

Atom absorption spectroscopy (AAS) FS13:

Determination of main- and trace elements in a seawater sample

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1. Theoretical Introduction

Atomic Absorption Spectrometry (AAS) is an analytical technique for the investigation of the elemental composition of a substance. The technique makes use of the fact that the atoms of each element in the electronic ground state can only absorb a characteristic energy which transfers the atom into the first electronically excited state. Therefore, in order to analyze a particular element of a sample, light that only contains the desired wavelength is needed. The easiest way to achieve this is to use excited atoms of the same element. For example in order to analyze copper, a lamp made from copper is needed. The light from this lamp is partially absorbed when passing through the sample by the corresponding element and the intensity of light reaching the detector is decreased. This decrease is measured and gives the AAS-signal.

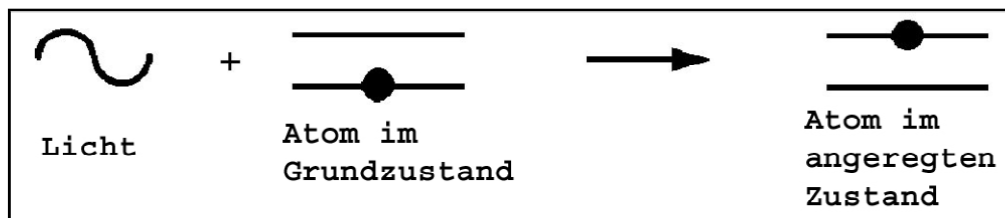


Figure 1 Excitation of an atom by absorption of electro-magnetic radiation.

1.1 Instrument

Basically an AAS unit consists of the following three components: light source, detector and atomizer.

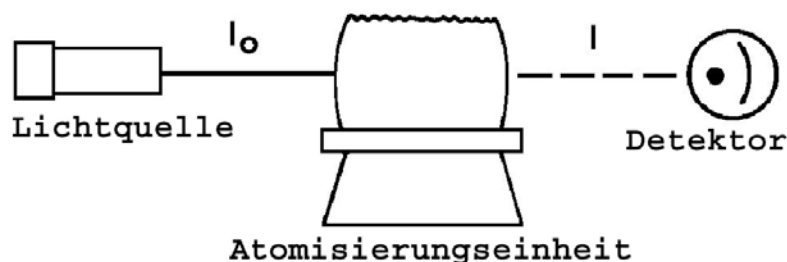


Figure 2 Overview of the setup of an AAS unit.

1.1.1 Light source

In most cases the light source used for AAS is a hollow cathode lamp (HKL). The cathode consists of the desired element. It immediately becomes clear what the great disadvantage of AAS is: for each element a separate lamp is needed. This is not only time consuming but it also means that only one element can be measured at a time.

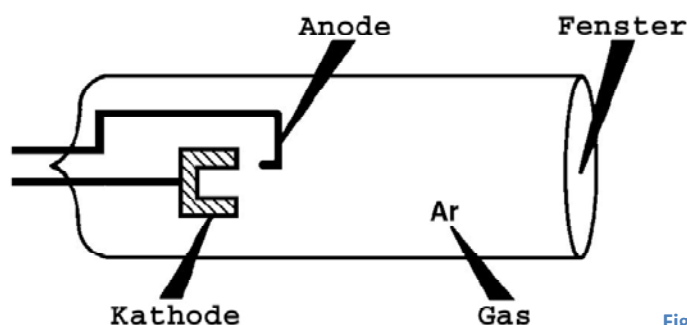


Figure 3 Image of a hollow cathode lamp.

In the lamp a voltage of several hundred volts is applied between the cathode and the anode. The lamp is filled with a gas, usually argon, which gets ionized at the anode. The Ar-cations are accelerated towards the cathode. Cathode atoms are ejected by this sputtering process and in further reactions with the argon ions they get excited. When going back to the ground state they emit the monochromatic light that is used for the excitation of the analyte. The processes in the lamp are shown in Figure 4.

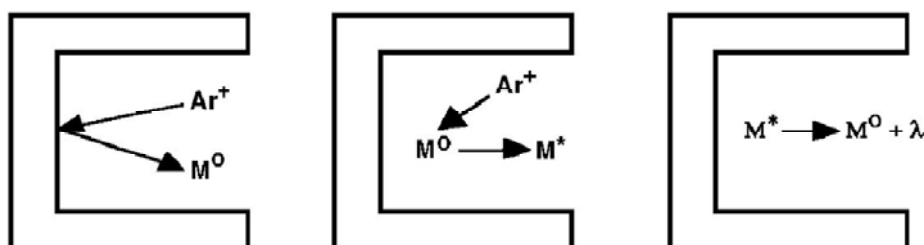


Figure 4 Processes that take place in a hollow cathode lamp.

For elements such as halogens or noble gases no cathodes can be produced. Therefore, electrodeless discharge lamps (EDL) are used. The atoms are transferred into the gas phase and excited by a radio frequency, emitting the characteristic wavelength when going back to the ground state.

1.1.2 Atomisation (Flame)

Gas mixture	Temp. (°C)
air-methane	1850-1900
air-gas	1700-1900
air-hydrogen	2000-2050
air-acetylene	2125-2400
Nitrous oxide-acetylene	2600-2800

Analyte atoms in the gas phase need to be present in the ground state so that they can absorb light. Different gas mixtures result in different flame temperatures. For the measurement it is important that the sample is mixed steadily with the combustion gas. This happens in the mixing chamber (Fig. 5). The

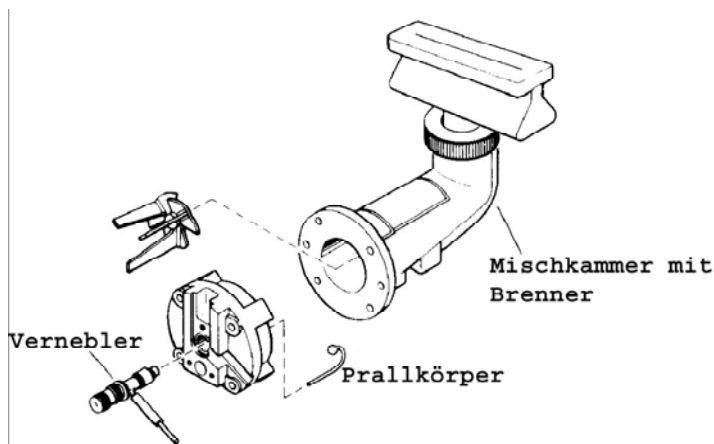


Figure 5 Nebulizer and mixing chamber of an AAS.

solution with the analyte is nebulized and transferred into the flame where the analyte is atomized. The disadvantage of this method is that fairly large amounts of sample are needed, as the efficiency of the nebulizer is only around one percent. The limit of detection for most elements in the lower ppm range.

1.1.3 Optical setup and detector

Since not only light of one wavelength is emitted by the flame, the specific spectral line of the analyte has to be separated from the other wavelengths. This is done by a monochromator placed after the atomizer as shown in Fig. 6. The light enters through a slit, is reflected on a grit and passes through a second slit with typical widths around 0.2-0.7 nm. It finally reaches the photomultiplier which converts the light intensity into a voltage.

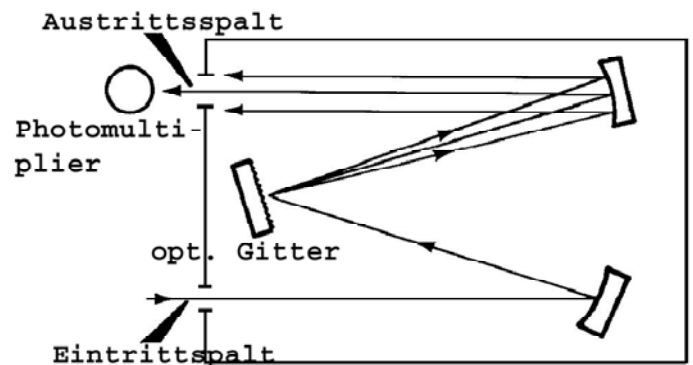


Figure 6 Monochromator and detector.

1.1.4 Instrument design

In modern AAS-instruments the optical setup is more complex. In order to balance fluctuations in the light intensity, so called "two beam devices" are used (Fig. 7). A rotating mirror (chopper) deflects the light alternating through the sample and around the sample. The light of the beam going around the sample is only depending on the intensity of the lamp. Intensity fluctuations can thus be corrected automatically.

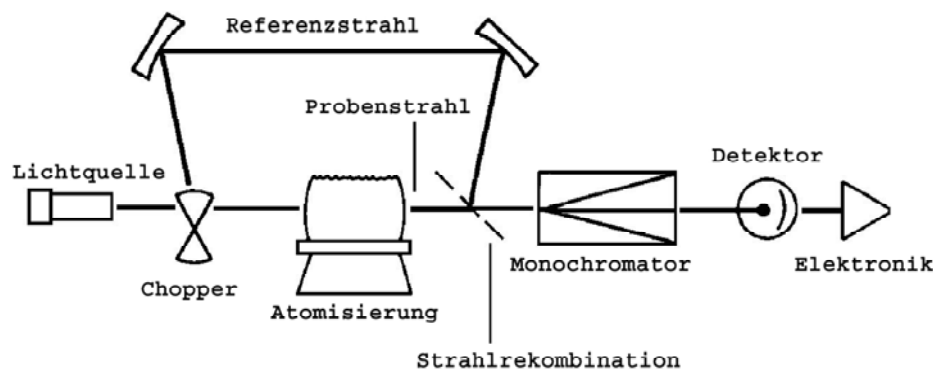


Figure 7 Setup of a two-beam device.

1.2 Definitions

Limit of detection

The definition of the limit of detection (LOD) according to the IUPAC is as follows: from at least 10 measurements of the background the standard deviation is calculated. The LOD is then 3 times the standard deviations above the mean of the background.

Absorbance

Light absorption is normally specified as the absorbance : $A = -\lg(I/I_0)$. I_0 is the intensity of the incident light, I represents the intensity of the light after absorption.

Characteristic concentration

The characteristic concentration C_{char} indicates which concentration is needed in order to result in 1% absorption (=0.0044 absorbance). This value indicates the sensitivity without giving information about the LOD as the signal noise is not taken into account:

$$C_{char} = \frac{C_{std} \left[\frac{mg}{l} \right] \cdot 0.0044}{absorbance}$$

2. Interferences

For (almost) every sample effects can be found that lead to the additional absorption of the characteristic wavelength of the analyte, for example by atoms, molecules or through the scattering of light at incompletely atomized particles. This is called "non-specific" absorption and needs to be distinguished from the specific absorption, otherwise a higher analyte concentration than actually present is measured.

2.1 Background correction with a continuum light source

It is assumed that the background absorption in the vicinity of the measured spectral line is the same as of the spectral line itself. By using a continuum light source (usually a deuterium lamp) with the same light intensity as the HKL the attenuation of the light from the HKL by the background can be estimated from the attenuation of the continuum lamp. The intensity of the continuum light source is attenuated only by the background, while the HKL is absorbed by both - background and analyte. By subtracting these signals, the background corrected signal of the analyte can be extracted. This type of background correction is used primarily for flame AAS.

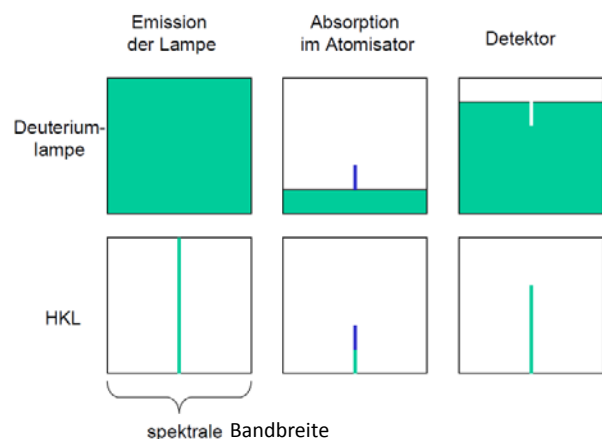


Figure 8 Background correction with a continuum light source.

2.2 Standard addition

There are, however, influences on the signal that cannot be compensated that easily. For example, if the solution is more viscous than the standard used for the calibration, the

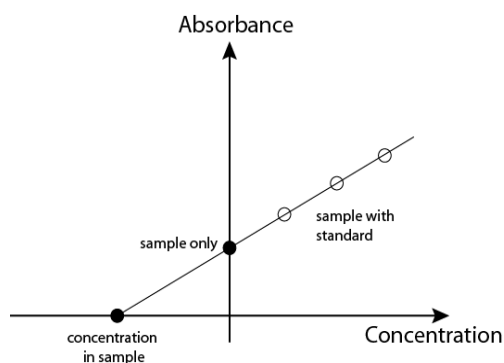


Abbildung 9 Standard addition method.

nebulization process is less efficient and the signals obtained are too low as less analyte is transported to the flame. Effects like this are called **matrix effects**. When working with a calibration curve one possibility is to separate the matrix. But this is often difficult or not possible because the analyte concentration will also be changed. Another possibility is to simulate the matrix, but this can be very complex, too. A good way to avoid the matrix problem is the standard addition method. The unknown concentration of an analyte can be determined by adding several known amounts of the analyte to the sample. The intersection of the resulting straight line with the x-axis gives the desired concentration (Fig. 9).

2.3 Chemical interferences

The best known example of a chemical interference is the determination of calcium when phosphate is present at the same time. The relatively stable calcium phosphate is formed which does not dissociate in the flame and, therefore, no absorption on the Ca-line can be observed. The problem can be solved in different ways. One possibility is to add an element which forms a salt with phosphate that is even less soluble than calcium phosphate, for example lanthanum. Another possibility is to increase the flame temperature in order to atomize the calcium. This can be done with a nitrous oxide- acetylene flame which overcomes the laborious use of lanthanum.

2.4 Ionisation interferences

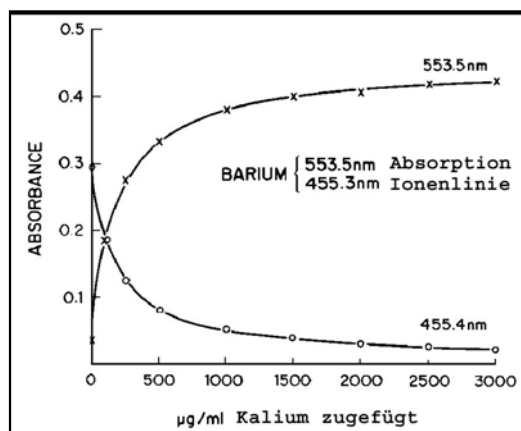


Figure 10 Ionisation interferences.

In hot flames easily ionizable species are often not present in the ground state but are ionized and can be found as cations. Ions have different electronic properties than atoms and, therefore, absorb light of different wavelengths than the neutrals. This makes them undetectable for AAS. The interference can be overcome by the addition of an element that is even easier ionizable. An excess of such an element will result in great amounts of free electrons which will impede the ionization of the analyte. An example is shown in Fig. 10. By adding potassium, barium can be measured.

3. Calibration

AAS is not an absolute measurement method. This means that from the signal no direct conclusion on the analyte concentration can be drawn. Therefore, a calibration is necessary which requires standard solutions with known concentrations for creating a calibration curve.

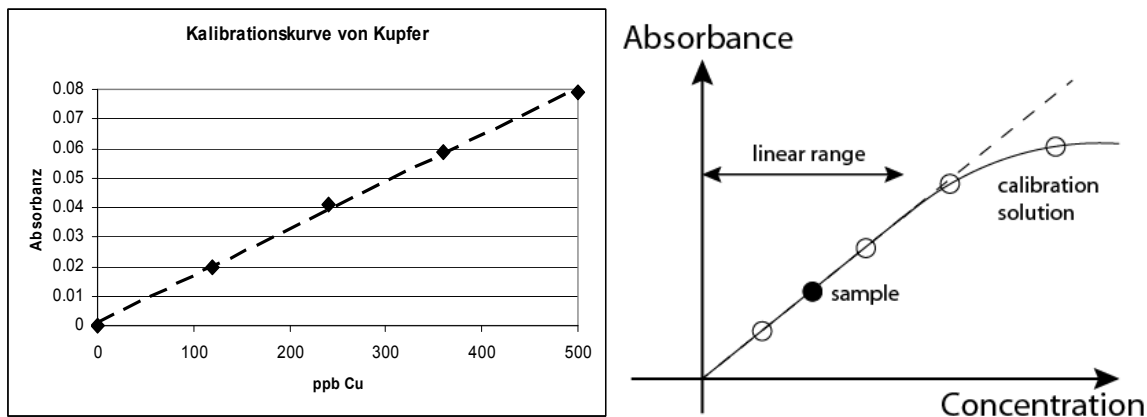


Figure 12 Calibration curve of copper (left). Linear range of the AAS (right).

In principle, there is no linear correlation between the concentration and the AAS signals. The linearity as assumed in the law of Lambert-Beer is a first approximation which is valid for low concentrations only. With higher concentrations a curvature becomes visible. Therefore, when working with AAS it is important to stay in the linear range. Samples should be diluted, if necessary!

The law of **Lambert-Beer** states:

$$I = I_0 e^{-\varepsilon'(\lambda) \cdot c \cdot d}$$

- d:** Thickness of the layer [m]
- I:** attenuated light beam [W]
- I₀:** incident light beam [W]
- ε'(λ):** extinction coefficient/ absorptivity of the absorber (depends on wavelength) [m²mol⁻¹]
- c:** molar concentration of the absorbing species [mol/L]

Mathematical conversion yields: $-\ln\left(\frac{I}{I_0}\right) = \varepsilon'(\lambda) \cdot c \cdot d$

By using the linear relation between the ln and the log $\varepsilon = \log(e) \varepsilon' \approx 0.434\varepsilon'$, we get:

$$-\log\left(\frac{I}{I_0}\right) = \varepsilon(\lambda) \cdot c \cdot d$$

which is equivalent to:

$$A = \log\left(\frac{I_0}{I}\right) = \varepsilon(\lambda) \cdot c \cdot d$$

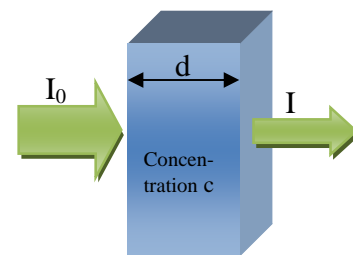


Figure 12 Parallele light passes through a layer of a thickness d. The absorbing solution with a concentration c attenuates the light according to the law of Lambert-Beer.

with the absorbance A . All constant terms can be combined into the sensitivity S and a linear relation between the absorbance and the concentration is yielded:

$$A = S \cdot c$$

From the sensitivity and the standard deviation of the background σ_{BG} the limit of detection can be determined: $LOD = \frac{3 \cdot \sigma_{BG}}{S}$

4. Task: determination of calcium and cadmium in a seawater sample

4.1 Motivation

The elemental analysis of seawater is an analytical challenge especially for trace elements due to its high salt concentrations. Strategies for the quantification of main and trace elements shall be developed using the example of calcium and cadmium. The goal of this lab course is to get familiar with the advantages and limitations of AAS and to compare the results with other methods for cation determinations.

4.2 Process of the lab course

- Theoretical introduction:
There will be a repetition of the theory before the practical part starts. The better prepared you are, the easier and shorter this part will be. In case you have questions about the theory, make a note so that we can discuss this before the experiments start.
- Discussion of the analytical problem and the analytical strategies
- Preparation of samples and calibration standards
- Measurements

4.3 Report

The report should contain a brief theoretical introduction, an experimental section and the results. All results have to be reported with the uncertainty (95%-limit) and a short discussion about how the errors were obtained.

4.4 Attestation condition

- repetition of the theory before the experimental part
- punctuality
- compliance with the laboratory rules and regulations (see laboratory safety concept D-CHAB)
- handing in the report and if necessary correcting it