Atom absorption spectroscopy (AAS) FS12:  
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 an element composition determination. It is exploited that the atoms of each element with the electronic ground state can absorb a characteristic energy. You get this in the first electronically excited state. To view a sample on a particular item needs to be able to analyze it such light, which only contains the desired wavelengths. The easiest way is to use excited atoms of the same element. For example, a Copper needs to analyze it a lamp, which contains copper. The light from this lamp partially absorbed by the element in the sample and the intensity of light at the detector weakens. This decreasing is measured and gives the signal.

![Diagram of AAS instrument](image)

1.1 Instrument

Basically there is an AAS unit from the three components: light source, detector atomizer.

![Diagram of AAS components](image)

1.1.1 Light source

As a light source is in the normal case, a hollow cathode lamps (HKL) is used. The cathode consists of the desired element. Here is visible also the great disadvantage of AAS, because of it takes for each element a separate lamp. This is not only cumbersome, but it also means that several elements cannot be measured simultaneously.
The lamp is inserted between the cathode and anode where voltage of several hundred volts is created. At the anode ionized argon atoms are accelerated to the cathode. Upon penetration, they free atoms, which further excited by Argon cations. In the transition from the excited state to the ground state element specific light is emitted, which is used for the excitation of the analyte. The processes in the lamp are shown below.

For elements such as halogens or inert gases, from which no filaments can be formed, EDL lamps are used (Electrodeless Discharge Lamp). The atoms are in the gas phase by a radiofrequency field stimulated and emit when falling back into the ground state radiation characteristic.

1.1.2 Atomisation (Flame)
In order to be able to absorb light, the analyte atom in the gas phase in the electronic ground state is available. The solution with the analyte is nebulized and the aerosol into a flame is transferred, where the analyte is atomized. There are different gas mixtures used to the optimum temperature to obtain flames.

<table>
<thead>
<tr>
<th>Gas mixture</th>
<th>Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air-methane</td>
<td>1850-1900</td>
</tr>
<tr>
<td>Air-gas</td>
<td>1700-1900</td>
</tr>
<tr>
<td>Air-hydrogen</td>
<td>2000-2050</td>
</tr>
<tr>
<td>Air-acetylene</td>
<td>2125-2400</td>
</tr>
<tr>
<td>Nitrous oxide-acetylene</td>
<td>2600-2800</td>
</tr>
</tbody>
</table>

The disadvantage of this method is the relatively large samples needed, since the efficiency of the spray only around one percent. The detection limits for most elements in the lower ppm range.
1.1.2 Optic and Detector
To select only a specific spectral line to measure the light after the atomizer into a monochromator (shown below) and split the desired wavelength by a gap (0.2-0.7 nm spectral bandwidth) to the photomultiplier steered which the light intensity into a voltage converter.

1.1.3 Instrument design
Modern AAS-optic devices is somewhat more complicated that described structure. To avoid fluctuations in lamp intensity offset usually two-beam devices are used. In a rotating mirror deflects the light of the HKL alternately through the sample or the sample around. The intensity of the light beam, which makes the sample is kept around, it just depends on the lamp intensity. Intensity fluctuations are corrected automatically by the device.
1.2 Definition

Limit of detection
The limit of detection (LOD) is defined according to IUPAC as follows: From at least 10 measurements of the blank is the standard deviation calculated. The LOD is 3 standard deviations above the mean of the blank.

Absorbance
Light absorption is determined as Absorbance: \( A = \frac{-\log (I / I_0)}{1} \). \( I_0 \) is the intensity of incoming light, while \( I \) is the intensity of light after the absorption.

Characteristic Concentration
The characteristic concentration indicates how high the concentration must be reduced by 1% absorption to generate (= 0.0044 Absorbance). This value indicates the sensitivity and makes no statement about the detection limit, because the signal noise in the calculation is not taken into account.

\[
Char.\text{Conc.}(\text{mg} / l) = \frac{\text{Conc. Std.}(\text{mg} / l) \times 0.0044}{\text{Measured absorbance}}
\]

2. Interferences
For (almost) every sample, there are effects, which in addition to the analyte sought to an additional absorption by atoms and molecules or scattering of light in incompletely atomized particles lead. This must be non-specific absorption of the specific distinction can be, otherwise a higher analyte concentration is measured as actually present in the sample.

2.1 Background correction with continuum light source
It is assumed that the substrate absorption in the vicinity of the measured spectral line is the same size as the place where the line itself. If the intensity of continuum radiation source (usually a deuterium lamp) is the same as the intensity of the HVAC, it may be from the weakening of the continuum radiation can be estimated how much the intensity of HKL by the underground weakened. The intensity of the continuum radiation by the analyte itself weakened only slightly (<1%), because the used bandwidth of the continuum radiation with 0.2-0.7 nm is much broader.
than the spectrum line width (0.002 nm). This type of background correction is used primarily in the flame AAS used.

2.2 Standardaddition

However, there are influences on the signal, which is not so easy to be compensated. For example, if the solution is more viscous than the standard, for which the calibration is needed, so does the spray less effective and it is too deep measured signal because less analyte in the flame is transported. These effects are generally described as a matrix effects. If you want to work a calibration curve, there are only the possibilities, off the matrix, which is often difficult or even impossible because the analyte is changed, or the matrix can be simulated.

However, there is a good way to address the problem of the matrix to avoid the standard addition method. An unknown concentration of an analyte (M0) is measured by the sample to be determined (Y0) several known quantities of analyte admits (Y1, Y2, Y3). The intersection of the straight line obtained with the x-axis gives the desired concentration.
2.3 Chemical Interferences

The best known example of a chemical interference, the determination of calcium, phosphate whilst still exists. It forms the relatively stable calcium phosphate, which is in the flame is not dissociated and therefore no absorption at the Ca-line makes. The problem can be solved several ways.

For one can be attached to an element which is supplied with a heavy soluble phosphate salt forms when the calcium. Lanthanum fulfilled this purpose very well. On the other hand, the flame temperature increases, because obviously the temperature is not sufficient to atomize everything calcium. It is now also standard with a nitrous oxide-acetylene flame is made, what the circumstances the use of lanthanum unnecessary.

2.4 Ionisation Interferences

Easily ionizable species are especially in hot flames often not in the ground state, but as cations before. The ions have different electronic properties and therefore absorb light at wavelengths other than the neutral atoms and are therefore not measurable with AAS. The interference can be configured by the content more easily ionizable elements to be monitored. A surplus of a very easily ionizable element generates a lot of free electrons, which prevents the analyte is ionized. An example is shown below: Barium can be measured by an excess of potassium is added.

![Graph of Barium Absorption](image)

3. Calibration

The AAS is not an absolute measurement method. This means that a signal is not measured directly on the analyte can be closed. It is always a calibration is necessary. This assumes that the standard solutions with known concentrations are available, a calibration curve incorporated.
Between the concentrations and the signals are, in principle, no linear dependence. The linearity, as in the Lambert-Beers’s law is assumed, is only a first approximation, which at low concentrations can be applied. With increasing concentration, a visible curvature. For AAS measurements is therefore to ensure that you always in the linear range, samples are too concentrated, where appropriate, diluted.

Lambert-Beer: \[ I = I_0 \cdot e^{-\kappa/l\cdot n} \]

It gives a linear relationship between the absorbance \( A \) and the particle density \( n \).

\[ A = -\lg \left( \frac{I}{I_0} \right) = 0.434 \cdot \kappa \cdot l \cdot n \]

All terms are constants in \( S (\text{=} \text{sensitivity}) \) and summed to obtain a linear relationship between the Absorbanz and concentration. In addition, the particle density, which by a dilution factor with the concentration of this site, replaced by this. The dilution factor is thus also a factor in the constant:

\[ A = S \cdot c \]

The sensitivity can be used in conjunction with the standard deviation of the blank, the limit of detection (LOD) to be determined.

\[ LOD = \frac{3 \cdot SD(Blank)}{\text{Sensitivity}} \]

\( I \) \( \text{escaping radiation power [W]} \)
4. Task: Determination of calcium and cadmium in a seawater sample.

4.1 Motivation
The elemental analysis of seawater is an analytical challenge due to its high total salt concentrations, especially for trace elements. Strategies for quantification of main- and trace elements in sea water should be worked out on the example of calcium and cadmium. The goal is to get familiar with the advantages and limitations of AAS and to compare the results with other methods for cation determination (e.g. polarography).

4.2 Process of Practicum
• Theoretical introduction
The theory is shortly before the trial reconditioned. The better prepared you are, the easier and shorter this part.
If you have questions about the theory, then you write it best, so we are in the preliminary experiment on it can be.
• Discussion of the problem and the analytic approach
• Preparation of samples and standards
• Measurements

4.3 Report
The report is to attempt a brief theoretical introduction, an experimental section and the results included. All results must be compatible with the uncertainty (95% limit) may be indicated.

4.4 Attestation condition:
• Theory is repeated before the internship
• Punctual appearance
• observance of the Labor Code (see Laboratory Safety Concept D-CHAB)
• Report, and, if necessary, corrected