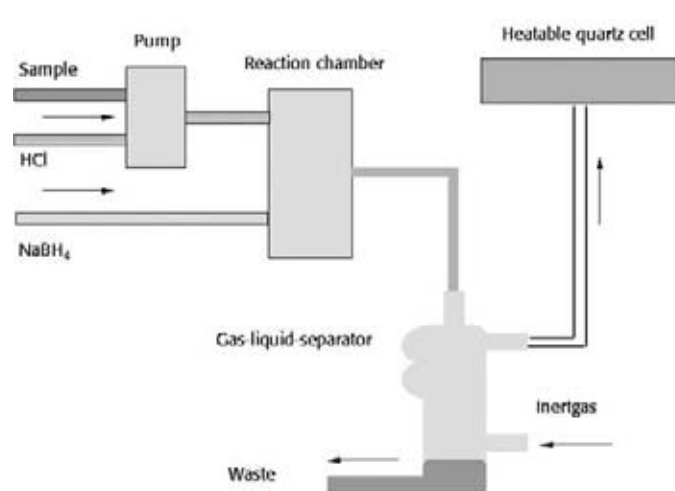
Fig. 5-4: Flow system

5.2.2   Flow systems

The great advantage of flow systems is the easy automation. The addition of the solution for measurement, the transport of reagents and the separation of the gaseous hydride can all be managed automatically.

In detail, the solution for measurement (sample or calibration solution), the reductant (usually $NaBH_4$) and the acid (HCl) are transported continuously in tubes by a peristaltic pump and mixed in a reaction tube. After their passage through the reactor the phases are separated in a gas-liquid separator; the gaseous hydride is transferred to the heated quartz tube by an inert gas flow and atomized. In this system continuous signals are generated that are proportional to the analyte concentration.

It is characteristic for flow systems that sensitivity increases with decreasing flow rate, i.e. increasing reaction time.

5.3 Influence of the analyte species in hydride generation

5.3.1 Oxidation state

Besides the design of the system the oxidation state of the analyte can play an important role in the formation and liberation of the hydride.

Selenium and tellurium in their hexavalent state do not form a hydride, and hence no detectable signal. For both elements a reduction to their tetravalent oxidation state is mandatory.

Arsenic and antimony in their pentavalent state produce a signal that might be 10-90% less sensitive than that of the trivalent state, depending on the system used (batch, flow, length of reaction tube) and on acid and reductant concentration. A reduction to the trivalent oxidation state is therefore highly recommended for these elements. Bismuth is usually present in its trivalent oxidation state, so that pre-reduction is not necessary for this element.

Tin requires very careful control of the pH and is best determined in saturated boric acid solution.

5.3.2 Sample pre-treatment

The significantly different behavior of the individual oxidation states requires a special pre-treatment for each analyte in order to determine its total concentration.

The necessary steps are summarized in the following Table:

Pre-reduction			Reducing agent
As (V)	$\longrightarrow$	As (III)	KI + Ascorbic acid
Sb (V)	$\longrightarrow$	Sb (III)	KI + Ascorbic acid
Se (VI)	$\longrightarrow$	Se (IV)	7 M HCl + 90°C
Te (VI)	$\longrightarrow$	Te (IV)	7 M HCl + 100°C

Arsenic and antimony require the same pretreatment with KI (5%) and ascorbic acid (5%) and can hence be determined from the same solution. Selenium and tellurium may also be determined from the same solution, considering the acid concentration and the heating time (30 min) to near boiling.

5.4 Cold vapor technique

The cold vapor technique is particularly suited for the determination of mercury, as this element can be reduced easily to the metal and does not require any atomization unit. In contrast to inorganic compounds, organic mercury compounds are problematic as they cannot be reduced to the element by sodium tetrahydroborate, and particularly not by stannous chloride. An acid digestion is therefore mandatory in this case prior to the actual determination. All this preparation has to be carried out with utmost care in order to avoid contamination, analyte loss, and to ensure complete digestion.

5.4.1   Digestion procedures

Some of the most common digestion procedures are summarized in the following Table. The choice of the method depends on the type of sample, the organic load and the reductant.

	DIN EN 1483	DIN EN 13506	US EPA 1631
Digestion solution	$KMnO_4$ + $K_2S_2O_8$ + H_2SO_4 + hydroxylamine hydrochloride	KBr + $KBrO_3$ + ascorbic acid (hydroxylamine hydrochloride)	KBr + $KBrO_3$ + hydroxylamine hydrochloride
Advantage	In case of high organic load; sulfides	No free halogens; in case of high organic load	Few reagents
Disadvantage	Laborious; high reagent consumption; stabilization of samples	High reagent consumption; high HCl concentration	Free halogens
Remarks	Alternative: ultrasonic bath may be used	Reduced HCl concentration in the presence of hydroxylamine hydrochloride	

5.4.2   Reductant

Two reducing agents became established for the determination of mercury. In addition to sodium tetrahydroborate, which is also used for the hydride-forming elements, stannous chloride ($SnCl_2$) is used as well, as it might offer better sensitivity and is less prone to foam formation. It has to be noted, however, that an interchange between the two reagents is not possible in the same apparatus.

Advantages and disadvantages:

	$SnCl_2$	$NaBH_4$
Sensitivity	+	-
Reduction capability for organic Hg-species	-	+
Low foam-generation	+	-
Low interferences caused by heavy metal ions	+	-
Low interferences caused by hydride forming ions	+	-
Costs	-	+
Handling	+	-

5.4.3   Analyte stabilization

Mercury may be stabilized using:
- Potassium dichromate $K_2Cr_2O_7$
- Potassium permanganate $KMnO_4$
- Potassium bromide KBr / potassium bromate $KBrO_3$

6 The HydrEA technique

6.1 Principle of the HydrEA technique

The HydrEA technique is the coupling of Hydride generation with Electrothermal Atomization. The hydrides are generated in a conventional hydride generation system. But instead of transporting the hydrides into a heated quartz tube for atomization, they are transferred with an inert gas flow into an iridium coated graphite tube, where they are collected. An element-specific temperature program is used for atomization, which can be optimized for minimum inter-element interferences.
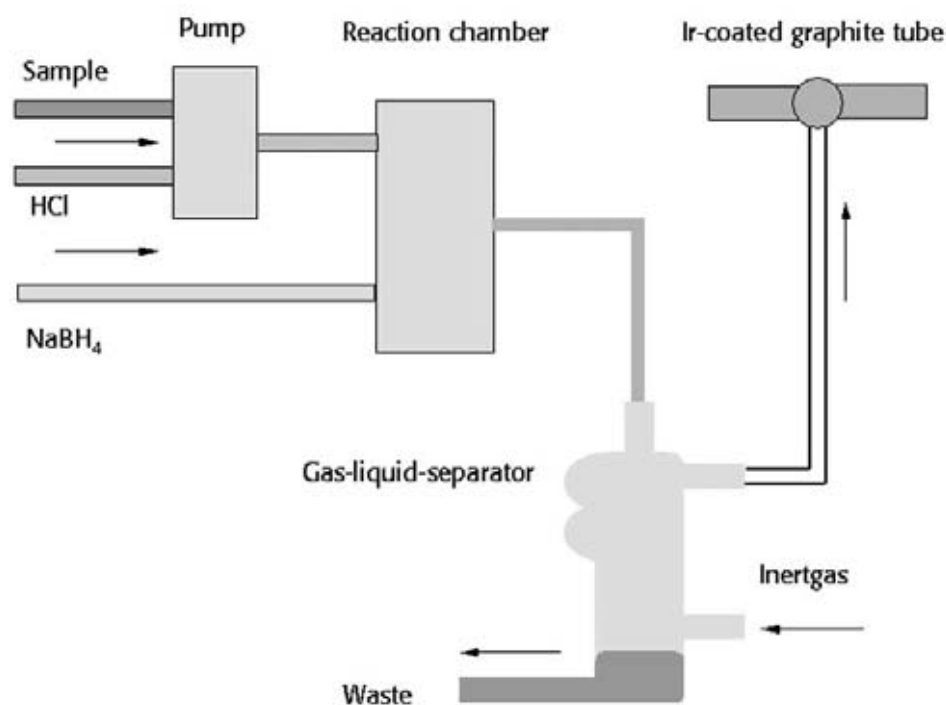

Fig. 6-1: Continuous HydrEA system

After the atomization the graphite tube and the iridium coating are cleaned in an additional heating step with the purge gas on, so that there is no risk for any carry-over. Care has to be taken only that this cleaning temperature does not exceed the volatilization temperature of iridium. The life time of iridium coated tubes is similar to that of pyrolytically coated graphite tubes.
The HydrEA technique can be used in continuous flow or in batch mode.

6.2 Advantages of the HydrEA technique

The main advantage of the HydrEA technique is the improved detection limits, which open new fields of application compared to the conventional hydride technique (e.g. drinking water analysis). In addition it is possible to separate the analyte from the matrix, as only few elements are forming volatile hydrides.
With its improved sensitivity and high precision the HydrEA technique offers an alternative to ICP-MS, which will be discussed in the next chapter.

7 Alternate techniques

7.1 *Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES)*

In optical emission spectrometry with inductively coupled plasma, in contrast to AAS, not only the atomic lines, but particularly ion lines play an important role. The technique is based on the use of very hot argon plasma (~6000-12000 K) to excite the analyte for optical emission. The temperature that can be reached depends on the power of the high-frequency generator.

7.1.1 Principle

Plasma is an ionized gas that in addition to atoms also contains electrons and ions. After ignition with a Tesla spark the energy transfer is via the high frequency field in the coil that is surrounding the plasma. Free electrons are accelerated and heat the plasma by collision with argon atoms. We distinguish between ionization, electron and excitation temperature, which are different at different locations of the plasma. The sample aerosol is introduced through the center of the plasma flow without affecting its stability and equilibrium.
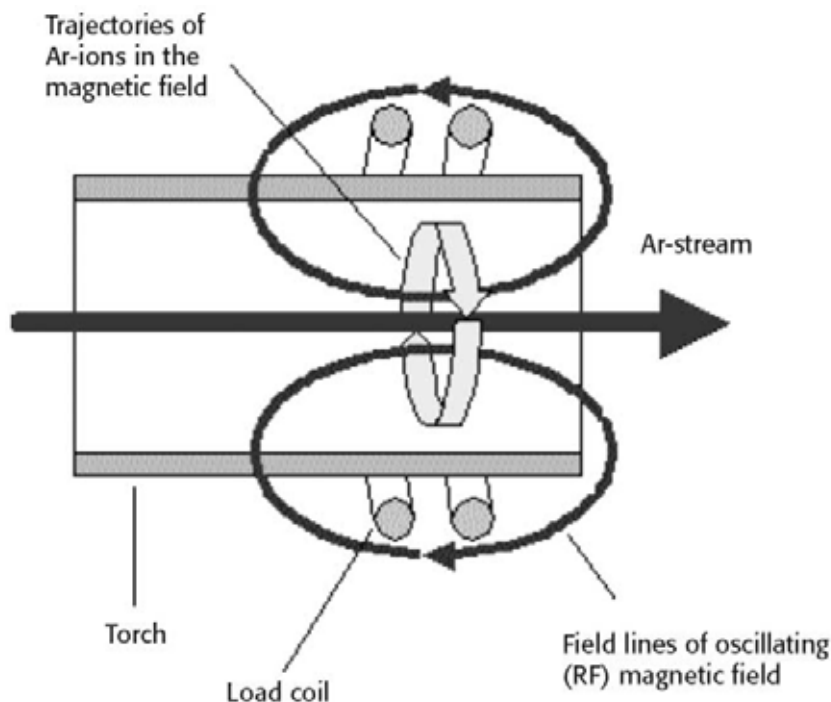

Fig. 7-1: Principle of ICP

In the plasma the atoms and particularly the ions are excited to emission. After spectral dispersion of the emitted radiation in a powerful optical system the element-specific wavelengths are used for identification and quantification.

7.1.2 Design

The most important components of an ICP spectrometer are the high-frequency generator, the plasma torch, the nebulizer and the spectrometer itself, which can be a monochromator (sequential spectrometer) or a polychromator (simultaneous spectrometer). An echelle mounting is typically used for the polychromator as much higher resolution is required than in AAS because of the much greater number of lines emitted by a plasma.

Fundamentals , Instrumentation and Techniques of Atomic Absorption Spectrometry   52/ 65

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7.1.3 Interferences in ICP OES

As in AAS we distinguish in ICP OES between spectral and non-spectral interferences. Non-spectral interferences are largely limited to transport interferences, as the vast majority of chemical compounds are completely dissociated at the high plasma temperatures. In order to minimize transport interferences pumps are normally used for sample introduction in ICP OES. The remaining interferences are usually compensated with an internal standard.

In contrast, spectral interferences due to direct line overlap are quite abundant due to the extremely high density of lines in the spectrum emitted by the ICP. To control for spectral interferences it is common practice in ICP OES to measure more than one line of the same analyte and to use least squares algorithms to correct for the interference.

7.2 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

7.2.1 Principle

In contrast to the above techniques in ICP-MS we do not observe radiation that is emitted or absorbed by atoms, but we measure the impact of ions on a detector, depending on their mass.
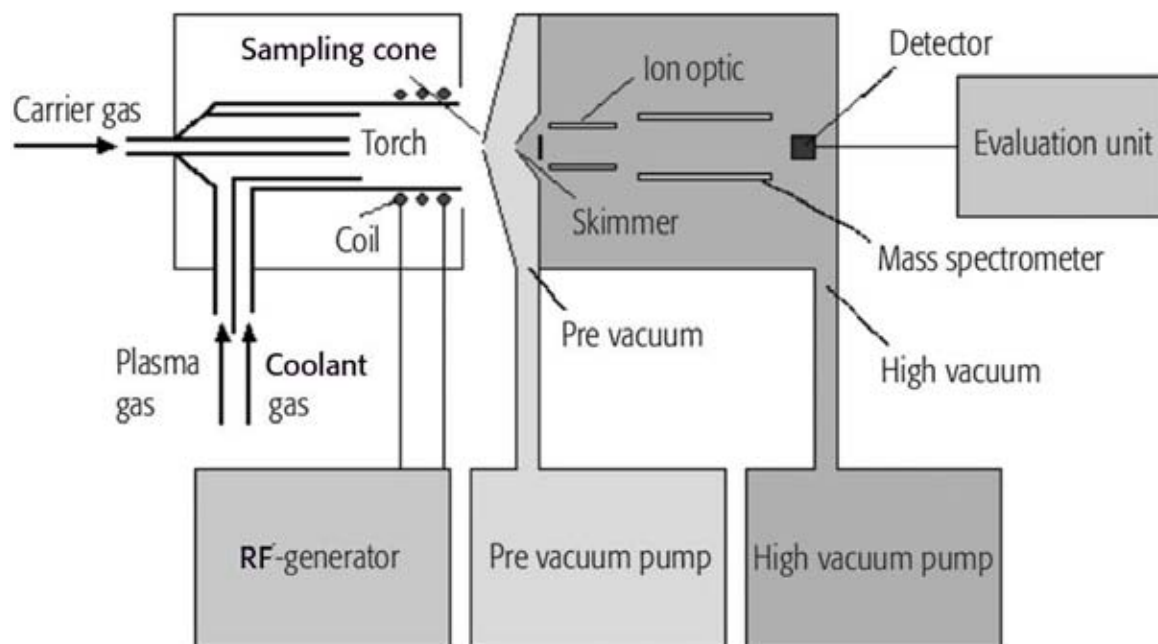

Fig. 7-2: Principle of ICP-MS

The ions generated in the plasma are extracted into high vacuum, focused in an electrical ion lens system and separated according to their mass/charge ratio in a quadrupole. The ions impact on a detector that records the number of ions per mass. This makes quantification of elements possible including isotope determination.

Advantages of ICP-MS compared to AAS:
- Fast sequential multi-element determination
- Excellent sensitivity

Disadvantages of ICP-MS compared to AAS:
- High purchase price and running cost
- Relatively low tolerance for high matrix concentrations

8 Difficulties of trace analysis

The concentration range of mg/L, as it is typical for flame AAS, is relatively easy to master nowadays. Major systematic errors should not be encountered if the necessary care is taken. The µg/L–range, which is typical for GF AAS, the hydride-generation and the HydrEA technique, in contrast is much more critical. The risk of systematic errors often increases exponentially with decreasing concentration. These errors can lead to low results because of analyte loss during sample preparation as well as high results due to contamination.

It is worth mentioning that systematic errors in AAS are usually made during sample preparation, so that the analytical technique cannot be blamed. For this reason direct procedures should be preferred in ultra trace analysis over those that require major sample preparation.

Volatile elements and those that form volatile compounds may be lost during open-vessel digestion. Fusions and dry ashing procedures are most critical. The best choice is a microwave-assisted pressure digestion in a closed system.

Adsorption of the analyte at container walls etc. is another source of error that can lead to analyte loss as well as contamination of the next sample.

Neutral solutions of many elements are not stable and show a tendency to hydrolysis. Very dilute solutions may be stable only for a short time even when they are acidified. It is not only the pH value that is of importance, but also the container material. A lead solution with 20 µg/L, acidified with HNO_3 for example is stable for several days in a PFA flask, whereas losses are encountered within a few hours when the same solution is stored in a glass container. Glass is in general not suitable for the ultra trace range. Silica and PFA in contrast are well suited to store solutions with very low analyte content.

Systematic errors due to contamination of the analyte with reagents, containers or the surrounding air are particularly frequent in trace analysis.

8.1 Water as a source of contamination

Water that is used in GF AAS for dilution and rinsing should always be deionized (high-purity water, conductance 0.055 µS cm^{-1}). Any contact with metal parts has to be avoided.

Fig. 8-1: Water purification system

The most widespread contamination elements are sodium, calcium, zinc, magnesium, aluminum, silicon and iron. It is obligatory to control the water quality before beginning a measurement. In addition it has to be assured that all materials that come into contact with water are made of inert plastic material (e.g. PFA).

Fundamentals , Instrumentation and Techniques of Atomic Absorption Spectrometry   54/ 65

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8.2 Reagents as a source of contamination

Reagents that are used for solvent extraction, acid digestion, fusion etc. are potential sources of contamination. For this reason reagents should be at least of analytical grade, preferably of higher purity. For many acids subboiling distillation is an economic alternative to purchasing the highest grade of purity. Liquid reagents, such as standards or acids should never be taken directly from the original container, but from an intermediate one-way container. The rest of the liquid should be discarded. For cost reasons only the required quantity should be drawn off. A dispenser can be very useful for this purpose, as only the pre-selected quantity is taken from the container. This helps to save time and money and keeps the risk of contamination low.
Solid reagents should be taken with a clean plastic spatula.

8.3 Laboratory equipment as source of contamination

Volumetric flasks, pipettes etc. of glass are sources of contamination for elements such as sodium or silicon. These two elements require special care for their determination. Pipettes with one-way tips have been found particularly useful. To rinse the pipette once with the solution for measurement is usually sufficient to remove potential contamination. The tips should be stored well packed until they are used.
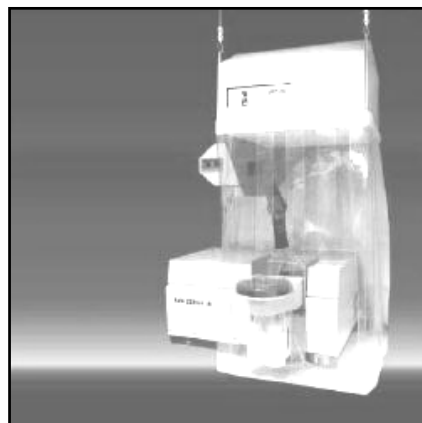

Fig. 8-2: Dispenser

Fig. 8-3: Pipette

Fig. 8-4: Laminar flow box

8.4 Ambient air as source of contamination

Atmospheric contamination by dust can become a major problem in trace element laboratories. Aluminum, iron, magnesium, silicon, sodium and zinc are among the elements frequently found in dust. The degree of contamination may vary with the location (vicinity of a metal-working factory, close to the sea).
Demanding tasks or work with lowest analyte contents might be better carried out in a laminar flow box.

9 Applications

9.1 *Example for flame AAS*

9.1.1 Determination of Na, K, Ca, Mg in pharmaceutical products

Experimental

The measurements were carried out using the novAA® flame atomic absorption spectrometer and the injection switch SFS 6.

Sample preparation

The samples could be measured without sample preparation. They were only diluted with a solution containing 0.2% CsCl and 0.2% $LaCl_3$ in order to bring them into a reasonable working range and prevent ionization of Na and K.

Instrument parameters

Element	Wavelength [nm]	Slit [nm]	Burner angle	Type of flame	Fuel flowrate [NL/h]	Burner height [mm]
Na	589.6	0.2	90°	Air / C_2H_2	65	8
K	769.9	0.2	90°	Air / C_2H_2	65	8
Mg	285.2	1.2	0°	Air / C_2H_2	65	8
Ca	422.7	1.2	0°	C_2H_2 / N_2O	195	6

Calibration

Na   Standard calibration procedure (Emission with 0.2% Cs/La)
Concentration of the standards: 0.022 / 0.044 / 0.065 / 0.087 / 0.131 / 0.218 mmol/L Na
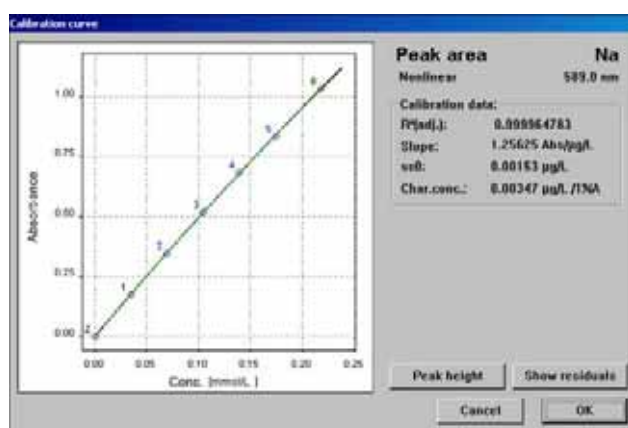6 Measurement cycles; 3 s Integration time, repeating mean

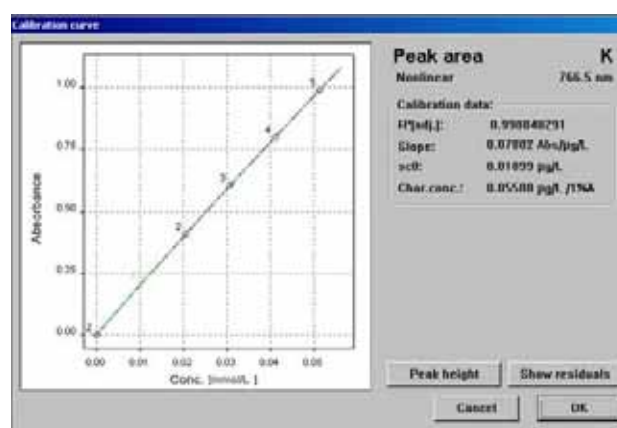*Fig. 9-1:* Calibration for sodium

Fig. 9-2: Calibration for potassium

K   Standard calibration procedure (Emission with 0.2% Cs/La)
Concentration of the standards: 0.0051 / 0.0102/ 0.0153 / 0.0205 / 0.0256 mmol/L K
6 Measurement cycles; 3 s Integration time, repeating mean

Mg   Standard calibration procedure (with 0.2% Cs/La)
Concentration of the standards: 0.0008 / 0.0016/ 0.0033 / 0.0049 / 0.0066 mmol/L Mg
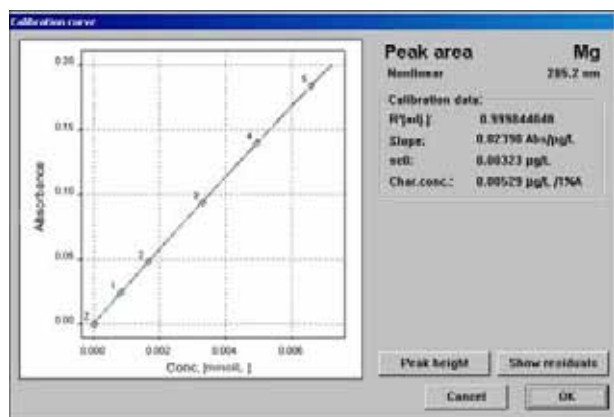6 Measurement cycles; 3 s Integration time, repeating mean
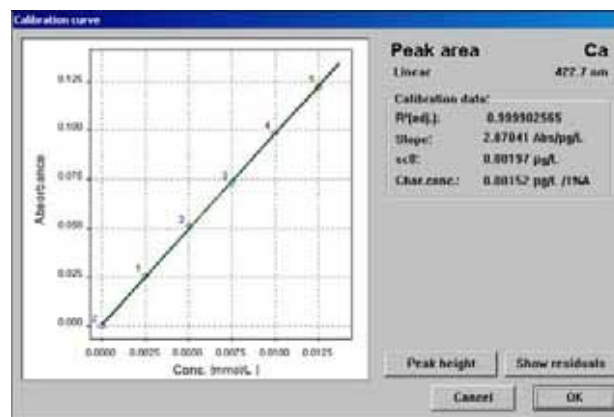

Fig. 9-3: Calibration for magnesium

Fig. 9-4: Calibration for calcium

Ca   Standard calibration procedure (with 0.2 % Cs/La)
Concentration of the standards: 0.0025 / 0.0050/ 0.0075 / 0.0100 / 0.0125 mmol/L Ca
6 Measurement cycles; 3 s Integration time, repeating mean

Results

Element	Sample	DF	Measured concentration [mmol/L]	RSD [%]	Certified concentration [mmol/L]	Recovery [%]
Na	Isoton.KS	1000	154 ± 1	0.6	154	100
	Sample 1 Na 100	1000	100 ± 1	0.1	100	100
	Sample 2	100	5.52 ± 0.04	0.7	< 6.5	-
	QC 0.217	1	0.2179	0.7	0.2175	100
K	Sample 1 Na 100	1000	19.8 ± 0.1	0.4	20	99
	Sample 2	10	0.14 ± 0.01	0.4	< 1.0	-
	QC 0.051	1	0.0511	0.5	0.0511	100
Mg	Sample 1 Na 100	1000	2.48 ± 0.01	0.4	2.5	99
	QC 0.007	1	0.0066	0.4	0.0066	100
Ca	Sample 1 Na 100	500	2.50 ± 0.02	0.8	2.5	100
	QC 0.012	1	0.01239	0.9	0.01247	99

Summary

The determination of Na, K, Mg and Ca in the investigated pharmaceutical products could be carried out without problems in spite of the high total salt concentration owing to the injection switch. The conventional air-acetylene flame was sufficient for Na, K and Mg, whereas the nitrous oxide-acetylene flame had to be used for Ca to compensate for up to 5% low recoveries. The same dilution solution of 0.2% CsCl and 0.2% $LaCl_3$ was used for all elements. No background correction had to be used. This application can be readily transferred to the daily routine using the integrated re-calibration function.

9.2 Example for graphite furnace AAS

9.2.1 Determination of Mn, Cr and Ni in plasma and urine samples

Experimental

The measurements were carried out using the AAS ZEEnit and the graphite furnace autosampler MPE 60z. The samples were measured directly after dilution with a mixture of HNO_3/Triton X 100.

Instrumental parameters

Element	Wavelength [nm]	Slit [nm]	Lamp current [mA]	Magnetic field strength [T]
Mn	279.5	0.2	6.5	0.8
Cr	357.9	0.5	4.0	0.8
Ni	232.0	0.2	5.0	0.8

Element	Graphite tube	T_{Pyr} [°C]	T_{Atom} [°C]	Ramp [°C/s]	Modifier
Mn	PIN-Platform	600/ 900	2300	1200	-
Cr	PIN-Platform	600/ 1100	2350	1200	5 µL $Mg(NO_3)_2$
Ni	PIN-Platform	600/ 1250	2400	1200	5 µL Pd

Several drying stages have been integrated in the temperature program (85 °C / 95 °C / 104 °C / 120 °C) in order to remove safely the various solvents and to transfer the sample without losses into the pyrolysis stage. In addition an oxygen ashing stage at 600 ºC was introduced to avoid carbon residues in the tube and hence increase its life time.

Calibration

Mn   Analyte addition technique
Concentration of the standards 0/ 3.0/ 6.0/ 8.0/ 10.0 µg/L Mn in 0.6% HNO_3 / Triton X 100
10 µL sample / max. 10 µL standard
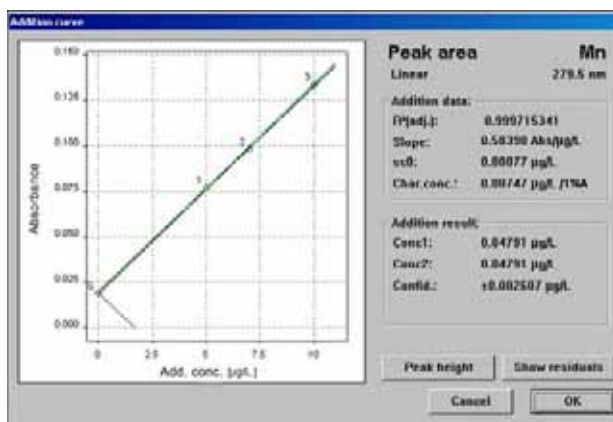2 Measurement cycles per statistic; peak area integration
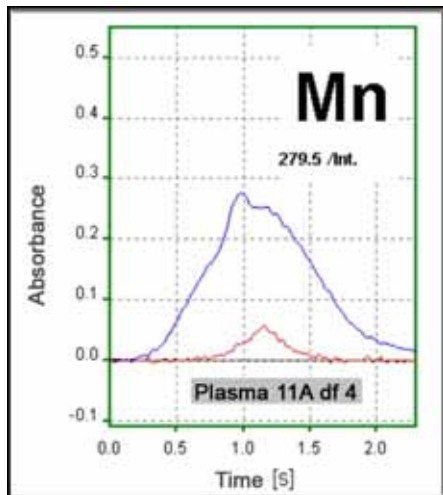

Fig. 9-5: Analyte addition for manganese
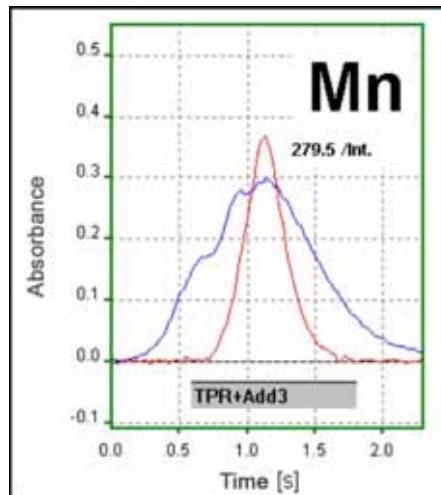
Fig. 9-6: Signal shape for test sample

Fig. 9-7: Signal shape for test sample + standard

Cr   *Plasma* – analyte addition technique
Concentration of standards 0/ 2.225/ 4.45/ 6.675/ 8.90 µg/L Cr in 0.6% HNO$_3$ / Triton X 100
12 µL sample / max. 12 µL standard
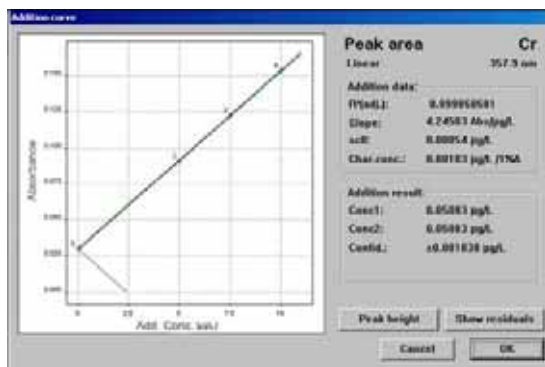2 measurement cycles per statistic; peak area integration
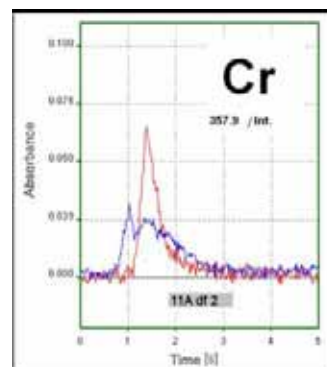

Fig. 9-8: Analyte addition for chromium

Fig. 9-9: Signal shape for chromium

Urine – standard calibration procedure
Concentration of standards 0/ 2.0/ 4.0/ 6.0/ 8.0/ 10.0 µg/L Cr in 0.6% HNO$_3$ / Triton X 100
20 µL Injection volume
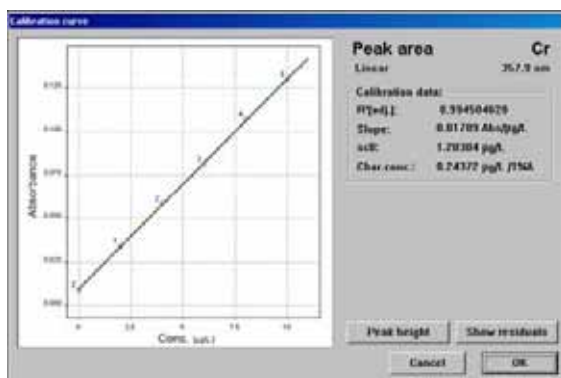2 measurement cycles per statistic; peak area integration

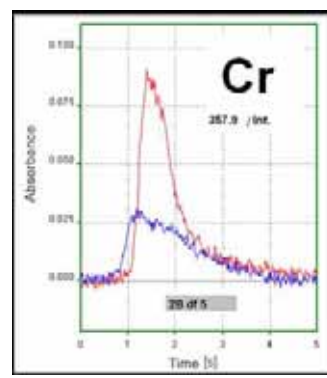Fig. 9-10: Standard calibration procedure for chromium

Fig. 9-11: Signal shape for chromium

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Ni   *Plasma* – analyte addition technique
Concentration of standards 0/ 6.67/ 13.33/ 20.00/ 26.67 µg/L Ni in 0.6% HNO_3 / Triton X 100
12 µL sample / max. 16 µL standard
2 measurement cycles per statistic; peak area integration

Fig. 9-12: Analyte addition for nickel
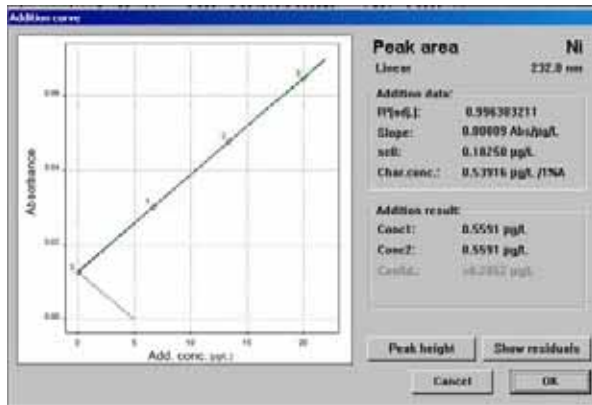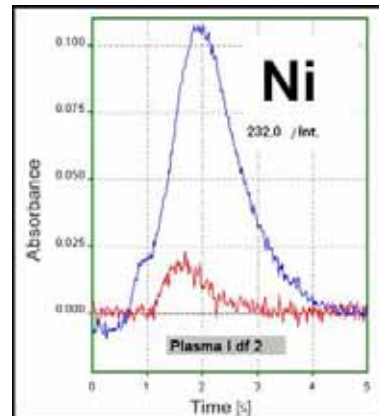

Fig. 9-13: Signal shape for nickel

Urine – standard calibration procedure
Concentration of standards 0/ 4.0/ 8.0/ 12.0/ 16.0/ 20.0 µg/L Ni in 0.6% HNO_3 / Triton X 100
20 µL Injection volume
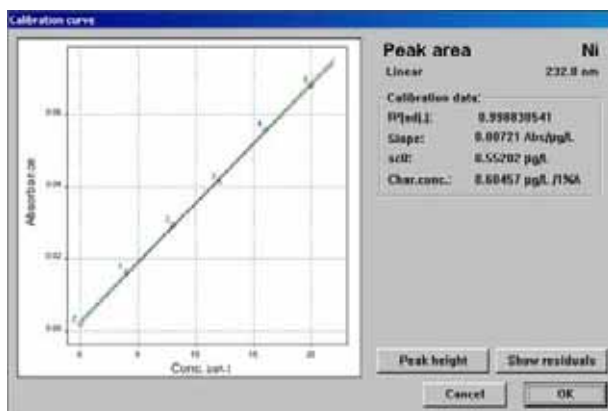2 measurement cycles per statistic; peak area integration

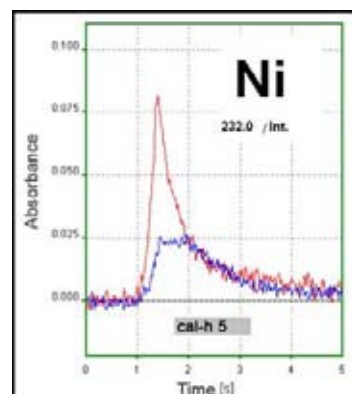*Fig. 9-14:* Standard calibration procedure for nickel

Fig. 9-15: Signal shape for nickel

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Results

Element	Sample	DF	Measured concentration [µg/L]	Certified concentration [µg/L]	RSD [%]
Mn	Control Plasma A	4	5.82 ± 0.53	5.5 (4.0 - 7.0)	-
	Control Plasma B	4	16.3 ± 0.1	16.0 (12.2 –19.8)	-
	Plasma 11A	4	6.79 ± 0.33		-
	Plasma 11B	4	13.7 ± 0.4 13.3 ± 0.6 (Add. Cal.)		2.8
	Urine 2A	2	3.18 ± 0.22 3.34 ± 0.80 (Add. Cal.)		3.0
	Urine 2B	2	5.73 ± 0.20		2.5
Cr	Control Plasma	8	17.1 ± 0.5	15.1 (11.4 – 18.8)	
	Plasma 11A	2	4.15 ± 0.14		1.1
	Plasma 11B	8	16.4 ± 0.5		0.9
	Control Urine	4	20.5 ± 0.2	20.2 (16.1 – 24.2)	0.1
	Urine 8A	2	0.54 ± 0.15		-
	Urine 8B	2	2.49 ± 0.14		6.8
	Urine 2A	2	15.9 ± 0.1		1.9
	Urine 2B	5	31.0 ± 0.3		1.7
Ni	Control Plasma	2	9.88 ± 0.20	8.0 (6.0 – 10.0)	
	Plasma 11A	2	6.30 ± 0.21		7.3
	Plasma 11B	2	17.5 ± 0.17		1.5
	Control Urine	2	20.8 ± 0.4	22.5 (18.0 – 27.0)	2.7
	Urine 8A	2	3.00 ± 0.48		15
	Urine 8B	2	4.38 ± 0.46		12
	Urine 2A	2	5.79 ± 0.45		11
	Urine 2B	2	37.2 ± 0.5 37.8 ± 0.3*		1.9

Summary

The determination of Mn, Cr and Ni in plasma and urine could be carried out without problems using GF AAS with Zeeman-effect background correction, which could remove any non-specific absorption caused by matrix components.

The results were in part double checked using the analyte addition technique or addition calibration. It was found that the standard calibration procedure could be used particularly for urine samples so that it was possible to do without the time consuming analyte addition technique. Utmost care has to be taken and only specially cleaned tools must be used for heavy metal determination at the lowest trace level.

9.3 Example for cold vapor AAS

9.3.1 Determination of Hg in the eluate of a textile sample

Experimental

Extraction solution:

- Synthetic sweat solution:
  0.5 g/L L-histidine monohydrochloride-1-hydrate
  5.0 g/L sodium chloride
  2.2 g/L sodium dihydrogen phosphate-2-hydrate
  Adjust solution to pH 5.5 with 0.1 mol/L NaOH

Sample preparation

- Weigh 5g of sample into an Erlenmeyer flask
- Add 100 mL of extraction solution (synthetic sweat solution)
- Extract for 1h at 40 °C in a water bath
- After cooling the sample is filtered and acidified with 1 mL HNO_3
- Ultrasound-assisted digestion of the organic matrix according to DIN EN 1483

Digestion procedure according to DIN EN 1483

- Transfer 20 mL of the sample into digestion flask
- Add carefully 200-400 µL of potassium permanganate solution (50 g/L; in H_2O); the solution must have rosy color after digestion; otherwise more permanganate solution has to be added
- Add 200 µL HNO_3 (65%)
- Add 200 µL H_2SO_4 (96%)
- Add 400 µL potassium peroxo disulfate (40 g/L; in H_2O)
- Tightly close the digestion flask and shake well
- Treat samples for 30 min at 50°C in ultrasonic bath (**Attention**: The solution must still show red/rosy color; more permanganate has to be added and the digestion continued if this is not the case)
- Short before the measurement add 40-100 µL hydroxyl ammonium chloride (120 g/L; in H_2O) until the solution is clear.

Determination

After the above-described pre-treatment samples are measured with the hydride system.

Instrumental parameters

Reducing agent:	0.3 % (m/V) $NaBH_4$ / 0.1 % (m/V) NaOH
	(Dissolve 7.5 g $NaBH_4$ and 2.5 g NaOH in water and complete to 250 mL. This solution is stable for 3 weeks at 4 ºC. Dilute the solution before measurement)
Carrier solution:	3 % HCl
	(Dilute 70 mL concentrated, Hg-free hydrochloric acid to 1000 mL with water)
Rinsing solution:	HCl/ HNO_3
	(Add 20 mL of concentrated HCl, Hg-free, and 20 mL concentrated HNO_3, Hg-free, to 2 L of distilled deionized water)

Instrumental parameters

Mode of operation:	continuous, without pre-concentration, FBR procedure		
Statistic:	1 Blank, 3 Measurement cycles		
Integration:	Peak area	Integration time:	25 s
Load time:	14 s	Gas flow (loading):	6 NL/h
Reaction time:	10 s	AZ waiting time:	10 s
Rinse time 1:	10 s	Rinse time 2:	6 s
Gas flow (Rinse 2):	31 NL/h	Rinse:	10 s after each sample

Calibration

Hg   Standard calibration procedure
Linear calibration curve
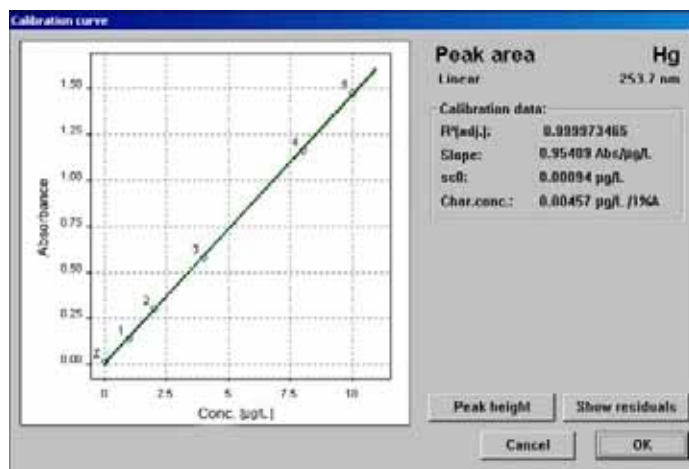Concentration of the calibration standards 1/ 2/ 4/ 8/ 10 µg/L Hg

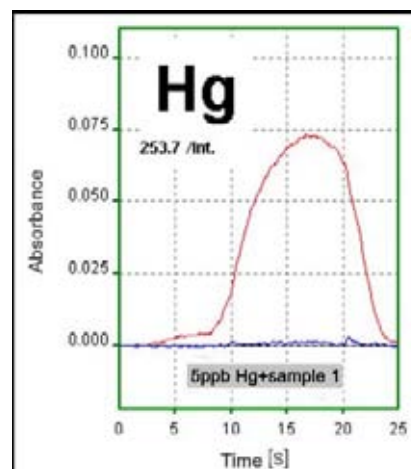*Fig. 8-16:* Standard calibration procedure Hg

Fig. 8-17: Signal shape addition of Hg

Results

Element	Sample	DF	Concentration	RSD [%]	Recovery [%]
Hg	Wool	1	<limit		
	Wool + 5ppb Hg	1	5.01 ± 0.05 µg/L	0.8	100.3
	QC Std 10ppb Hg	1	9.93 ± 0.07 µg/L	0.2	99.3

Summary

Mercury can be determined in samples with high organic load without problems after an appropriate digestion. Complete digestion of the organic matrix is important (rosy color of the sample solution after digestion)
The accuracy of the procedure could be demonstrated by a spiking experiment (100.3 % recovery) and a quality control standard (99.3 % recovery).

9.4 Example for the HydrEA technique

9.4.1 Determination of Se in plant materials

Experimental

The measurements were carried out using an AAS ZEEnit and a hydride system HS 55.

Sample preparation

The samples were already supplied in digested form.

1 g of plant material has been digested with 5 mL HNO_{3conc} and 2 mL H_2O_2 in a microwave oven. The resulting solutions were completed to 50 mL with $H_2O_{tridest}$.

For the determination by hydride-generation selenium has to be present as Se(IV). For the pre-reduction of Se(VI) 12.5 mL of the sample solution were transferred to a 50-mL flask, 25 mL of concentrated HCl were added and completed to volume with $H_2O_{tridest}$ (dilution factor 4). The flasks were heated in a water bath at 90° C for at least 30 min. The solution was measured after cooling to room temperature.

Instrumental parameters

Element	Wavelength [nm]	Slit [nm]	Lamp current [mA]
Se	196.0	0.8	5.5

Element	Graphite tube	$T_{Pyr.}$ [°C]	$T_{Atom.}$ [°C]	Ramp [°C s^{-1}]
Se	Standard tube Ir coated	300	2100	1300

Hydride generation parameters

Mode of operation	Batch	**Purge time**	10 s
Sample volume	10 mL	**Pump time**	10 s
Pump speed	5	**Reaction time**	20 s
Enrichment cycles	1	**Purge time**	10 s
Gas flow	6 NL/h	**Reduction medium**	3% NaBH$_4$ in 1% NaOH

Calibration

Se Standard calibration procedure
Concentration of standards: 0.05/ 0.1/ 0.25/ 0.5/ 1.0 µg/L Se
The standards were prepared in the same way as the samples
(12.5 mL of an acid mixture of 5 mL HNO_3 / 2 mL H_2O_2 add 25 mL of concentrated HCl; dilute to 50 mL with water; keep at 90° C for 30 min)
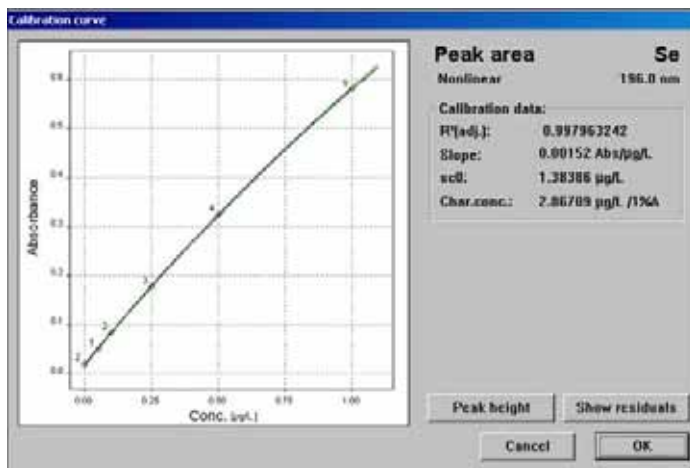Peak area integration; non-linear calibration; 3 Measurement cycles.
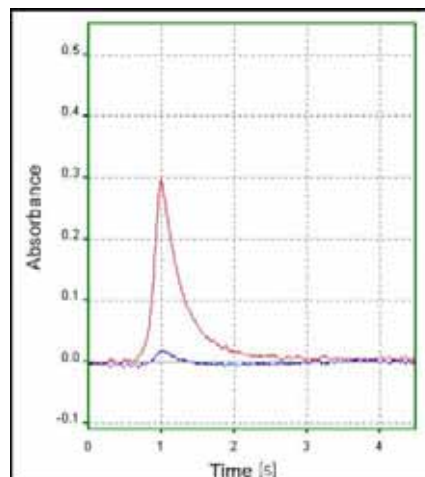
Fig. 8-18: Standard calibration procedure for Se

Fig. 8-19: Signal shape for sample

Results

Sample	Description	Concentration [µg/kg]	RSD [%]	Interlaboratory comparison [µg/kg]
7d	dandelion	30.3 ± 0.8	4.3	30.6
8	grass	38.8 ± 0.8	0.9	48.9
10	lucerne	99.1 ± 1.1	0.6	120
27	dandelion	30.4 ± 0.8	2.8	30.6
28	grass	39.5 ± 0.8	1.4	48.9
30	lucerne	95.1 ± 1.1	2.5	120
1	Hay sample	23.6 ± 0.8	4.4	
4	Hay sample	9.84 ± 0.9	2.5	
7h	Hay sample	10.3 ± 0.9	3.8	

Summary

The standards have been prepared in the same way as the samples in order to take into consideration potential interferences on hydride generation due to the high HNO_3 concentrations. Low recoveries might also result from an insufficient microwave digestion of organic selenium compounds and/or an incomplete pre-reduction of Se(VI) to Se(IV). The completeness of the digestion could be checked by an addition of vanadium pentoxide as catalyst. The efficiency of the pre-reduction could be increased by a higher dilution of the digestion solution, which, however, also affects sensitivity. All in all the HydrEA technique is offering an extremely sensitive technique for the determination of selenium traces in plant materials.

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