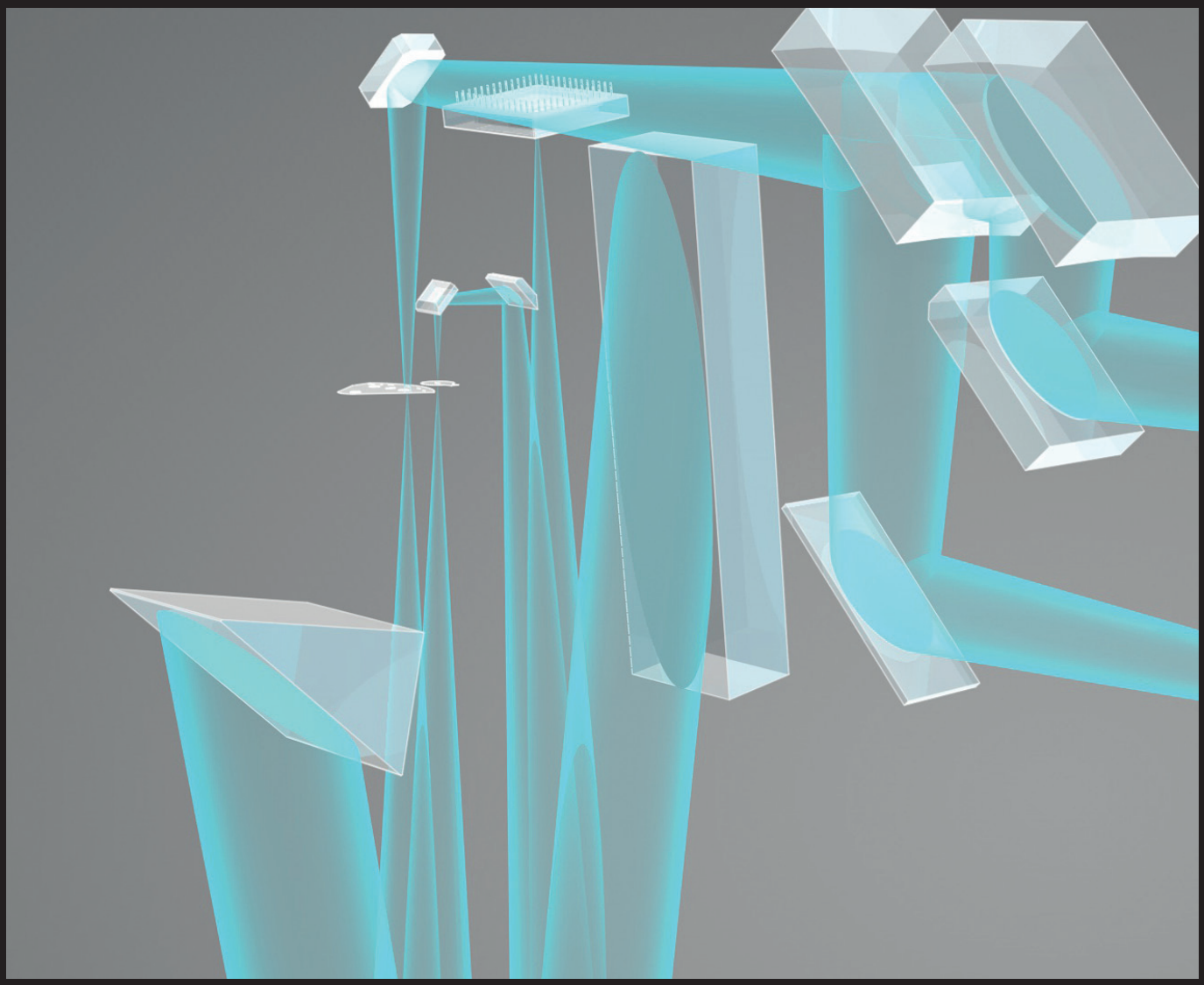
analytikjena

FUNDAMENTALS

Instrumentation and methods of Optical Emission Spectrometry using Inductively Coupled Plasma (ICP-OES)



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1 Fundamentals and definitions

1.1 Structure of the atom

According to Rutherford and Bohr, every atom is composed of a positively charged nucleus and negatively charged electrons circling the nucleus on defined trajectories (orbitals). According to Bohr, an atom can absorb or emit energy only in discrete amounts. If an atom collides with another particle or with a quantum of radiation that has a suitable amount of energy, it can absorb its energy. When this occurs, an electron jumps from its ground state in an outer orbital to a more outward lying, more energetic orbital. This process, referred to as excitation, can be triggered by the supply of thermal, electrical or optical energy (electromagnetic radiation).

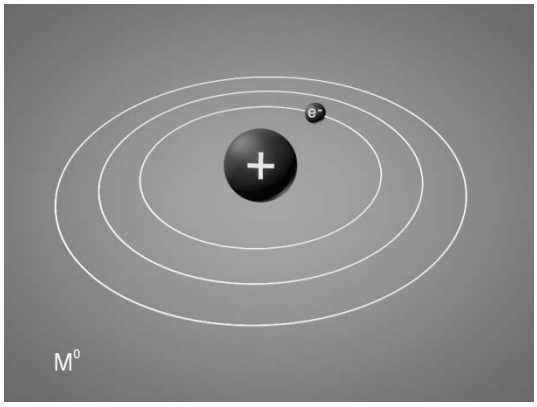


Figure 1-1 Atom in ground state

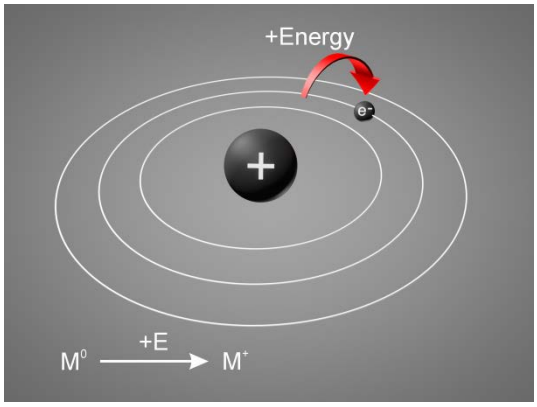


Figure 1-2 Excited atom

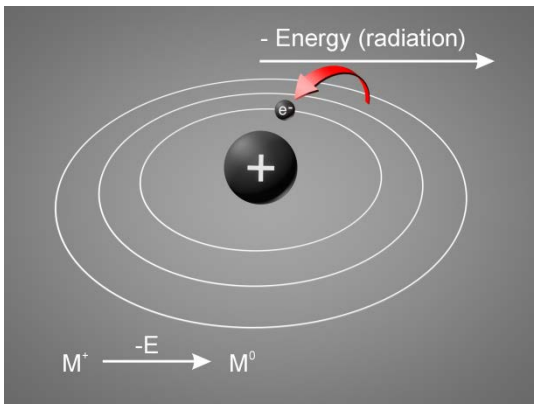


Figure 1-3 Return to ground state

Note: These illustrations only show the nucleus and, as the inner orbital, the ground state. Lower lying, completely filled orbitals are not depicted.

Absorption of photons (or of electromagnetic radiation) forms the basis of **atomic absorption spectrometry**. After a short dwell time in a more energetic orbital, the electron returns to its ground state. The energy difference released by this process is emitted in all spatial directions in the form of electromagnetic radiation (or as a photon). This is the fundamental principle underlying **atomic emission spectrometry**. When the amount of energy added by absorbing electromagnetic radiation is emitted in all spatial directions in the form of electromagnetic radiation, this is referred to as **atomic fluorescence**.

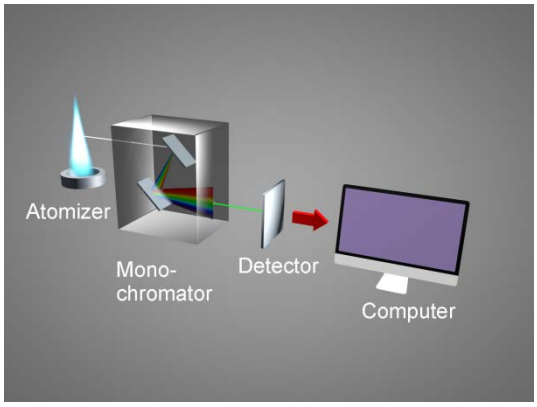


Figure 1-4 Atomic emission

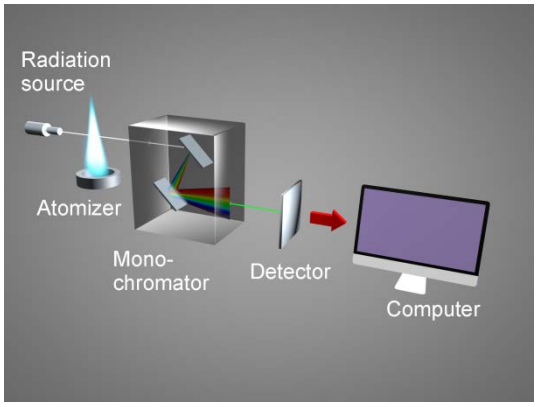


Figure 1-5 Atomic absorption

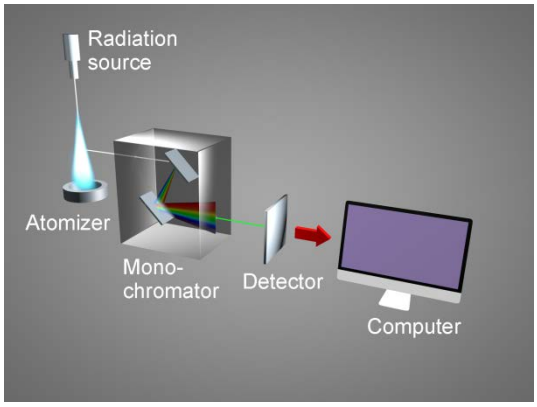
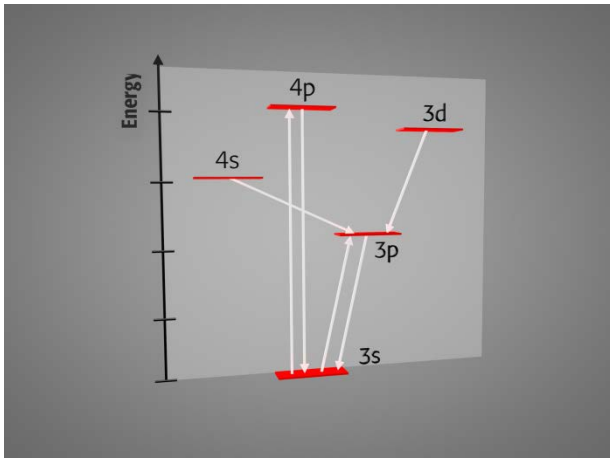


Figure 1-6 Atomic fluorescence

If an amount of energy exceeding the binding energy of an electron is supplied to an atom , the electron is removed from the region of electrical attraction exerted by the nucleus, i.e. it is dissociated from the atom. This process is referred to as **ionization**. The outermost electron of an atom has the least binding energy and therefore is the one that is most easily dissociated.

1.2 Absorption, emission and fluorescence spectrometry

Atomic spectrometry is a branch of spectrometry examining the line spectra resulting from the interaction between electromagnetic radiation and free atoms. Since free atoms are able both to absorb and emit radiation of the same wavelength, atomic spectra can be observed as emission, absorption or fluorescence spectra.



The arrows indicate the transitions that can be performed by electrons. Down means emission of energy (relaxation), up means absorption of energy (excitation).

Figure 1-7 Energetic layout of the electron shells

The energy that was absorbed or emitted can be represented as a line spectrum in the form of absorption or emission profiles, respectively. Since the energy differences between orbitals are different for each element, each element emits a characteristic line spectrum. This can be used for the qualitative detection of elements.

The **energy difference** between two orbitals can be described using the following equation:

$$\Delta E = h * \nu$$

ΔE	energy difference
h	Planck constant
ν	frequency

Since, for historical reasons, ICP emission uses the wavelength rather than the frequency of the light, the equation can be transformed as follows:

$$\Delta E = h * c / \lambda$$

c	velocity of light
λ	wavelength

It follows that the difference in energy is inversely proportional to the wavelength. To put it another way: a relatively small amount of energy is required for the transition of a line in the long wave range (e.g., visible light), whereas a large amount of energy is required for the transition of a line in the short wavelength range (e.g., UV of 200 nm).

An examination of various atomic spectra reveals that the pattern of the spectral lines of an element depends on its position in the periodic system. Elements that have only one valence electron (e.g. the alkali metals) are characterized by spectra that have relatively few lines, whereas elements that have multiple valence electrons (e.g. the transition elements) have very line-rich spectra.

In absorption spectrometry, the atoms are generally in the ground state, at the lowest possible energy level. Through resonance interaction with a photon an electron can be lifted to a higher orbital. Under these conditions, i.e., ground state and resonance, only a relatively small number of transitions is possible. In atomic emission, by contrast, electrons are distributed at significantly higher temperatures (flame, arc, spark, plasma) in higher orbital, from which a large number of drops back to the start level (ground state) are possible. As a consequence, emission spectra are significantly more line-rich than absorption spectra.

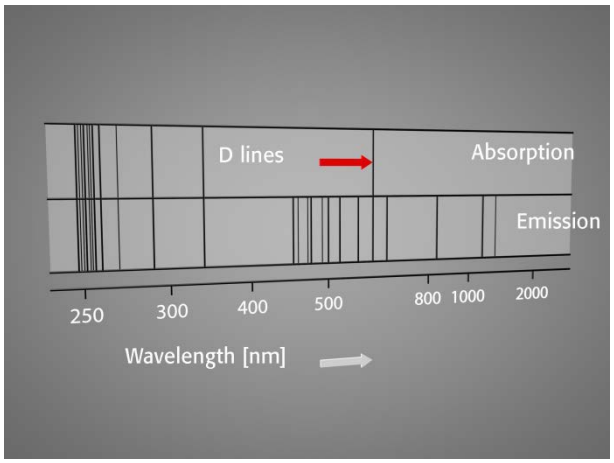


Figure 1-8 Absorption and emission spectra of sodium (schematic)

In addition to the fact that extremely diverse states of excitation are reached, ionization can and typically does occur. Since these ions are also excited, emission spectra are for two reasons very line-rich compared with absorption spectra.

The emitted radiation is spectrally resolved by means of a monochromator or of a polychromator and correspondingly measured sequentially or simultaneously, respectively, by a detector. Provided that only element specific light falls on the detector, element assignmentaccording to the line position is possible. If this is not the case, spectral interference is said to occur. Based on the relationship between the line intensity and the concentration of calibration standards, it is possible to perform quantitative analyses of the sample solution. This form of quantification is called spectrometry as opposed to spectroscopy, which is a qualitative method.

Related method: Atomic absorption spectrometry

Free atoms (gas phase) are generated by temperatures that are moderate compared with those used for emission spectrometry and can be excited to higher energy levels by energy supplied in the form of radiation: Electrons of the outer shell are raised to higher energy levels, and the atom is in what is known as an excited state. Since only discrete amounts of energy can be absorbed by an atom, only radiation of definite wavelengths can be absorbed. The attenuation of the radiated intensity of a selected line is correlated in the form of extinction (absorbance) with the number of atoms in the absorption chamber and thus with the concentration of these atoms in the sample.

Related method: Atomic fluorescence

Intense monochromatic excitation radiation, as can be produced by discharge lamps (e.g. low pressure mercury vapor lamps), is focused onto an atomic cloud, which, as in atomic absorption spectrometry, is generated by low-background flames or by electrothermal excitation. Because this method uses relatively low temperatures, the atoms are mostly in ground state. As a result of the absorption of the excitation radiation, the atoms transition to an excited state. Emitting the excitation energy (or parts of it) in the form of fluorescence radiation, the atoms return to ground state or to a lower energy level. The fluorescence radiation is usually collected at a right angle to the excitation radiation in order to avoid direct irradiation, spectrally resolved by means of a monochromator and the intensity measured using a suitable detector. If the background radiation is negligible, the monochromator can be dispensed with for fluorescence measurements.

1.2.1 Quantitative analysis in emission spectrometry

The intensity of the radiation from the emitting element that falls on the detector depends on a number of factors (sensitivity of the line, efficiency of the sample introduction system, transmission of the optics, quantum efficiency and amplification of the detector, and others). For this reason, it is necessary to calibrate the spectrometer used for quantification by means of samples of known concentration. In general, a linear relationship extending over up to six orders of magnitude can be observed, which, owing to various apparatus-related limitations (e.g. carry-over effect), typically dwindles to 4 to 5 orders of magnitude. Because the linear range is so large, only the linear range is normally used for quantification. Where higher concentrations are to be measured, a less sensitive emission line is selected or, if possible, radial observation is chosen instead of axial observation.

As has already been mentioned, the linear range extends over several orders of magnitude, starting at the detection limit. Since the detection limits are generally very low, the linear relationship should be verified exemplarily, normally as part of the validation process.

When using linear calibration functions, it is not permitted to extend a large linear range into the non-linear range because it is not possible for such functions to describe the actual behavior.

1.2.2 Background equivalent concentration

In ICP emission spectrometry, the analysis lines used for quantification are superposed on a background consisting of continuum radiation originating from the plasma. This background increases as the temperature of the plasma increases. Also, the background radiation is relatively low for short wavelengths (ca. 200 nm) and increases as the wavelength increases.

In many instrumental analytical methods it is customary to express the sensitivity as a signal/background ratio. In ICP Emission, this would be impractical, since the lines are extremely variable in terms of sensitivity: some lines are used with concentrations in the upper mg/L range, at which other lines are clearly outside the linear range. In order to be able to use the concept of the signal/background ratio for emission as well, it would be necessary in each case to state also the concentration of the analyte that led to the corresponding signal, making it difficult to handle. Therefore, in ICP emission spectrometry the concentration is normally included in the signal/background ratio, resulting in the background equivalent concentration (BEC) value. This is the analyte concentration at which the intensity of the generated signal matches the background. To determine the BEC, the

intensity of the background is divided by the net intensity of the signal and multiplied by the concentration of the analyte used in the measurement

$$BEC = c_{analyte} * I_{BG} / I_{net}$$

Thus, the BEC value is a reciprocal signal/background ratio standardized by concentration. While the highest possible numerical value is desirable for the signal/background ratio, a low BEC value indicates good sensitivity.

When comparing BEC values, it should be noted whether they are for radial or for axial observation. Values in older tables are always for radial observation.

1.2.3 Detection limit

The detection limit is a further essential characteristic value of an analytical method. It is a measure of the content of analyte above which the concentration of analyte in the sample will, with a certain statistical confidence, be found to be greater than that in the blank. Since the measured signal must be distinguished with a certain assurance from the signal of the blank, it is statistically related to the precision of the determination of this blank.

In the case of an unstable or noisy signal, it is difficult or almost impossible to determine whether it is due to a small change in the emission (and thus a change in the concentration of the analyte) or to a fluctuation in the baseline.

According to IUPAC, the limit of detection is defined as the concentration of the analyte that yields a signal corresponding to 3 times the background noise (3σ criterion, or k = 3) of the blank.

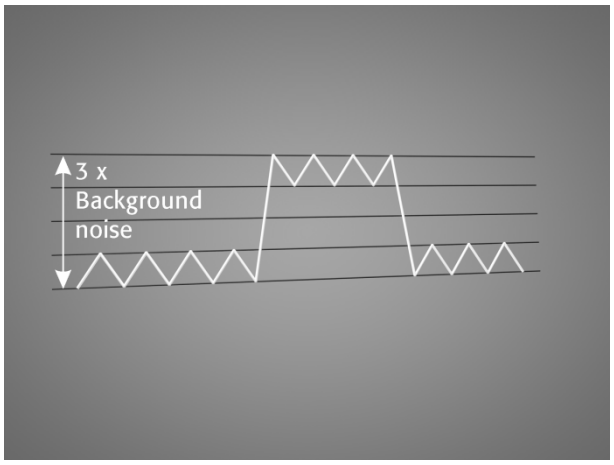


Figure 1-9 Detection limit with 3σ criterion Peak to Peak noise !?

In Germany, analyses are often performed according to the DIN 32645 standard, which defines two methods that are known as the blank value method and the calibration line method. The blank value method is relatively easy to handle: after calibration, a blank value solution is measured 11 times. The standard deviation SD (in intensity) determined for these measurements is multiplied with the statistical safety factor k (typically = 3).

$$c_{LOD} = k * SD / \text{slope of calibration curve}$$

The measured background noise value can be decreased by measuring the analysis and background signals simultaneously, so that variations from external sources (e.g. sample introduction system) compensate each other to a large degree. Simultaneous measurneant can be achieved by using a semiconductor detector (e.g. CCD).

The limit of detection c_{LOD} depends on the sensitivity of the analysis line (good BEC value) and on the reproducibility (low noise) of the background. It can also be calculated using the equation:

$$c_{LOD} = BEC * RSD_{BG} * k$$

RSD_{BG} is given as a ratio, i.e., % value / 100

This relationship can also be used to extrapolate, by way of an estimation calculation, from a tabulated or measured BEC to the expected limit of detection. The RSD value of the background is then assumed to be 1 % (i.e., 0.01). 3 is substituted for k. Thus one obtains

$$c_{LOD} \approx BEC / 30$$

It should be noted that the value obtained in this way can only be regarded as a rough guide, since the assumption regarding the background noise does not strictly apply: for a low background (short wavelength range) it must be assumed that the RSD is much greater.

1.2.4 Limit of quantitation

In this connection, it is important to point out that although a numerical value is assigned to the limit of detection, this does not mean that it is admissible at this limit to make a statement regarding the concentration in the sample. This is only possible if the measured concentration is greater than the limit of quantitation.

Within the concentration range of the limit of quantitation, the presence of the analyte is presupposed. It is the smallest concentration of an analyte that can be quantitatively determined with a certain degree of precision. If the measured value is in the range between the limit of detection and the limit of quantitation, the analysis is positive, but a quantitative statement is not permissible.

As a “quick estimate”, the limit of quantitation is three times the detection limit or ten times the noise of the blank.

The detection and quantification limits must be determined and stated separately for each sample type (matrix) and method.

When comparing the detection and quantification limits of different laboratories or device manufacturers, it is important to indicate how these parameters were determined and to which matrix they correspond.

1.3 Plasma

In an ICP (**i**nductively **c**oupled **p**lasma), excitation for light emission is achieved by adding sufficient energy to a gas to transform it into a plasma, the next higher state of matter. A plasma is characterized by the fact that the disorder on the atomic level is so great that electrons dissociate from the atoms resulting in the formation of ions. A plasma can also be said to be an ionized gas. The plasma used for analytical purposes reaches temperatures in the range between 5,000 and 10,000 K.

The energy is providedby means of an induction coil, through which a large current alternating at high frequency flows. The current induces a magnetic field that accelerates electrons and ions. When these collide with neutral atoms, they in turn knock electrons out of their atomic shells, so that new ions are generated. Together, ions and electrons form the plasma.

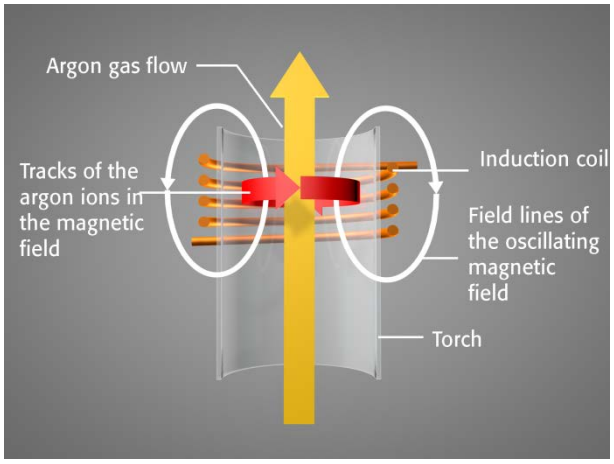


Figure 1-10 Functional principle of ICP

In order for the inductive coupling of energy into the plasma to function permanently, the direction of the current must change continually. This occurs at radio frequency: 27 or 40 MHz. Investigations carried out at the outset of the commercialization of ICP indicated that the transfer of energy increases with the frequency. Ideally, the frequency would be in the order of 100 MHz, but this band is reserved for FM radio stations. Only the 27 MHz and 40 MHz frequency bands are internationally released.

Argon is used as the operating gas. As an inert gas, argon has a very low tendency to form ions. For this reason, initial ignition is needed to create in a small space an energy density that is sufficient to ionize even argon. Once a sufficient number of ions is present, the collisions described above are sufficient to maintain the plasma. (It is sometimes erroneously said that a plasma is “burning”. “Burning”, however, denotes a chemical reaction involving oxygen. A plasma, by contrast, is the next higher state of matter beyond the gas phase.)

2 Layout of an ICP-OES device

2.1 Components of an ICP-OES device

The central feature of an ICP emission spectrometer is the plasma. It is maintained inside a **plasma torch**. The energy needed to maintain the plasma is provided by a radio frequency generator. A nebulizer turns the measuring solution into an aerosol, the larger droplets of which are subsequently removed inside the **spray chamber**. The **injector** of the torch injects the aerosol into the plasma, where the substance is dried extremely quickly. The dried solid residue is melted and finally vaporizeds. The gas molecules are then atomized and the atoms ionized. The electromagnetic radiation which is emitted as a result of the simultaneously occurring excitation is directed by the **transfer optics** to the dispersing (wavelength-resolving) optics. The optics separates the light by wavelength, and the intensity of the radiation for each wavelength is registered by a detector.

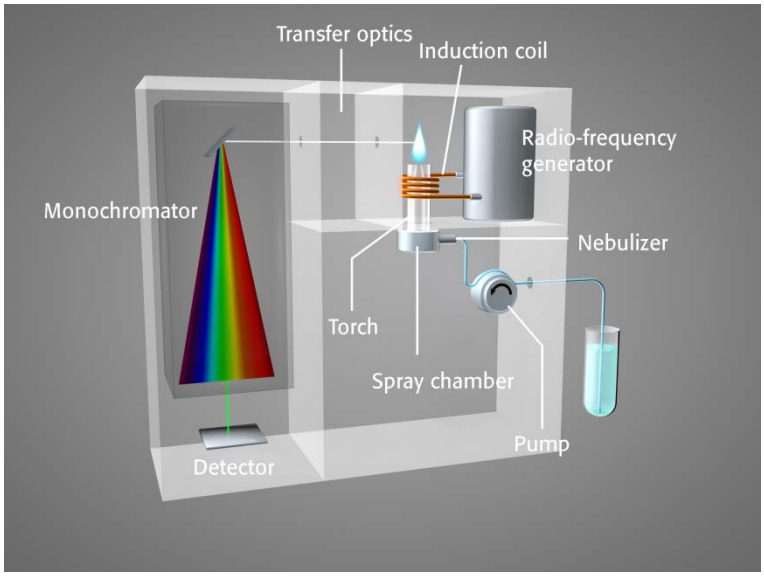


Figure 2-1 Schematic structure of an ICP emission spectrometer

Splitting into wavelengths with subsequent detection can occur sequentially or simultaneously. Accordingly, a distinction is classically made between two types of spectrometer: monochromators (sequential spectrometers) and polychromators (simultaneous spectrometers). A special case are devices that, like a classic sequential spectrometer, address the wavelengths one after the other, but at the same time also measure a spectral range on both sides of the analysis line. This type of device is called a Scanning Array Spectrometer.

Owing to geometrical limitations and to the limitations of the detector, only devices working sequentially can achieve the best separation of neighboring wavelengths, so that these have the advantage of a high spectral resolution. Simultaneous spectrometers usually have no or only a small number of moving parts. Consequently, simultaneous devices are associated with greater speed of analysis and stability. Scanning Array Spectrometers combine the benefits of the sequential device (best spectral resolution) with the benefits of simultaneous devices (stability).

Echelle grating based configurations provide good spectral resolution in as small a space as possible. l Such designs make use of two wavelength dispersing optical elements. Typically these are a prism and a grating. The characteristics of the dispersive elements are selected in order to produce an unambiguous spectrum. In polyschromators, the dispersing elements are arranged perpendicular to each other so that a two-dimensional spectrum with rows

corresponding to the orders of the grating is produced. For example, the. approximately the 30th to 130th orders might be used to cover a range from 165 to 900 nm.

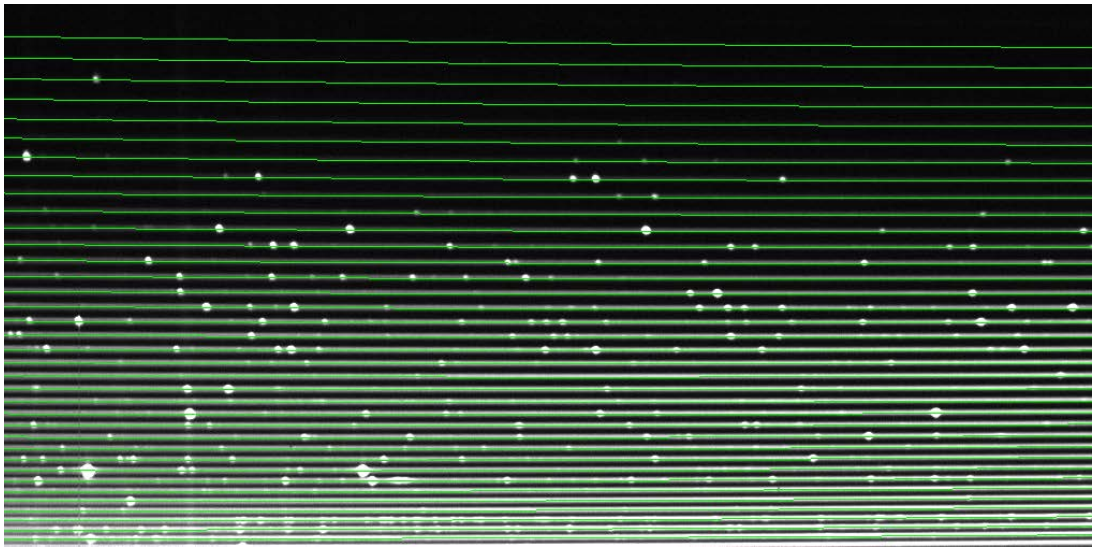


Figure 2-2 Section of an echellogram (spectrum generated by means of echelle optics)

The green lines in Figure 2-2 indicate the expected locations of the order bands are expected to occur. The actually measured order bands are superimposed as gray stripes, on which the emission lines appear as brighter spots. In the spectrum as used for analysis the spots are displayed as peaks.

The prism and grating can also be located in the same plane, with the prism deigned to function as a wavelength filter which only lets through a wavelength range corresponding to order containing the wavelength of interest. This optical configuration is called a double monochromator.

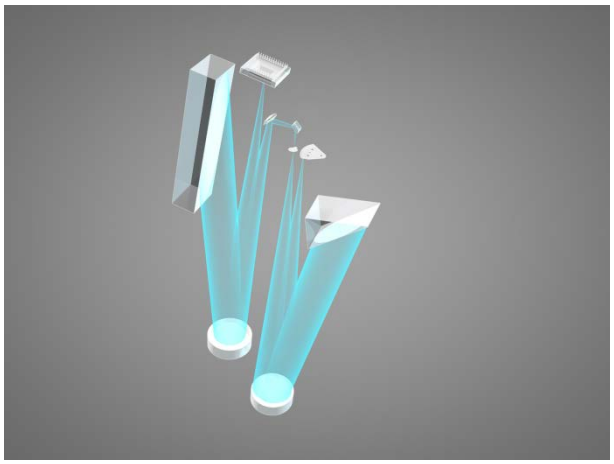


Figure 2-3 Example of a double monochromator as used in the PlasmaQuant PQ 9000

2.1.1 Plasma torch

The inductively coupled plasma is maintained inside a **torch** consisting of three concentric tubes. The outer tube functions as electrical insulation between the two electrical circuits, i.e., **coil** (primary circuit) and **plasma** (secondary circuit), both of which have very high voltages so that arcing would occur if they were not separated by an insulator. The electrical insulation is reinforced by the **bonnet**, which is inserted between **coil** and **outer tube**.

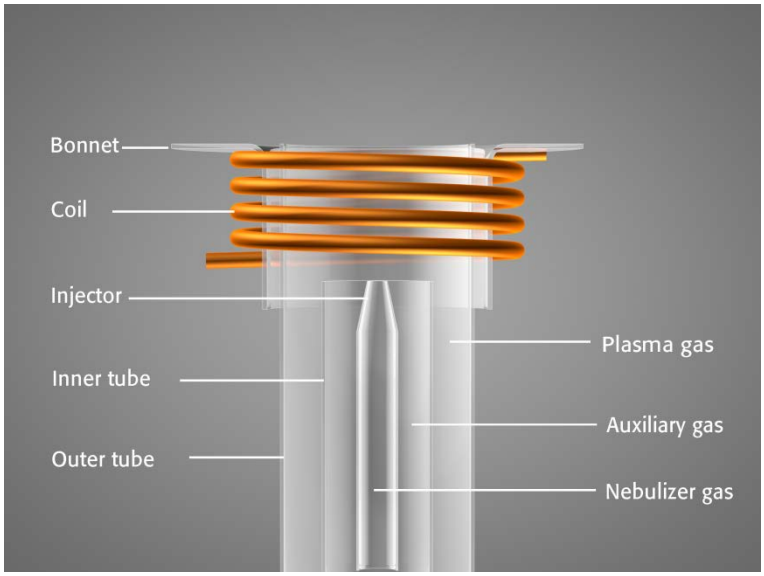


Figure 2-4 Layout of the torch

The material used is normally quartz. However, quartz gets soft above approx 2,000 K and needs to be cooled intensively because of its proximity to the plasma, which in this part of the torch has a temperature of approx. 10,000 K. This is done by means of argon gas, which is guided in such a way that it flows as close a possible to the inner wall of the outer tube, carrying away the heat that is transported there by radiation. Depending on the plasma power, this requires a flow of 10 to 20 L/min. The inner tube helps to guide the flow of the coolant gas. The distance from the outer tube is very small, so the coolant gas is forced to flow close to the outer tube. Since this gas by itself is sufficient to maintain the plasma, it is called **plasma gas.**

The injector is used to introduce the measuring solution into the plasma. Here, argon combined with the measuring solution, which has been nebulized to form a fine aerosol, flows into the center of the plasma. The radio frequency plasma has an annular form, ie. there is a gap at the center into which the aerosol can be injected relatively easily. As the aerosol-loaded gas passes through the plasma, it absorbs energy from the plasma ring surrounding it and is rapidly heated. During this process, the aerosol is dried, the resulting solid matter melts, the resulting fluid evaporates, the freed gas molecules dissociate into atoms and eventually form positively charged ions. The gas transporting the aerosol into the plasma is the same as that is used to form the aerosol. For this reason, this gas is called **nebulizer gas**. Typical gas flow rates are 0.5 to 2 L/min.

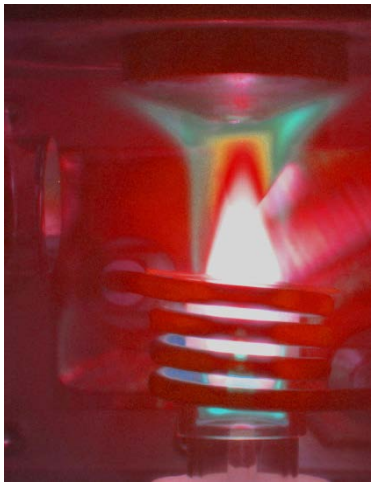


Figure 2-5 Plasma temperature profile for 1 g/L Y

The lower the nebulizer gas flow, the longer the residence time in the plasma, and the higher the temperature in this part of the plasma. This part of the plasma contains the elements that are to be measured (the analytes) and is therefore called the **analyte channel**.

The space between the inner tube and the injector can be filled with gas. This gas is called **auxiliary gas**. Its flow is laminar, keeping the plasma away from the tip of the injector and from the inner tube. This can be necessary if salt deposits are formed because of high salt concentrations in the measuring solution, or if soot deposits are formed when certain organic solvents are used. Increasing the flow of auxiliary gas, typically from 0.5 L/min to 2 L/min, can prevent these deposits. Another way to prevent these deposits is to increase the clearance between injector tip and plasma by lowering the entire torch.

Figure 2-6 Carbon deposits at the injector tip

Normally, all three tubes are made of quartz, but they can also be made of other materials that are both electrically insulating and can withstand high temperatures. In particular when solutions containing hydrofluoric acid are used, ceramic materials offer advantages; however, these are significantly more expensive.

Typically, the outer tube is exposed to the greatest stress through heat and vapors from the sample. The high temperatures lead to recrystallization of the amorphous material, which manifests itself by white crystal structures. These crystals slow down the flow of the coolant

gas, causing the outer tube to melt in extreme cases. To avoid this, the outer tube should be replaced if the inner wall of the outer tube has become very rough. Especially with fully demountable torches, this can be done easily and at low cost.

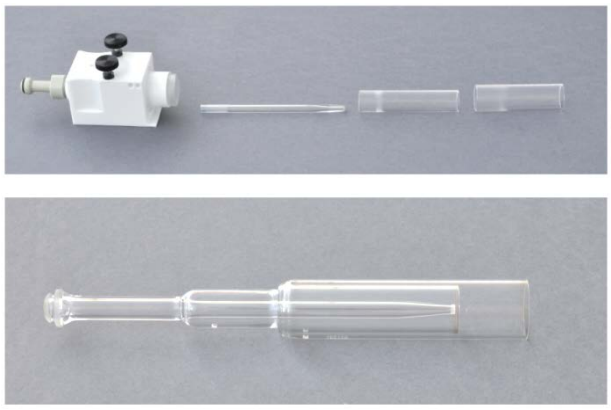


Figure 2-7 Demountable torch (top) and non-demountable torch (bottom)

This option of easy replacement does not exist for non-demountable torches, which were used especially in the early days of ICP. As regards demountable torches, a distinction is made between fully and partially demountable torches. In a fully demountable torch, all 3 tubes can be replaced independently of each other, whereas in a partially demountable torch, the outer and inner tubes are rigidly connected. Therefore both tubes must be replaced if the outer tube needs to be replaced because of recrystallization.

The temperature of the plasma, and particularly the temperature of the analyte channel, which is crucial for excitation, depends on a number of parameters. By far the most important of these are the power coupled into the plasma and the speed of passage through the plasma. The latter depends on the nebulizer or carrier gas flow speed and on the diameter of the injector nozzle. The slower the speed at which the analytes are transported through the plasma, the more time is available to absorb energy from the surrounding plasma and the more the analyte channel is heated up. However, if the nebulizer gas flow is too low, the momentum will not be sufficient to allow the nebulizer gas to enter the plasma. It will then rebound from the bottom of the plasma and flow around the outside of the plasma instead. Above a certain nebulizer gas flow rate, this gas and the sample aerosol will enter the plasma completely. If the nebulizer gas flow rate is further increased, the sensitivity will increase up to an analysis line dependent maximum. The higher the amount of energy required for excitation, the sooner will the cooling effect caused by increased speed of movement through the plasma manifest itself, which in turn will lead to decreased sensitivity.

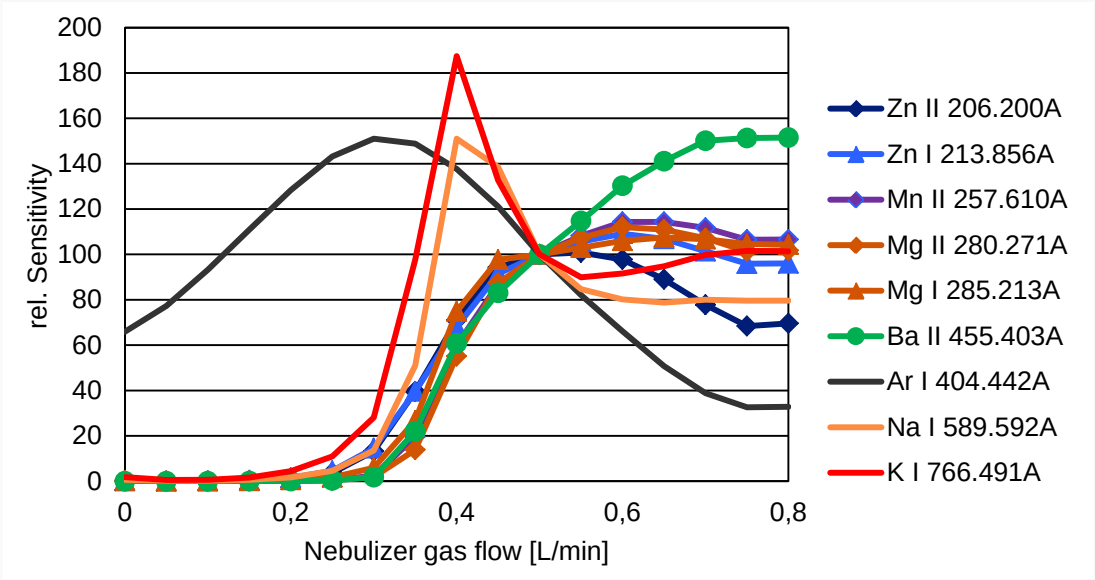


Figure 2-8 Sensitivity of selected emission lines as a function of nebulizer gas flow in axial observation

It is apparent that the temperature of the analyte channel also depends on the power input. The temperature of the analyte channel increases as the power increases. Increases in temperature result in increased sensitivity especially for lines that need very high amounts of energy, whereas the lines that are easy to excite exhibit decreased sensitivity.

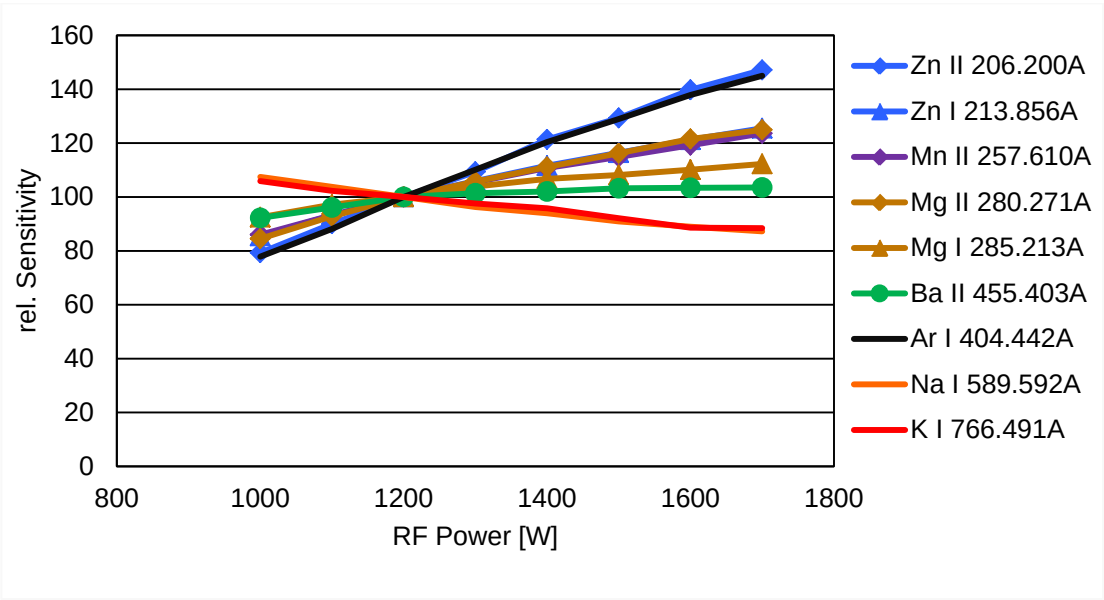


Figure 2-9 Sensitivity of selected emission lines in axial observation as a function of power input

The other two gases, i.e. the plasma gas and the auxiliary gas, have a much lower impact on analyte sensitivities. Normally, the rates of flow are changed only as required due to the characteristics of the sample. Examples are organic solvents or high-saline solutions.

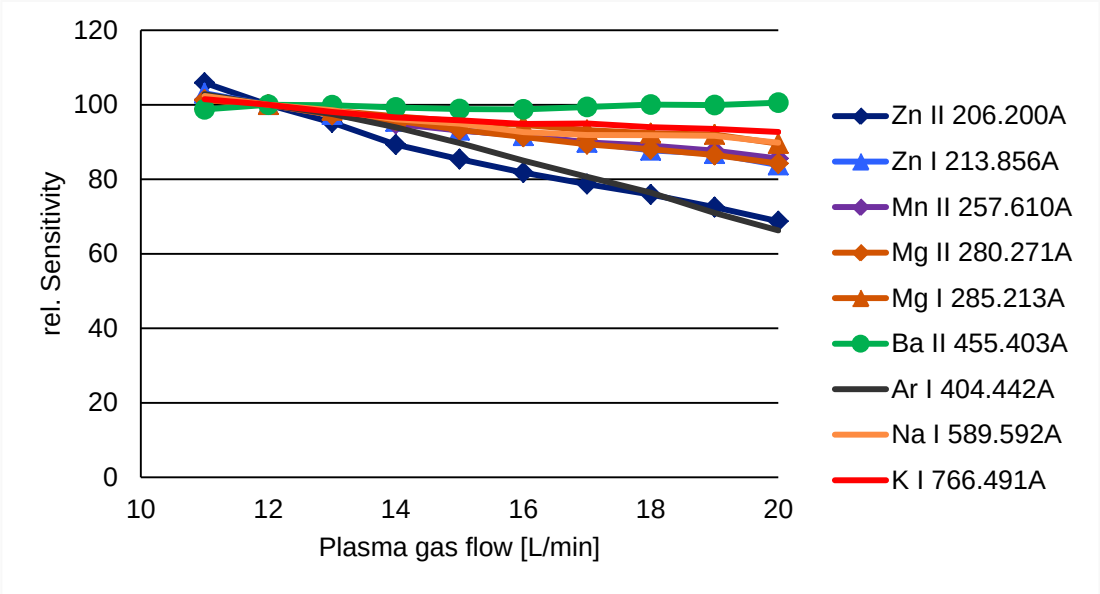


Figure 2-10 Sensitivity of selected emission lines in axial observation as a function of plasma gas flow

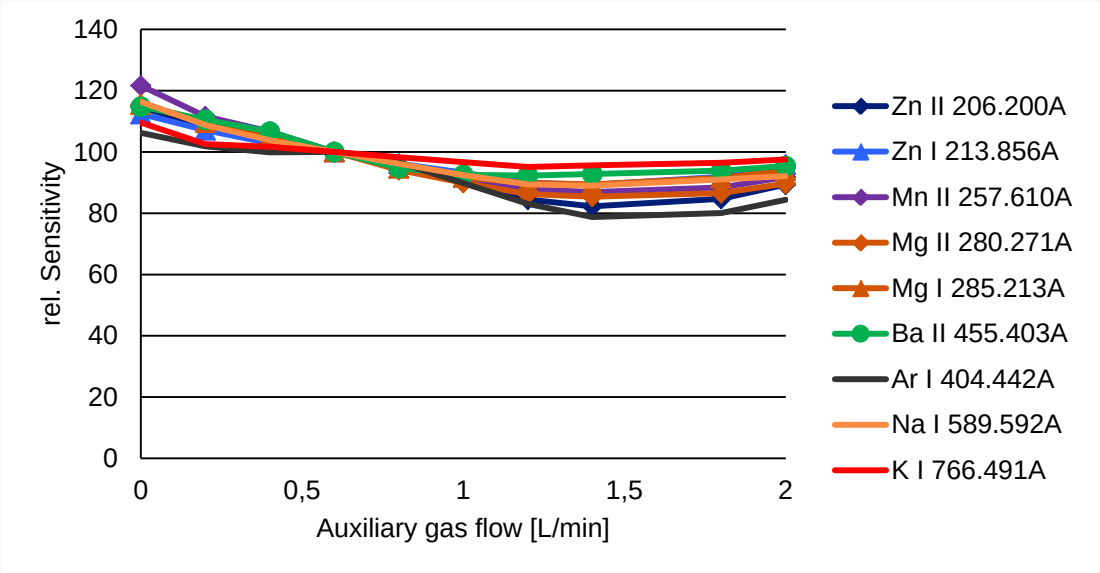


Figure 2-11 Sensitivity of selected emission lines in axial observation as a function of auxiliary gas flow

2.1.2 Sample introduction system

As mentioned, the measuring solution is introduced into the plasma in the form of an aerosol. The aerosol is created by means of a **nebulizer**, which typically uses a gas jet to break the measuring solution up into small droplets. These droplets are of different sizes, which is disadvantageous for the subsequent processes that will eventually lead to excitation and emission of light: Excitation only occurs in free atoms or ions. These can only be created if the solvent, usually water, evaporates from the droplets. The remaining solid matter melts, the resulting liquid evaporates. The vapor consists of molecules, which are then split up into atoms. The atoms are then excited to emit radiation, or are transformed into ions, which in turn are able to emit radiation. All these different processes take time to be completed. As such, it is not possible to dry, melt, evaporate, dissociate, ionize and excite larger droplets within the relatively short residence time in the plasma. For this reason, only very small droplets can be allowed to enter the plasma. The **spray chamber** is designed to ensure that this is the case. Making use of centrifugal force, it rejects the larger droplets, while the smallest ones enter the plasma via the **injector**. The efficiency of a nebulizer/spray chamber system is in the region of approx. 2 %. The remainder of the measuring solution (98 %) is drained from the spray chamber, usually by pumping out the excess solution.

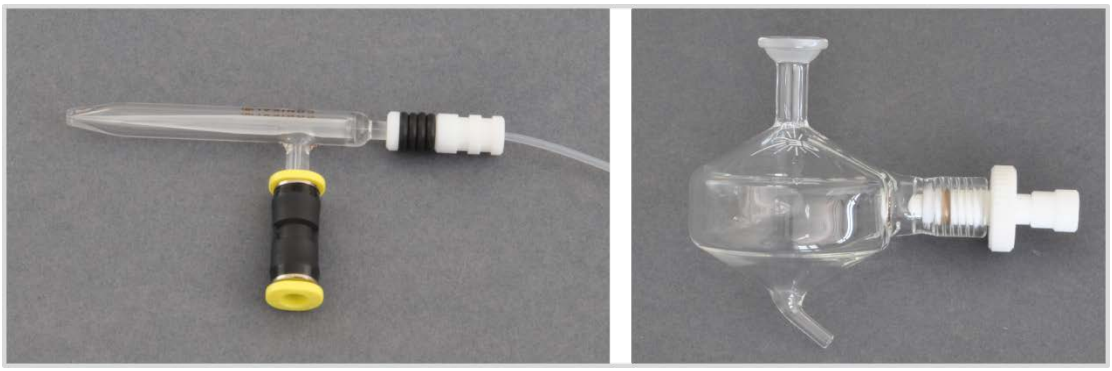


Figure 2-12 Concentric nebulizer and cyclone spray chamber

Since the droplets are separated based on their mass, the density of the solution influences the quantity of aerosol that enters into the plasma and hence the sensitivity. The greater the density, the lower the intensity at the same analyte concentration.

The viscosity is another influencing factor, since it is more difficult to transport a viscous solution through the narrow capillary tubing and capillaries of the nebulizer. A pump can mitigate the viscosity effect, but is not able to prevent it entirely. The greater the viscosity of a solution, the lower the intensity at the same analyte concentration.

Reducing the surface tension will facilitate nebulization so that more aerosol will enter the plasma. Addition of surface-active substances will increase the intensity at a given analyte concentration.

There is a number of nebulizer types, since some nebulizers get more easily clogged at increased salt concentrations or particle loads than others. Since nebulizers that can accommodate more difficult solutions are, as a rule, more expensive (and sometimes also have other disadvantages, such as compromised precision), the most suitable nebulizer should be selected for each application.

If hydrofluoric acid is required in order to dissolve a solid substance or to stabilize certain analytes, the components of the sample introduction system should also be made of HF resistant materials (plastics for nebulizer/spray chamber and ceramics for the torch).

2.1.3 Plasma observation

As has already been mentioned, the analytes move through the plasma along the analyte channel. As they move through the plasma, the originally injected extremely small aerosol droplets are strongly heated, and excited atoms and ions are eventually created. All this happens in the analyte channel, which runs through the center of the plasma, from the bottom to the tip of the plasma. A temperature gradient can be observed: at first, the temperature rises rapidly to a maximum value of approx. 6,000 to 7,000 K. This is the hottest section of the analyte channel. It is located slightly above the induction coil. Beyond that point, the analyte channel gets cooler, because the energy is radiated into the surrounding space.

The radiation emitted by the analytes in the analyte channel can be observed from two directions: From the side (called radial observation) or along the analyte channel (called axial observation). Radial observation offers the advantage of it being possible to observe a specific section (normally, this will be the hottest section, but in special cases it can also be a cooler one) and thus to improve both the sensitivity and the quality of the results e.g. in terms of absence of interference.

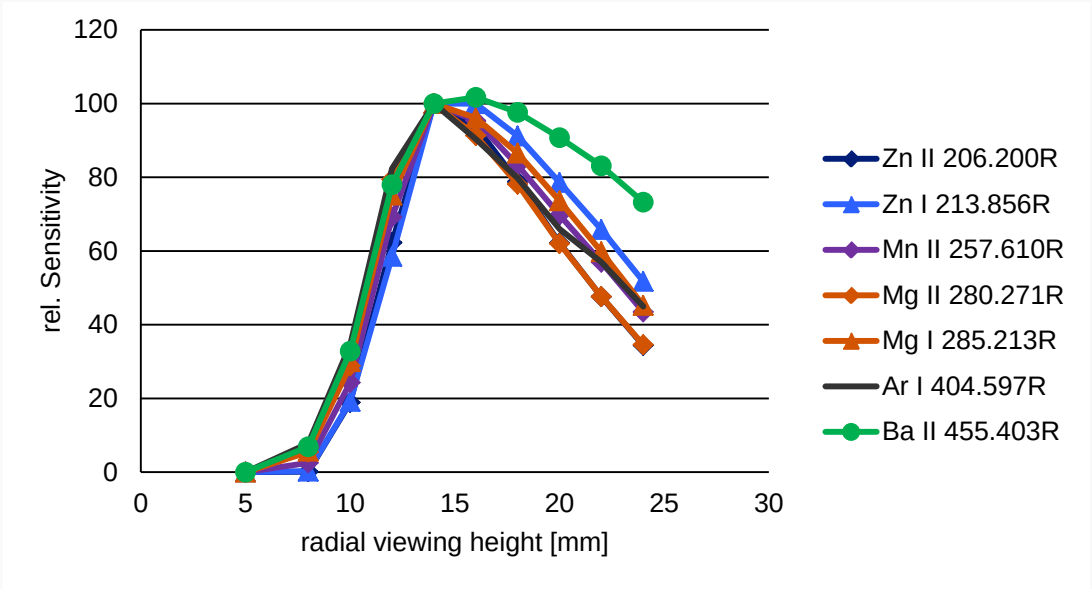


Figure 2-13 Relationship between sensitivity and radial viewing height for various emission lines

Axial observation, by contrast, encompasses a larger section of the analyte channel, resulting in increased sensitivity and thus lower limits of detection. However, since it is inevitable that the cooler regions are also observed, it is not possible to completely avoid interferences originating in the cooler section of the analyte channel. The interferences originating from the upper region of the plasma (where the plasma has already cooled down) can be reduced by removing the tip of the plasma. This is normally done with the help of a cone, on which the plasma impinges. The radiation from the plasma goes through an opening in the middle of the cone and is directed to the dispersing optics and to the detector. A counterflow of argon through this hole (cone gas) is used to cool the plasma down rapidly and to protect the optics located behind the cone.

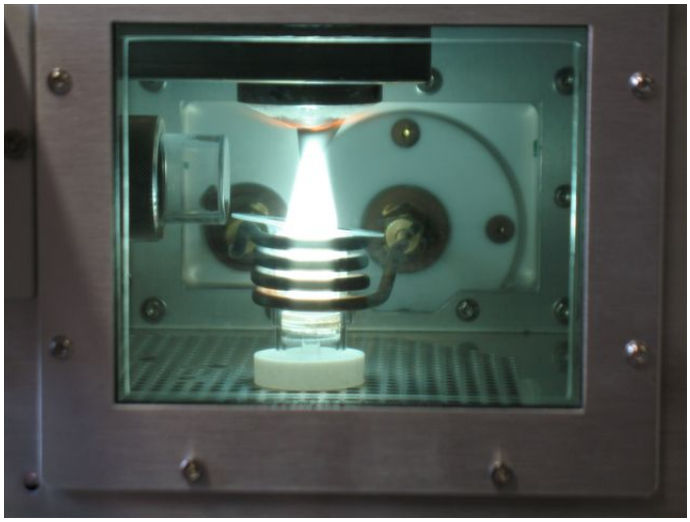


Figure 2-14 Tube for radial observation (left) and cone for axial observation (top)

By means of **dual view optics** it is possible to select, controlled via the method, the ideal observation direction for each analysis line. In the context of method development, it can be advisable to measure a line from both observation directions in order to select, based on experimental results, the observation direction best suited for routine work.

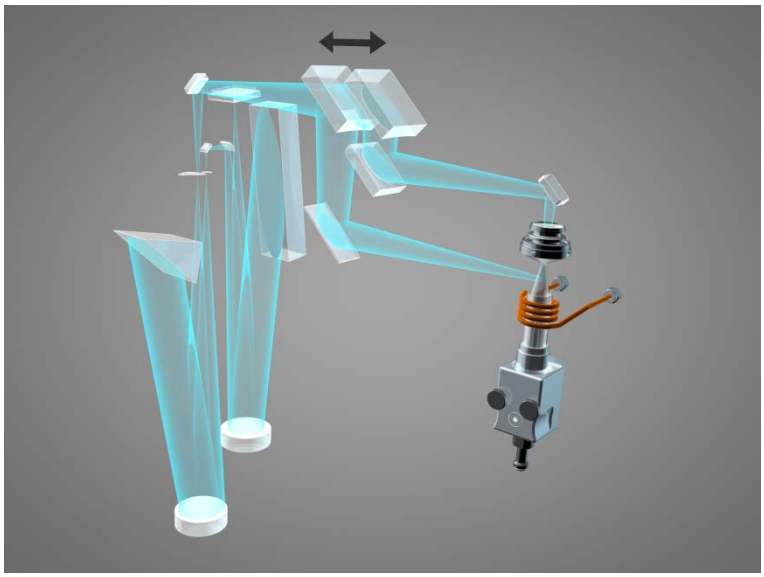


Figure 2-15 Dual view transfer optics with double monochromator

The mirror marked with a double arrow in Figure 2-15 can be shifted by means of a stepping motor controlled mechanism to activate either axial observation (from the top) or radial observation (from the left).

2.1.4 Dispersing optics

The radiation emitted by the plasma is separated by the optics into its constituent wavelengths (dispersed). The dispersing optics of an ICP emission spectrometer must be capable of clearly separating lines that are very close to each other. This is necessary because ICP spectra are very line-rich, resulting in the relatively frequent occurrence of spectral overlap.

A very good separation (resolution) is achieved by means of a compact double monochromator (for illustrations see chapters 2.1 and 2.1.3). The first monochromator uses a prism to pre-disperse the radiation, which is then further dispersed by a grating in the second monochromator. Both monochromators are in a Littrow configuration, using a focal length of approximately 400 mm. The radiation from the plasma passes through the entrance slit into the first monochromator and is redirected to the prism by the first parabolic mirror. The prism is mirrored on the reverse side, so that the radiation passes through it twice before it falls, now spectrally dispersed, onto the parabolic mirror again, which directs the radiation, via a plane mirror, to the intermediate slit. The prism is adjusted in such a way that the spectral range surrounding the analysis line passes through the intermediate slit into the second monochromator. The second parabolic mirror directs the radiation onto the echelle grating, where the selected spectral range is resolved to a high degree. The entire highly resolved subsection of the spectrum is then reflected onto the detector by the parabolic mirror. The resolving power of the double monochromator is in the region of 140,000, which at 200 nm corresponds to a bandwidth of 1.6 pm or to a spectral resolution of approx. 3 pm.

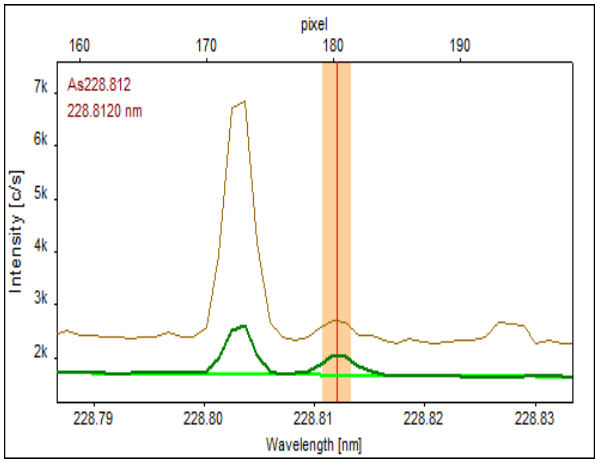


Figure 2-16 Spectrum of Cd (left) and As (right) at 228.8 nm

Since the two peaks are baseline separated in Figure 2-16, both elements can be analyzed free from interference at 228.8 nm.

2.1.5 Detector

The detector used is a linear CCD (Charge Coupled Device) array with, for instance, 576 pixels, of which 200 are used for analytical purposes by default. All pixels are exposed and read out simultaneously. In order make optimum use of the detector, a short-time exposure of 10 ms takes place before the actual measurement starts. The information gained in this way is used to determine a suitable exposure time for the detector in the range between 1.6 and 5,000 ms. This exposure time is determined by the system - in contrast to the measuring time, which is specified by the user as part of method development. If the measuring time defined by the user is longer than the optimized exposure time determined by the device, the

measurement will be repeated a corresponding number of times. If, for instance, the user specifies a measuring time of 3 s (the default value of the method) and the exposure time is determined at 100 ms, the measurement will be repeated 30 times. Together, these 30 measurements yield the spectrum which will be used by the software to calculate the intensity.

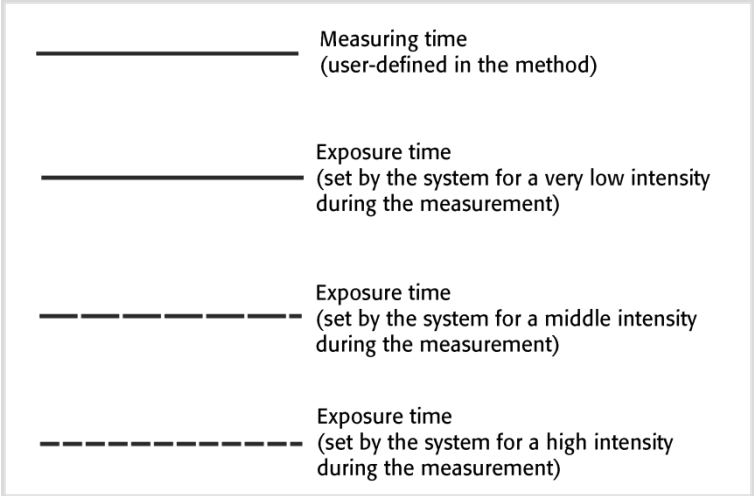


Figure 2-17 Measuring and read-out time at the CCD detector

The measuring time has a strong influence on the reproducibility of a measurement. A longer time can be used to average out fluctuations. This manifests itself particularly clearly in the lowest intensity range, i.e. near the limit of detection. Quadrupling the measuring time lowers the limit of detection by 50 %.

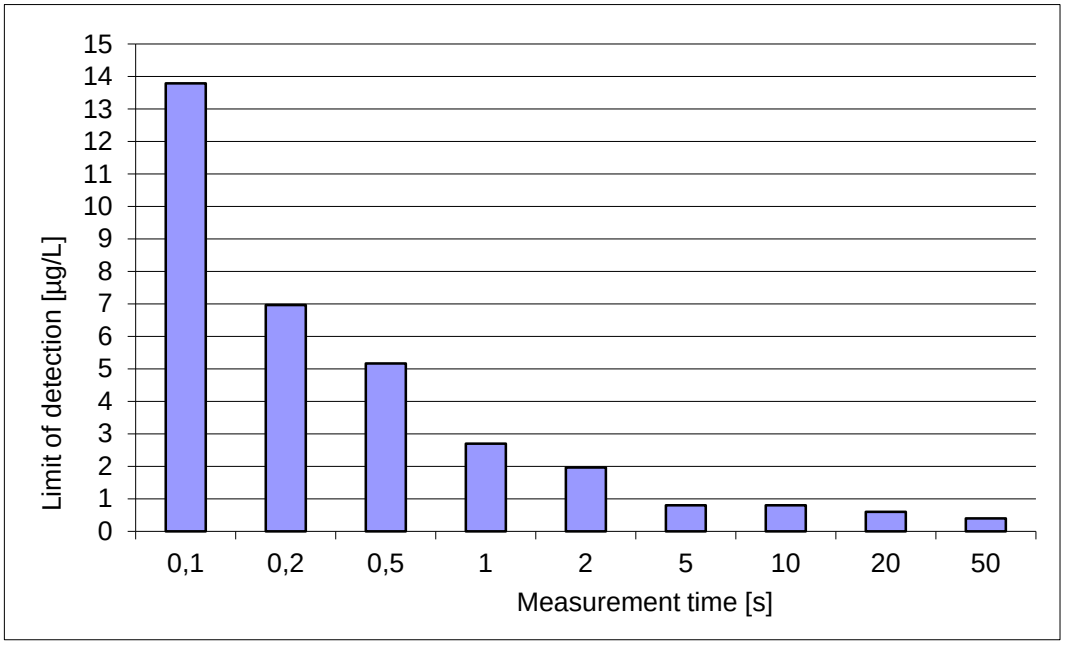


Figure 2-18 Limits of detection for Pb at 220.353 nm as a function of the measuring time

While the signal is being processed, the next exposure already commences, allowing for a rapid succession of measurements.

2.2 Method development in ICP-OES

2.2.1 Method parameters

A method defines the measuring and evaluation parameters for a specific sample matrix. With regard to the measuring parameters, these are primarily the selected analysis lines and surrounding spectral range, the measuring times, the parameters determining the plasma temperature and the observation direction and position. The main evaluation parameters are the number of pixels used to determine the intensity as well as background correction. In some cases, additional corrections for spectral and non-spectral interference are also defined. Furthermore, a method defines the calibration, including, primarily, the number and concentration of calibration solutions as well as the evaluation algorithm. Quality control measures are also defined as part of a method.

A method also comprises a precise description of the sample preparation process including sampling, preservation and, if applicable, preparation of a solution, e.g. by means of digestion. These are of crucial importance for correct results. A method also defines interference correction or compensation measures, such as matrix adjustment or the use of an internal standard.

2.2.2 Selection of lines

The selected analysis line should be free of spectral interference and suited to the expected concentration range of the samples. Wavelength tables, which are also integrated in the software, offer a first guide for the avoidance of spectral interference. In addition, exact observation and assessment of the spectra of all measuring solutions is required. A shoulder on an analysis line, for instance, indicates the presence of spectral interference. If spectral interference is suspected, a comparison should be made with the spectrum of a single element solution in order to determine whether this is in fact the case or whether the analysis line itself has a shoulder.

If the suspected interference is confirmed, this line cannot be used with classical evaluation techniques. The usual strategy to avoid incorrect measurements is to use another, interference-free, line of the analyte. Only if such an interference-free line cannot be found, correction procedures should be considered. Furthermore it is important to assess whether the sensitivity range of an analysis line matches the expected concentration range. In doubtful cases, this should be verified by means of a linearity test.

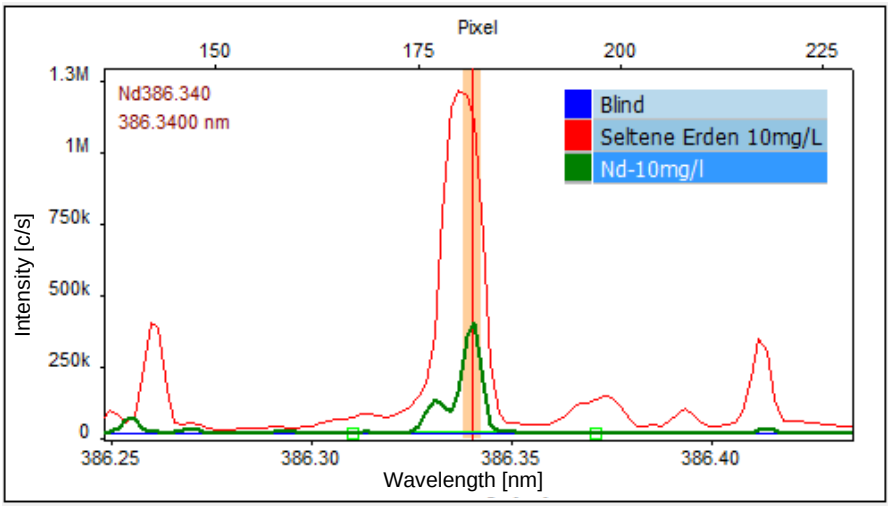


Figure 2-19 Overlaid lines in the spectra of neodymium and a rare-earths-multi-element-solution

In the spectrum of Nd at 386 nm, the peak marked in red (Figure 2-19) appears when the rare-earths-multi-element-solution is introduced. A comparison with the spectrum of the pure Nd solution reveals that it is due to spectral interference.

2.2.3 Plasma excitation and observation parameters

A method defines the parameters determining sensitivity. The temperature of the analyte channel is a decisive factor. It primarily depends on the power input and on the nebulizer gas flow. The other gas flows, such as plasma gas flow and auxiliary gas flow, do not affect the sensitivity of an analysis line strongly so that they are normally changed only if this is made necessary by other factors e.g. saline content of the measuring solution (see also Chapter 2.1.1).

The direction of observation, however, significantly influences sensitivity and can also affect the accuracy, so that it must be defined in a method. The same applies to the position of observation (viewing height) in the case of radial observation.

2.2.4 Peak and background evaluation

In addition to the measurement parameters, a method also defines the evaluation modalities. This concerns the evaluation of the analyte peak, the most important parameters being the type of evaluation (peak height or peak area) and the number of pixels used to determine the intensity. Since the peak shape does not change in ICP-OES, evaluation of peak height would be the ideal type of evaluation - particularly, since peak height evaluation achieves the best signal/background ratio and hence the best limit of detection. Since determination of peak height would require narrower pixels then are practicable, , area or partial area evaluation typically are the preferred approaches in ICP-OES. If one takes the smallest possible partial area resulting from the charge of a single pixel, one obtains (in analogy to peak height evaluation) the best signal/background ratio and hence the best limits of detection. Since the detection limit is not only influenced by the sensitivity but also by the reproducibility, a certain amount of averaging of the noise is advisable. One finds that the best limits of detection are obtained when 3 pixels are used. Further, the risk arising from

drift phenomena increases for 1 pixel evaluation, since minute external influences, such as temperature or pressure changes, can cause a slight shift of the peak position. Especially when high-resolution optics are used, such a hardly perceptible shift of peak position will lead to a changed peak intensity measurement. Minimizing this risk is another reason why 3 pixels are used to determine peak intensity. Increasing the number of pixels results in increased intensity, but at the same time the intensity of the background also increases, leading to a deterioration of the signal/background ratio and hence also of the limit of detection. When 3 pixels are used, this effect is still acceptable as compared with one pixel. However, if an even greater number of pixels is used, the signal/background ratio deteriorates disproportionately, since the added pixels hardly contribute to the peak intensity, while the background intensity proportionately increases with each additional pixel.

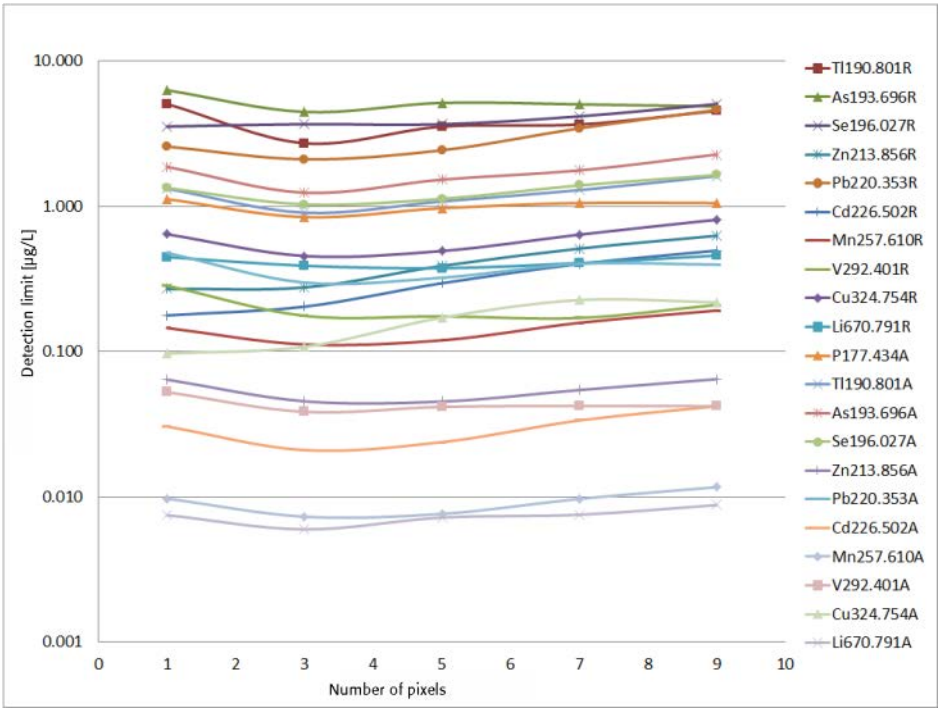


Figure 2-20 Limits of detection as a function of the number of pixels used for peak evaluation in logarithmic scaling

Figure 2-20 shows a minimum for 3 pixels. If only one pixel is used, the influence of the noise is stronger, since no averaging takes place. If more than 3 pixels are used, the limits of detection deteriorate because the signal/background ratio deteriorates

The analyte peaks are, as has already been mentioned, superposed on a background. The intensity of the background changes with the temperature of the plasma. The temperature, in turn, is influenced by the quantity of matter inserted into the plasma: The more matter introduced into the plasma, the more the plasma is cooled and the lower the background intensity.

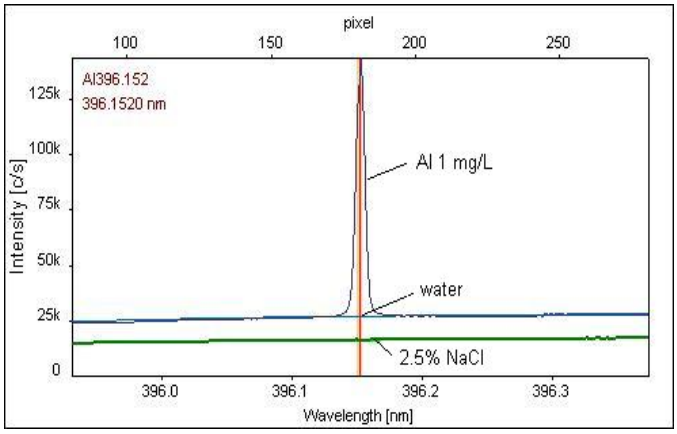


Figure 2-21 Lowering of the background resulting from the introduction of a matrix cooling the plasma (2.5 % sodium chloride solution)

Also, the wings of extremely intense peaks lead to a raised background at a somewhat greater distance.

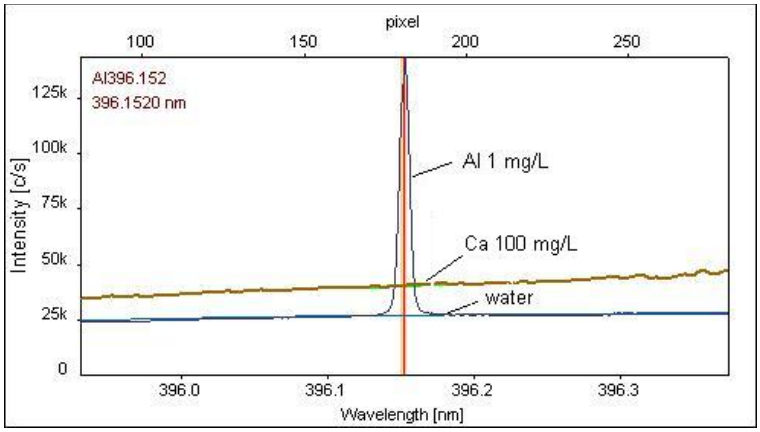


Figure 2-22 Raised background caused by the wings of a very intense emission line in the extended neighborhood (here: Ca line at 396.847 nm)

Since the intensity of this background radiation depends on the quantity and type of sample composition (matrix), the level of the background needs to be quantified for each individual measurement. This background intensity is then subtracted from the gross intensity of the analyte peak. Background correction performed in this way is crucial for the accuracy of the analysis. The followings options are available for the definition of background correction:

- Static
  The user defines points, normally on both sides of the analysis line, representing the background for a specific analysis line and all sample solutions
- Dynamic
  The software automatically determines for each spectrum the ideal points for background correction.

2.2.5 Correction of spectral interference

If, as part of the process of assessing the relevant potential emission lines, spectral interference is found to be present, a different line of the analyte should be used. Normally, there are alternatives. If there are no alternative lines, the influence of spectral interference can be corrected by means of mathematical methods.

2.2.5.1 Inter element correction (IEC)

Inter element correction (IEC), the mathematically simplest method, is not always ideal in terms of accuracy. It presupposes that the analysis line and the interference line are practically at the same wavelength, caused by direct overlapping or coincidence. An interference-free wavelength of the interfering element is then sought, and the intensity ratio between the line interfering with the analysis and the interference-free line is determined. This quotient is then used to calculate from the intensity of the interference-free line of the interfering element measured during the analysis, the part of the total signal measured for the analysis line of interest that is due to the interfering element. The difference between the total intensity and the intensity of the interfering element corresponds to the interference corrected intensity of the analysis line.

2.2.5.2 Multivariate evaluation

Multivariate evaluation is another type of correction method. If the difference in wavelength between analysis line and interference line is more than one fourth of the half width, it makes possible the correction of spectral interference by means of adaptation calculation. The spectra of the sample and of pure solutions of the background, analyte and interfering components are required. A spectrum is treated as a column in a (mathematical) matrix. By means of a matrix transformation it is then possible to calculate the proportion of the analyte in the total spectrum. This type of calculation generally leads to more accurate and more reproducible results.

2.2.6 Non-spectral interference

In addition to spectral interference, there is also non-spectral interference. While spectral interference on the analysis line manifests itself by a high reading, non-spectral interference changes the slope of the calibration function. Non-spectral interference is normally recognized by the fact that when sample solutions are spiked or diluted the recovery rate significantly differs from 100 %.

2.2.6.1 Sample transport related interference

Deviations from the optimum recovery rate are often due to changes in the transport of the aerosol into the plasma. These sample transport problems can be caused by variations in the physical properties of samples, such as viscosity, density or surface tension. For this reason, these problems are also referred to as sample transport related interference. In order to minimize the effects caused by reduced supply rates owing to increased viscosity, a pump is used or supply sample to the nebulizer even if the nebulizer is self-aspirating.

2.2.6.2 Excitation related interference

Another type of non-spectral interference is caused by changes in the excitation conditions within the plasma. This type of interference is also called excitation related interference. One cause of such interferences can be changes in the plasma temperature resulting from varying cooling effects arising from the introduction of different quantities of matter into the plasma. Further, since different elements release different amounts of electrons into the plasma, the concentration of electrons depends on the type and quantity of the substances contained in the sample.

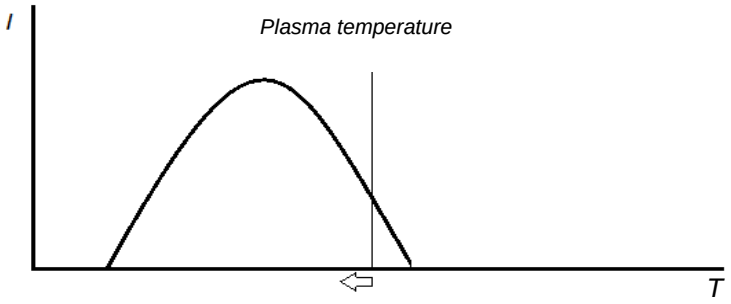


Figure 2-23 Change in intensity as a function plasma temperature

The temperature of the analyte channel is reduced as a result of the introduction of matter. If the optimum temperature for the analysis line is below the plasma temperature, this results in increased sensitivity. However, at a plasma temperature higher than that of the optimum temperature, the temperature decrease results in decreased sensitivity. Ideally, both are the same. The changes in temperature caused by the introduction of matter will then have no or only insignificant influence on the results

While sample transport related interference has the same impact on all analytes, excitation related interference is not only element dependent, but also analysis line dependent. This tends to make it difficult to correct or compensate for this type of interference.

2.2.6.3 Correction of non-spectral interference by means of matrix adjustment

The measures frequently employed to correct non-spectral interference are various variants of matrix matching as well as the use of one or more Internal Standards. Matrix matching means that the standard solutions are adapted to the specific properties of the sample solutions. As a first step, this means that acid is added to the calibration solutions at the concentration at which it is present in the sample solutions. In some cases this is not sufficient, so that it is also necessary to add essential matrix components. Normally, it is sufficient to add the approximate concentrations. Simplifications are also possible. For instance, it will normally be sufficient to add, for Ca and Mg, only the sum of the two as one element (e.g. Ca). In very rare cases this is still not sufficient. In these cases, a well-characterized sample (e.g. after measuring with the help of standard addition or of the resulting spiked solutions) must be used. Standard addition (also referred to as analyte addition) is, essentially, a special (a perfect) form of matrix matching, since the calibration takes place within the sample, as it were.

Adding identical quantities of an ionization buffer (typically a Cs solution) to all measuring solutions is a very special variant of matrix matching. It suppresses excitation related interference, particularly for elements that are easily excited and ionized (e.g. alkali metals).

Diluting the measuring solutions is yet another variant of matrix matching. By this means the physical properties of the sample solutions become more like those of water. Provided that

this does not result in concentrations of the elements of interest becoming too low, diluting the sample solutions is the most elegant strategy for correction of non-spectral interference. Normally, diluting by a factor of 10 will be sufficient to eliminate most non-spectral interferences. This is normally done as part of the digestion procedure for the samples, so that an additional step is not required.

2.2.6.4 Correction of non-spectral interference by means of an Internal Standard

Matrix matching attempts to minimize physical differences between standard and sample solutions. By contrast, the concept of the Internal Standard employs correction of the measured raw data. With the help of an added quantity of an element the change in sensitivity for each sample is determined. Working on the assumption that the effects have identical impacts on the analytes and on the added element (= Internal Standard), this change is used to correct the slope of the calibration line.

While in the case of matrix matching a little additional effort is required only in the preparation of the calibration solutions, exactly the same quantity of an element must be added to each solution when applying the Internal Standard concept. Moreover this element must not already be present in any of the solutions. Y is often used as Internal Standard. It is advisable to use an element with highly detectable lines, for the quantity of this element that is added to all solutions should be sufficient to ensure that a well quantifiable peak is obtained. On the other hand, the quantity of the additive should not be too great in order to make sure that both the risk of contamination and of spectral interference by the Internal Standard element on the analysis line are as low as possible. Also, it is important to make sure that the linear range is not exceeded.

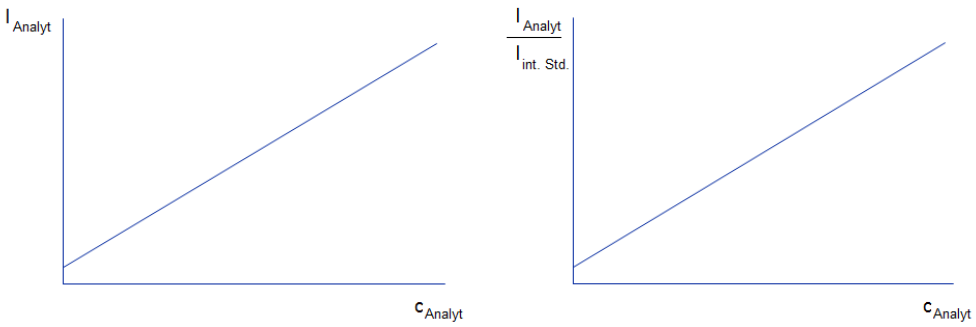


Figure 2-24 Calibration diagrams without and with Internal Standard

The intensity of this element is determined in each measuring solution. If, for instance, low readings of this element occur in a solution, this reduction of intensity is used to correct the analyte intensities accordingly. This presupposes that Internal Standard and analytes are affected in the same way by the interferences. This is true in the case of sample transport related interference, not however in the case of excitation related interference. Since a combination of the two often obtains, the use of one line for the Internal Standard will not be sufficient in some cases. It may be necessary to use different excitation types (atom/ion lines), or perhaps to work with multiple Internal Standards.

If an element is added to the measuring solution as an Internal Standard, one should be aware that this changes the matrix composition and that new spectral interference can occur as a result. The table lists some analysis lines that are spectrally interfered with by frequently used Internal Standard elements.

Selected spectral interference caused by typical Internal Standard elements on frequently used analysis lines

Analyte	Wavelength [nm]	Internal Standard	Wavelength [nm]
Au	267.595	Ta	267.590
Ca	396.847	Dy	396.839
Cd	228.802	Sc	228.803
Dy	364.540	Sc	364.531
Ge	265.118	Hf	265.116
Ge	265.118	Ta	265.122
Na	330.298	La	330.311
Pd	324.270	Y	324.227
Sr	232.235	Hf	232.247
Tb	384.873	La	384.902
Ti	336.121	Sc	336.127
Ti	337.279	Er	337.271
Zn	213.857	Hf	213.857
Zr	339.197	Sc	339.253

2.2.7 Calibration

As in many other instrumental analytical methods, there is no immediate correlation in ICP-OES between intensity and concentration. Instead, the relationship depends on a number of factors that change over time (e.g. condition of pump tubing) or according to the parameters used (sensitivity of an emission line at a specific plasma temperature). To account for this, a conversion factor between intensity and concentration is determined before the start of a series of measurements by means of calibration solutions (also called reference solutions or standards).

ICP-OES is a sample oriented multi-element method and accordingly multi-element solutions are used for calibration. Nevertheless, in the following reference will mostly be made to just one analyte. This is because these issues can be described more clearly if only one analyte is discussed. Of course, the statements apply to all analytes contained in the multi-element solution.

2.2.7.1 Number of calibration solutions

Under ideal conditions, one calibration solution would be sufficient to model a linear function going through the origin of the co-ordinate system. Since the signal evaluation generally involves background correction, the resulting difference for the blank value must be (zero (nil). Since the background is frequently structured, the difference between the intensity at the evaluation position for the signal and the positions for the background can be deviate from zeroth. The assumption that the function passes through the origin is therefore not justified, and the axis intercept must be measured by means of a blank value.

If it has been verified that the operating range is within the linear range, it is sufficient to work with 2 calibration solutions (a blank and a standard). Whether more than 2 calibration solutions are used depends on constraints such as applicable standard methods and regulations. Generally, the calibration standards used should always consist of independently prepared solutions.

2.2.7.2 Concentrations of the analytes

The upper calibration solution should contain a concentration of the analyte high enough to cover the entire measurement range. If the expected range of concentrations in the samples is very small (from below the limit of detection to approx. 3 times the limit of quantitation), a higher concentration should nevertheless be selected for the upper standard, so that it is possible to achieve acceptable reproducibility (« 5%) for the measurement.

The concentration in the upper standard can be higher by several orders of magnitude than the expected concentrations in the samples. However, carry-over effects must be avoided. Whether carry-over occurs should be tested experimentally.

2.2.7.3 Calibration algorithm

A large majority of emission lines have a linear range extending over several (up to 6) orders of magnitude. In these cases, it is clear that the calibration function should be linear. For each emission line used this should be experimentally verified for the desired operating range by means of single element solutions. . If this is not the case, it is advisable to use a less sensitive line. If, in exceptional cases, this is not practicable (for instance because the non-linear range starts at a very early stage), non-linear calibration must be considered as a last resort. (Of course, this will then require multiple reference solutions.)

Non-linear calibration is an exception in ICP-OES, which normally applies to lines involving the easily excitable transitions in atoms of alkali and alkaline earth metals. In many cases, a non-linear calibration function covers up faults in the development of the method. For instance, influences of viscosity in a dilution series can dissemble non-linearity unrecognized spectral interference cause a non-linear progression or carry-over, which has a stronger impact on smaller concentrations, can be interpreted as non-linear behavior.

As has been mentioned above, it is advisable to include a measured value for the blank solution. A calibration function that is forced through the zero point normally also masks l faults in the method.

Aside from the usual standard calibration algorithm, the standard addition method (also known as analyte addition method) is used to compensate for non-spectral interference. Here, one or more known analyte quantities are added to the samples. Based on the slope of the added quantities, the software calculates the concentrations in the samples. If a very large number of samples of the same matrix composition are to be analyzed in this way, this means an enormous amount of effort for sample preparation. This can be minimized by thoroughly analyzing one sample using the standard addition method and then using this sample itself or the spiked samples as perfectly matrix matched calibration solutions for the standard method. This method is referred to as addition calibration.

2.2.7.4 Quality control

The continued validity of the calibration is verified by means of known solutions (quality control samples or standards). These solutions must be prepared independently of the calibration standards in order to be able to recognize faults in the production process of the calibration solutions.

2.3 Automation in ICP-OES

ICP emission spectrometry is usually employed as a routine method for processing the main load of elemental analysis. In most cases, this involves analysis of large numbers of samples. Often, an automatic sample feeder (autosampler) is employed in order to streamline the workflow. In many cases, these autosamplers use x/y co-ordinates for positioning and work with the same tablets s are also used to store samples.

2.4 Problems of trace analysis

2.4.1 Water as a source of contamination

Deionized water should be used for diluting and rinsing (ultrapure water18 MOhm). Any contact with metallic materials must be avoided.

2.4.2 Stabilizing and digestion reagents as sources of contamination

The purity of the reagents must be such that, taking into account the required limits of quantitation and the quantities of the reagents used, no measurable contamination will be introduced.

2.4.3 Ambient air as a source of contamination

Contamination by dust can adversely affect the results of trace analyses. Elements that are often found in dust include aluminum, calcium, magnesium, sodium, silicon, zinc and iron. The degree of contamination can vary depending on the properties of buildings (e.g. ceilings) and the location (laboratory in the immediate vicinity of metal processing operations or close to the sea).

If very low element contents are to be determined, it may be advisable to use a cover for the autosampler or a laminar flow box.

2.4.4 Vessels and pipettes as sources of contamination

Metal ions can be adsorbed onto the surfaces of glass vessels. If the glass is wetted with an acidic solution, these ions may be released. This risk is particularly present in volumetric flasks which are used for a variety of solutions. In this case, a significant contamination risk can result. Aged glass in particular has a micro-roughness that significantly increases the effect described above.

For this reason it can be advisable NOT to pour solutions that are to be analyzed for trace elements into volumetric flasks made of glass, but directly into the plastic vessels used with the autosampler. The potential volume error caused by this procedure will normally be smaller by magnitudes than the error that can result from carry-over between vessels.

If the use of glass volumetric flasks cannot be dispensed with, it is essential for work in the trace and especially in the ultra-trace range, that the same volumetric flasks are always used for specific solutions. (def?)

In the case of the noble metals and Hg, the use of glass has proven to be advantageous.

Owing to the production process, plastic materials can also contain traces of elements that may be eluted by acidic measuring solutions. Therefore it is advisable to check the purity of the materials of vessels and pipette tips by means of leaching tests.

3 Applications

The chapters dealing with interferences show that samples containing as little matrix as possible have the least risk of interference and thus are the ones which are most easily analyzed correctly. Drinking water, waste water with low levels of contamination or digests of samples of biogenic origin are cases in point. However, the concentrations to be analyzed in drinking water are very low, so that an ultrasound nebulizer is often employed, which can lead to increased excitation related interference. One great advantage of ICP emission spectrometry in particular is that it allows the use of highly matrix loaded measuring solutions with which however the known interferences can occur.

Spectral interference can occur with elevated frequency if the matrix contains one or more elements belonging to the transition metals or lanthanides, since the spectra of these elements are very line-rich. Whether interference occurs or not must be examined in each specific case as part of method development.

In particular the fact that highly matrix loaded samples are used in ICP emission, does also result in a general increase of viscosities and densities of the measuring solution compared with purely aqueous solutions, so that increased sample transport related interference is to be expected, which normally leads to low readings. In some sample types, the surface tension can also change. In particular, this occurs in electroplating baths or the resulting waste water. Here, high readings frequently occur.

In addition, the higher matrix supply leads to increased cooling of the plasma. Potentially, this can result in either an increased or a reduced signal. Finally, easily ionizable elements (such as the alkali and alkaline earth metals) easily release ions into the plasma. As a result, owing to the law of mass action, there is a shift in favor of atoms and their emission lines.

Very high sample weights (from approx. 10 g/L) can affect the plasma torch and the cone. Especially alkali ions lead to accelerated devitrification of the quartz glass, which manifests itself as a milky-white coating on the quartz parts, particularly on the inside wall of the outer tube. High concentrations of noble metals lead to a metal film, which should be removed at regular intervals by means of acid baths.

High sample weights can also lead to clogging of the nebulizer and/or injector. Any deposits forming at the injector tip should be removed. Deposits are an indication that the distance between the bottom of the plasma and the injector tip is too small for the matrix of the solutions being analyzed. In this case, the distance should be increased mechanically, or the auxiliary gas flow should be increased. If none of these measures alone yields the desired success, both measures can be combined. It should be born in mind that the ignitability of the plasma decreases as the distance between injector and plasma increases. Here, it may be necessary to find a compromise.

If the nebulizer becomes clogged repeatedly owing to a very high matrix concentration, it may be advisable to use a better suited nebulizer. Each combination of nebulizer and spray chamber has an optimum nebulizer gas flow and sample pump rate , Thus, these two parameters should be optimized and the values found used in future for this nebulizer/spray chamber combination.

In contrast to AAS, where only a small number of lines is often available, the selection of lines in ICP-OES significantly depends on the accompanying elements. For this reason it is not possible to give a general recommendation regarding a specific wavelength for an element that is to be analyzed. However, for certain areas of application, where the matrix compositions are considered to be known and of small variability, it is possible to indicate lines that are suitable in many cases. Since the recommendations are periodically adjusted as additional applications are developed, these are by their nature best maintained in the operating software.

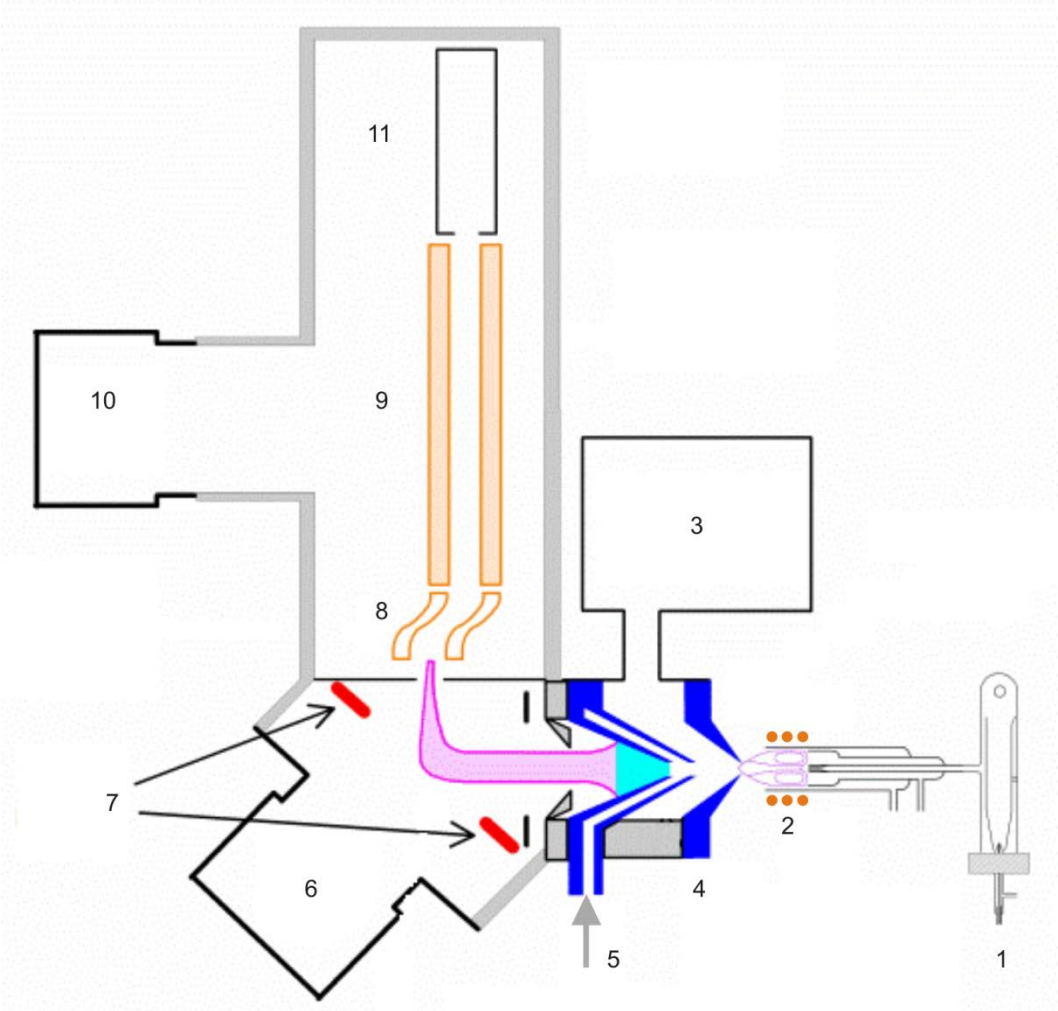
A challenge with regard to accuracy is posed by those elements which at can occur in compounds of different volatility. This primarily applies to non-metals and metalloids. It should be recalled that the efficiency of a conventional nebulizer/spray chamber system is in the region of approx. 2 % for aqueous measuring solutions, while gases enter the plasma quantitatively. Accordingly, a substance of higher volatility will lead to high readings if a non-volatile substance was used for calibration. In this connection, possible reactions in the spray chamber must be taken into account. For example, when iodine is analyzed, iodide and iodate can react to form elemental (gaseous) iodine. Small quantities of the iodide that was used for the calibration, may for instance remain in the spray chamber owing to memory effects and then react with iodate from the digested sample solutions. Another example is the analysis of sulphate as sulphur in drinking water. In drinking water, sulphur is present as sulphate. On the other hand, hydrogen sulphide may be present in non-acidified ground water. This then causes sulphur concentrations to appear to be substantially too high.

Since many metals have a tendency to be adsorbed or even to precipitate in neutral and particularly in alkaline milieu, it is strongly recommended to stabilize aqueous measuring solutions by means of acidification.

4 Alternative methods

4.1 Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)

Like ICP-OES, ICP-MS uses an inductively coupled plasma and components that are needed to maintain the plasma, as well as the sample introduction system.



1	Nebulizer and spray chamber	6	Turbomolecular pump
2	Virtually center grounded coil	7	ReflexION Ion Mirror
3	Rotary vane vacuum pump	8	Curved pre-filters
4	Sampler cone	9	HD Quadrupole mass analyzer
5	Skimmer cone with iCRC	10	Turbomolecular pump
		11	ADD[10] - All-digital detection system

Figure 4-1 Functional principle of ICP-MS

Positively charged ions formed in the plasma at standard pressure are drawn by means of a vacuum pump through a small hole (sampler) in a cone that juts out into the plasma. Immediately behind this, there is a second cone with an aperture (skimmer), behind which a high vacuum is maintained. Only in high vacuum are the ions sufficiently stable to cover the distance to the detector. The positively charged ions are focused by means of an electrical lens or mirror and in most cases separated according to mass/charge ratio. Typically a scanning quadrupole is used; the fields generated by the quadrupole electrodes are varied rapidly so that ions are selectively transmitted and impinge on a detector, which records the

number of ions per mass. This allows quantification of elements as well as isotope determination.

Typically, liquid samples are used; however, with the aid of appropriate accessories it is also possible to introduce solid samples (e.g. laser ablation) or gaseous samples (e.g. hydride and Hg cold vapor methods) into the device.

Advantages of ICP-MS:

- quick multi element method
- excellent sensitivity
- ideal detector for coupling techniques and laser ablation

- Disadvantages of ICP-MS:
- high investment and operating costs
- low tolerance for higher matrix content

4.2 Atomic absorption spectrometry (AAS)

AAS is used to measure the absorption of radiation by an atomic cloud generated from the measuring solution. The atom vapor can be produced inside a flame, in a graphite furnace or in a (heated) quartz cell (Hg and hydride methods).

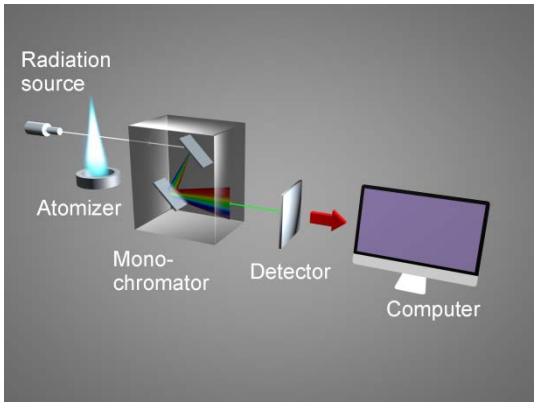


Figure 4-2 Schematic structure of a conventional atomic absorption spectrometer

Line Source AAS (LS-AAS) normally uses hollow-cathode lamps as sources of radiation (a)?, with the cathode consisting of the element to be analyzed. The atomization device (b) ?has the task of producing element atoms in the ground state. After transversing the atomization device, the attenuated radiation passes, in form, through the monochromator (c)? consisting of entrance slit, dispersing element (grating) and exit slit. The grating has the task of spectrally dispersing the radiation And the exit slit selects the analysis line from the total spectrum, rejecting other lines emitted by the source of radiation. The detector (d)? then photoelectrically registers the attenuation of the analysis line.

High-Resolution Continuum Source AAS (HR-CS-AAS) uses a Xenon short-arc lamp as the source of radiation. As in the classic form of AAS, the atomization device has the task of producing ground state atoms. After traversing the atomization device, the attenuated

radiation is passed through a double monochromator, consisting of entrance slit, pre-monochromator prism, intermediate slit and echelle grating monochromator. The intermediate slit has the task of selecting from the spectrum generated by the prism the segment containing the analysis line. This part of the spectrum enters the second monochromator, where it falls on the detector in highly resolved form. The detector consists of a linear CCD array that not only registers the intensity of the analysis line, but also of its spectral neighborhood.

AAS typically uses liquid samples. A special variant (hydride or cold vapor method) uses gases for quantification. The graphite furnace method also enables analysis of solid matter in powdered form.

Advantages:

- low investment and operating costs
- easy operation
- anchored in many standard methods

Disadvantages:

- small linear range
- chemical interference
- Line Source: single element oriented operating principle

4.3 X-ray fluorescence analysis

In X-ray fluorescence analysis, the sample is irradiated with x-rays. Electrons are knocked out of the inner orbitals. As a result, electrons from higher energy levels fall into the vacated orbital. The energy released in this way is emitted as element-specific fluorescence radiation.

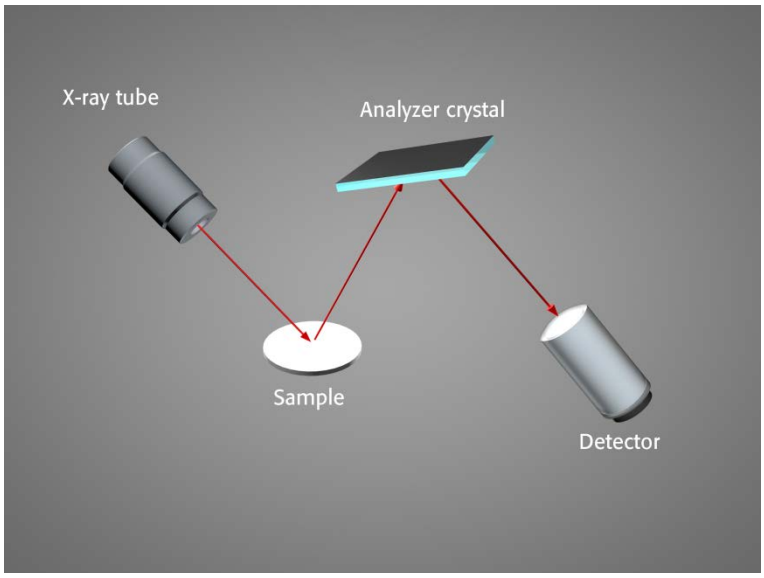


Figure 4-3 Schematic structure of an X-ray fluorescence analyzer

X-ray fluorescence analysis is a typical analytical method for solids.

Advantages:

- non-destructive solids analysis
- no memory effects

Disadvantages:

- matrix adjusted calibration standards required

4.4 Total reflection x-ray fluorescence

In this method of surface analysis, the x-ray beam is directed onto the sample at glancing incidence, so that total reflection occurs.

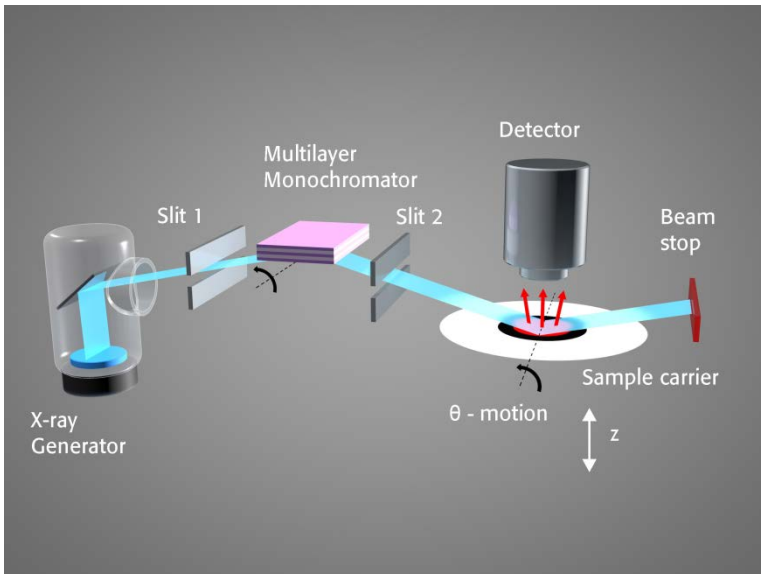


Figure 4-4 Schematic structure of a TXRF Spectrometers

For analysis by total reflection x-ray fluorescence, liquid samples are evaporated onto a carrier.

Advantages:

- small sample volume
- low cost of reagents
- no memory effects

Disadvantages:

- liquid nitrogen required
- only for elements from atomic number 16 upwards

5 Futher References

European Norm: "Water quality – Determination of 33 elements by inductively coupled plasma atomic emission spectroscopy (ISO 11885 : 2007)".

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