Determination of heavy metals in natural waters and sediments by high resolution-continuum source flame and graphite furnace atomic absorption spectrometry

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Reviewers:

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Dedicated to:

My mom Nurasni, my wife Noormaisyah

and our children

Nada & Syifa’

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Abstract

The determination of Cu and Fe in natural water samples and water certified reference material water CRM 1643e using Line Source Flame Atomic Absorption Spectrometry (LS FAAS) and High Resolution Continuum Source Atomic Absorption Spectrometry (HR-CS AAS) with the graphite and the flame techniques in this study showed very good results. The use of the matrix modifiers proved to be very helpful for eliminating the interferences from the matrix. In general, the filtration of sample did not result in significant differences, but the addition of HNO_3 to the sample lead to a significant increase of the analyte absorbance, whereas the addition of H_2O_2 did not cause any increase.

The use of HR-CS AAS with the graphite and the flame techniques as well as the LS FAAS for the determination of the relevant metals (Cr, Fe, Ni, Cu, Cd and Pb) in the sediment standard reference materials and in the SETOC sediment samples using microwave assisted dissolution was described. The slurry sampling analyses and the direct solids sampling HR-CS GFAAS were also performed in this work, namely for the case of the three sediment certified reference materials IMEP-14, CRM-320 and PACS-1. Two SETOC sediment samples were used as real samples. No stabilizer was used in the slurry technique. Therefore, the slurry technique was only applied to the sample with a very fine particle size (37-125 µm). Analyses of sediment samples with the slurry sampling and direct solids sampling with matrix modifiers $NH_4H_2PO_4$, $Mg(NO_3)_2$, $Pd/Mg(NO_3)_2$ and NH_4F were also performed. The appropriate matrix modifiers for the different elements were determined.

The results showed that the optimum temperature program and matrix modifier varied for each analyte. Influences of the drying treatment at a temperature of ±110ºC during 5 hours for sediment CRMs decreased the statistical errors for all elements in all CRMs. The percentage of error in the sample without drying is slightly higher and was found to be in the range of 1 to 19% and 1 to 14% in the dried sample. The weight of samples in the direct solids sampling technique has an impact on the analysis results. Increasing amounts of sample which are introduced into the graphite furnace tend to produce higher measurement errors. These errors came from the memory effects and incomplete atomization of the sample. For all analytes in CRMs the recoveries were above 80%, except for Ni in the case of the slurry technique. Although the same procedure was used for each CRM sample, the recovery of Ni was different. For Ni in IMEP-14 and PACS-1, a recovery of 60–66% was obtained, whereas, for

CRM-320, a recovery of 101% was found. The recoveries for Cr, Fe, Ni, Cu, Cd and Pb in CRMs were found to be in the range of 81–105%, 60–129% and 81–107% by the dissolution sampling, the slurry sampling and by direct solids sampling technique, respectively.

Zusammenfassung

Die Bestimmung von Cu und Fe in natürlichen Gewässern und im zertifizierten Referenzmaterial CRM 1643e mittels Linienstrahler Flammen-Atomabsorptionsspektrometrie (LS FAAS) und High-Resolution Continuum Source Atomabsorptionsspektrometrie (HR-CS AAS) mit Graphitrohr und Flamme ergab sehr gute Ergebnisse. Die Verwendung von Matrix-Modifiern erwies sich sehr hilfreich für die Beseitigung von Störungen aufgrund der Matrix. Die Filtration von Proben lieferte im allgemeinen keine signifikante Unterschiede, aber die Zugabe von HNO_3 an der Probe führte zu einer signifikanten Erhöhung der Absorption bei den Proben, wobei die Absorption bei der Probe durch die Zugabe von H_2O_2 nicht erhöht wurde.

Die Anwendung von HR-CS AAS mit Graphitrohr und Flamme und LS FAAS zur Bestimmung der relevanten Metalle (Cr, Fe, Ni, Cu, Cd und Pb) in Sediment Standard Referenzmaterialien und in den SETOC Sedimentproben nach Mikrowellenassisteirten Aufschluß verbesserte die Ergebnisse. Analysen von Slurries der Proben und direkte Feststoff analysen mit der HR-CS GFAAS wurden für die drei zertifizierten Referenzmaterialien IMEP-14-, CRM-320 und PACS-1 in dieser Arbeit durchgeführt. Zwei SETOC Sedimentproben wurden als reale Proben analysiert. In der Slurry-Technik wurde kein Stabilisator verwendet. Daher wurde der Slurry-Technik nur für die Probe mit einer sehr feinen Korngröße (37 bis 125 µm) verwendet. Die Analysen von Sedimentproben mittels der Slurry-Technik und mit direkter Feststoff-Probenahme wurden auch unter Verwendung von Matrix-Modifiern $NH_4H_2PO_4$, $Mg(NO_3)_2$, $Pd/Mg(NO_3)_2$ und NH_4F durchgeführt. Für die verschiedenen Elemente wurden die geeigneten Matrix-Modifiern ermittelt.

Die Ergebnisse zeigen, dass das optimale Temperaturprogramm und der optimale Matrixmodifier für jeden Analyten unterschiedlich waren. Die Auswirkungen von der Trocknung bei einer Temperatur von ± 110 ° C während 5 Stunden führte zu geringeren statistischen Fehlern für alle Elemente bei allen CRMs. Der prozentuale Fehler bei den Proben ohne Trocknung ist etwas größer (1–19%) als bei den getrockneten Proben (1–14%). Das Probengewicht hat bei der direkten Feststoff-Probenahme Auswirkungen auf die Analyseergebnisse. Steigende Mengen an Probe, die in das Graphitrohr eingebracht werden, führen tendenziell zu höheren Messfehlern. Diese Fehler resultierten aus den Memory-Effekten und aus einer unvollständigen Atomisierung der Probe. Für alle Analyten betrug die

Wiedergewinnungsrate bei den CRMs über 80%, außer für Ni bei der Slurry-Technik. Obwohl das gleiche Verfahren für jede CRM Probe verwendet wurde, ergab zu sich für die Wiedergewinnungsraten bei Ni verschiedene Ergebnissen. Für Ni in IMEP-14-und PACS-1 wurde Wiedergewinnungsraten von 60 und 66% erhalten, während für CRM-320 die Wiedergewinnungsrate von 101% war. Die gesamten Wiedergewinnungsraten für Cr, Fe, Ni, Cu, Cd und Pb in CRM waren nach Aufschluß jeweils im Bereich von 81–105% mit der Slurry-Probenahme 60–129% und mit der direkten Feststoff-Probenahme 81–107%.

Chapter 1. Introduction

1.1 Environmental analysis

Environmental analysis is very important, especially with respect to the presence of contaminants and toxic elements. As a matter of fact every form of human activity is a potential source of pollution and accordingly, all the compartments of the earth's atmosphere, the hydrosphere and the geosphere have the potential to be exposed to pollution. In the environment, materials are constantly transported between these three spheres of the environment. At each stage of the transportation, the concentration of the compounds will be changed either by phase transfer, dilution or preconcentration. Both the atmosphere and the hydrosphere are major routes for the dispersal of compounds. Dispersal of a pollutant in water or in the atmosphere will inevitably lead to a dilution of the pollutant. The effect of a chemical compound in the environment is related directly to its concentration, so the dispersing process not only will spread out the pollutant but it also might have a lower effect away from the source. This would especially be the case when we consider that most pollution is broken down by microbial attack, photochemical or other degradation during the displacement processes, and so there would be little chance of building up the concentrations for toxic levels [**1**,**2**]. The processes also are related to the low solubility of high-molecular-mass organic compounds in water together with the hydrophobicity of organic compounds which do not contain polar groups. Indeed, here organic materials are precipitated in water but they also will adhere to any available solid material found in sediments [**3**].

Trace metals contaminations in soil and sediments are a far more serious problem than either air or water pollution because here pollutants are usually tightly bound and they may persist for a long period, depending on the conditions. Moreover, the soil is an important geochemical sink which rapidly accumulates heavy metals and usually depletes them very slowly by leaching into the ground water aquifers or bioaccumulating into plants. Uptake, translocation, and accumulation of potentially toxic trace metals in plants widely differ depending on the type of soil, the pH, the redox potential, the moisture and the organic contents. Plants grown on soils which are either naturally enriched or highly contaminated with some heavy metals can bioaccumulate to levels, which are high enough to have toxic effects on animals or human beings who consume them. So the element determinations in soil and sediment samples more reliably trace the pollution than water, since sediments can be considered to be a record in terms of environmental changes [**1**].

The metals which are of most environmental concern are the transition metals. These elements often enter the environment in an insoluble form as a result of industrial waste, deposition discarding manufactured products, or as parts of naturally occurring mineral deposits. Deposition from the atmosphere often occurs in the form of insoluble salts. However, the solubility of metals increases with a decrease in pH. Some of the problems are related to the fact that acid rain causes leaching of toxic metals from the soil. Solubilization is often enhanced by the formation of complexes with organic materials such as humic and fulvic acids produced by the decay of organic material [**1**].

Accurate determinations of some elements are not an easy task, due to high risks of sample contamination, loss of the analyte, and the presence of structures in the sample matrix which are difficult to be dissolved. This should be carefully considered in the preparation of the samples [**3**]. However, a better homogeneity is attained for the analytes in an aqueous sample and accordingly we generally aims at performing a sample decomposition process. The demand for rapid analyses tends to simplify the analytical process and asks for sophisticated instruments in order to minimize or even avoid sample decomposition. Here, direct solid analysis methods were developed such as slurry sampling for powders.

The identification of contaminants and the establishment of their toxic level in soils are very important and need our attention nowadays. The requirements for the determination of trace and ultratrace elements ask for improvements in instrumental sensitivity and elemental coverage. For environmental pollution studies, flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), and inductively coupled plasma optical emission and mass spectrometry (ICP-OES and MS) are the most commonly used methods for elemental determinations in environmental analysis in the case of soils and sediments [**4**]. In the analysis of a variety of complex environmental samples we needs to consider the interferences and the type of sample. A fundamental problem in the determination of traces of heavy metals in the environment is the optimization of both the sample treatment and the measurement methods so that the results really represent the real values for the analytes in the sample [**5**].

Elemental speciation also is a concern in the analysis of the environmental samples. This is because the various species of an element can have a totally different effect in terms of essentiality or toxicity on our ecology system as a result of their differences in physico-chemical properties. Elemental speciation in this sense still represents a great challenge, because of the low concentration of the species, their poor stability and the matrix interferences. In addition, some aspects have to be solved, such as understanding their role in physiological and pathological processes, the availability and practicability of analytical methods and finally considerations for sampling [**6**,**7**]. Elemental speciation often makes use of a chromatographic method in order to separate the individual species prior to their detection. A number of high performance liquid chromatography methods coupled online with ICP-MS detection was developed for the study of the speciation of trace metals of environmental interest [**8**,**9**].

1.1.1 Problematic interferences in the determination of Cd, Cr, Cu, Fe, Ni and Pb in environmental samples

A complete environmental analysis can be very complex, involving effects of physical, chemical, biological and instrumental factors. Various methods for the determination of environmentally relevant substances in the environment as well as elemental determinations themselves may suffer from interferences despite the use of sophisticated tools. The interferences in the determination of Cd, Cr, Cu, Fe, Ni and Pb in environmental samples depend on the method being used. When solid samples are analyzed by atomic absorption spectrometry, we often have to bring the metals in solution or to dissolve the samples through some form of sample preparation. Solvents, reagents, glassware and other sample processing hardware may cause contamination of the samples. Therefore the handling and cleaning of all the tools before their use must be in accordance with the analytical requirements.

The determination of some elements by flame atomic absorption spectrometry (AAS) may be prone to interferences when the flame is not sufficiently hot to dissociate the molecules, as it is the case for phosphate interferences with magnesium, or when the atoms are immediately ionized. These phenomena are known as chemical interferences. Chemical interferences may be eliminated by separating the metal to be determined from the interfering materials with the aid of complexing agents. Whereas the complexing agents are primarily employed to increase the sensitivity of the analysis, they also may be used to eliminate or to reduce interferences.

In analyses by AAS spectral interferences often occur, when the analytical lines of other elements fall within the width of the absorption line of the element of interest. The results of the determination will then be erroneous as a result of the contribution from the interfering element to the atomic absorption signal. Interferences can also occur when a resonant line of another element in a multielement lamp, or from a metal impurity in the lamp cathode, falls within the slit bandpass, provided the other metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width [**3**,**10**,**11**]. Furthermore, physical matrix effects, resulting from variations in the physical characteristics of the sample such as particle size, homogeneity, surface conditions and moisture content may affect the accuracy of the measurements. The interferences caused by contaminants such as humic acids also may cause a problem. The presence of high concentrations of dissolved solids in the sample may result in interferences by non-element specific absorbance such as light scattering [**1**,**12**].

Meanwhile, interferences in elemental determination by ICP-MS also often are found both in the determination of the elements and in speciation analysis. Elemental determinations by ICP-MS and speciation analysis can be used in complement to confirm species recovery and to determine mass balances. Interferences in ICP-MS unlike in AAS and ICP-AES, may be related to voltages applied to the ion lenses of the ICP-MS [**13**]. Further interferences may be caused by polyatomic ions. In the case of Se e.g. Ar dimers cause some interference with some isotopes of the element Se. When determining ^{52}Cr interferences from the isobars ^{40}Ar^{12}C^{+} and ^{35}Cl^{16}OH^{+} may occur, because of the limited resolution [**14**,**15**].

1.1.2 Methods for elemental determinations

In analytical chemistry many methods are known to be of use to determine the elements in various samples. The respective instruments are produced and used nearly all over the world. These instruments continue to become more sophisticated so as to meet the analytical requirements. A brief survey of these methods is given below.

1.1.2.1 Atomic spectrometry

In atomic spectrometry the measurement is based on the interaction between matter and electromagnetic radiation. Electromagnetic radiation covers about six orders of magnitude in frequency or wavelength.

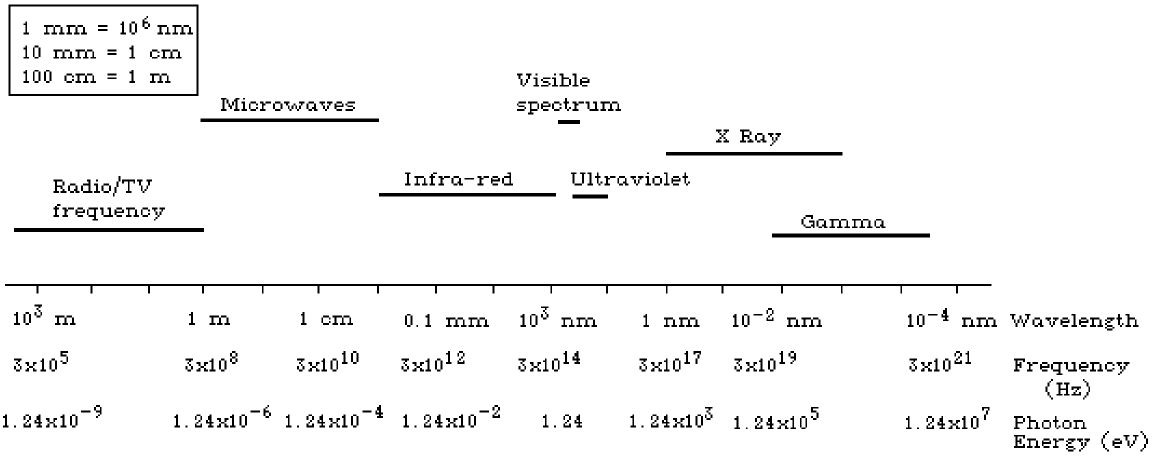


Fig.1 Electromagnetic spectrum with types of radiation.

Atomic spectrometry primarily makes use of the measurement of the energy absorbed or emitted when atoms or molecules change from one distinct energy level to another. Each such change involves a fixed amount of energy, which as a package is called a quantum or photon. While these photons can be considered as elemental particles, it is often convenient to think of them as having a wave character with specific frequencies and wavelengths which are linked to their energies according to Planck's law:

$$E = h\nu \tag{1}$$

E is the amount of energy (erg s), *h* Planck's constant ($6.62 \cdot 10^{27}$erg s), ν is the frequency (s^{-1}). Frequency (v) and wavelength (λ) are inversely related as:

$$c = \lambda v \tag{2}$$

c is the velocity of light in vacuum, ($3 \cdot 10^{10}$ cm s^{-1}).

In the optical absorption spectrometry the radiation from a tungsten lamp or a hydrogen or deuterium arc passes through a monochromator. The selective wavelength is sent through the sample to a detector. The amount of radiation absorbed is proportional to the concentration of atoms or molecules being determined. If the intensity of the radiation entering the sample is I_0, and the intensity after passing the absorption reservoir is I:

the transmittance is $T = I/I_0$ (3)

and the % transmission = $100 \cdot T$ (4)

The absorbance (A) = $\log_{10} (I_0/I) = - \log_{10} T = a . b . c$ (5)

A = a . b . c is the Bouguer-Lambert-Beer's law. According to Beer's law the absorbance is proportional to the concentration and this is particularly important for chemical analysis.

The energy level in atomic spectrometry deals with changes in the atom electron energies. The radiation is treated more like high-energy particles than like waves. Atomic spectrometry methods in this way distinguish the particles by their energies. Atomic spectrometry includes emission, absorption and fluorescence spectrometry. Emission spectrometry occurs when radiation is emitted by matter, absorption spectrometry take place when radiation is absorbed by matter and in fluorescence spectrometry the radiation absorbed in part is emitted again almost immediately, at a longer wavelength or with lower energy.

Further, at lower energies, microwaves, radiowaves and magnetic resonance radiation are used, which give information about the molecular structure because some atomic nuclei have a nuclear spin. Those are primarily ordinary hydrogen (^{1}H, protons) and secondarily ^{13}C, ^{19}F, and ^{31}P. Typically nuclear magnetic resonance (NMR) spectrometry uses a fixed radio frequency under a careful control of the magnet current. Because individual protons in a molecule are influenced by adjacent protons, they absorb at different magnetic fields and an NMR spectrum is produced [**16**].

Meanwhile, mass spectrometry is included in the spectrometry but it does not involve electromagnetic radiation. The spectrum here contains signals at different masses of atoms molecules or fragments of molecules. The sample substance is introduced and broken down into charged fragments by electron impact or chemical ionization under vacuum. The fragmentation is accelerated when applying a voltage and the ions passing through a mass analyzer are separated according to their ratio of mass to charge.

1.1.2.2 Electrochemical methods

In electrochemistry voltammetry is very important and it developed from the discovery of polarography in 1922 by the Czech chemist Jaroslav Heyrovsky, for which he received the 1959 Nobel Prize in chemistry [**5**]. The common characteristic of all voltammetric techniques is that they involve the application of a potential (E) to an electrode system and a monitoring of the resulting current (i) flowing through the electrochemical cell. In many cases the applied potential is varied or the current is monitored over a period of time (t). Thus, in all voltammetric techniques the measurement signal is some function of E, i, and t. Voltammetric techniques are considered as active techniques opposed to passive techniques such as potentiometry. Indeed, the applied potential forces a change in the concentration of an electroactive species at the electrode surface by electrochemical reduction or oxidation [**10**].

The analytical advantages of the various voltammetric techniques include excellent sensitivity with a very large useful linear concentration range for both inorganic and organic species (10^{-12} to 10^{-1} M), a large number of useful solvents and electrolytes, a wide range of temperatures, short analysis times (seconds), the sensibility of a simultaneous determination of several analytes, the ability to determine kinetic and mechanistic parameters, a well-developed theory and thus the ability to reasonably estimate the values of unknown parameters and the ease with which different potential waveforms can be generated and small currents can be measured.

The electrochemical cell, where the voltammetric experiment is carried out, consists of a working (indicator) electrode, a reference electrode, and usually a counter (auxiliary) electrode. In general, in the interface between the electrodes a charge can be transferred or its effects felt. Because the reaction or transfer of interest is taking place at the working electrode, we refer to the working electrode, when we speak of the electrode. The reduction or oxidation of a substance at the surface of a working electrode at the appropriate applied potential, results in a mass transport to the electrode surface and the generation of a current. Even though the various types of voltammetric techniques may appear to be very different at a first glance, their fundamental principles and applications are based on the same electrochemical theory [**5**,**10**].

In voltammetry, the reactions between the applied potential and redox current are described by several well-known laws. The applied potential controls the concentrations of the redox species at the electrode surface ($c_O{}^0$ and $c_R{}^0$) and the reaction constant (k^0), is described by the Nernst or Butler–Volmer equations, respectively. In the cases where diffusion plays a decisive role, the current resulting from the redox process (known as the Faraday current) is related to the material flux at the electrode–solution interface and is described by Fick's law. The interaction between these processes is responsible for the characteristic features observed in the voltammograms of the various techniques. For a reversible electrochemical reaction (that is a reaction, which is so fast that equilibrium is always reestablished as changes are made), which can be described by $O + ne^- \rightleftharpoons R$, the application of a potential E forces the respective concentrations of O and R at the surface of the electrode (that is, $c_O{}^0$ and $c_R{}^0$) to a ratio in compliance with the Nernst equation:

$$E = E^{\circ} - \frac{RT}{nF} ln \frac{C_R 0}{C_O 0} \qquad (6)$$

Here R is the molar gas constant (8.3144 J mol$^{-1}K^{-1}$), T is the absolute temperature (K), n is the number of electrons transferred, F is the Faraday constant (96,485 C/equiv) and E^0 is the standard reduction potential for the redox couple. When the potential applied to the electrode is changed, the ratio $c_R{}^0/c_O{}^0$ at the surface will also change according to Eq. (6). When the potential is made more negative the ratio becomes larger and O is reduced, whereas when the potential is made more positive the ratio becomes smaller and R is oxidized.

For some techniques it is useful to use the relationship that links the variables current, potential, and concentration:

$$\frac{i}{nFA} = k^0\{c_O{}^0 \exp[-\alpha\theta] - c_R{}^0 \exp[-(1-\alpha)\theta]\} \qquad (7)$$

In this so called Butler-Volmer equation q = $nF(E - E^0)/RT$, k^0 is the heterogeneous rate constant, a is known as the transfer coefficient and A is the area of the electrode. This relationship allows us to obtain the values of the two analytically important parameters, i and k^0.

Finally, in most cases the current flow also directly depends on the flux of material to the electrode surface. When new O or R is created at the surface, the increased concentration provides the force for its diffusion towards the bulk of the solution. Likewise, when O or R is destroyed, the decreased concentration promotes the diffusion of new material from the bulk solution. The resulting concentration gradient and mass transport is described by Fick's law, which states that the flux of matter (F) is directly proportional to the concentration gradient:

$$\Phi = -AD_0(\partial C_0 - \partial_x) \qquad (8)$$

Here D_O is the diffusion coefficient of O and x is the distance from the electrode surface. An analogous equation can be written for R. The flux of O or R at the electrode surface controls the rate of reaction, and thus the Faraday current flowing in the cell. In the bulk solution, concentration gradients are generally small and ionic migration carries most of the current. The current is a quantitative measure of how fast a species is being reduced or oxidized at the electrode surface. The actual value of this current is affected by many additional factors and most importantly by the concentration of the redox species, the size, shape and material of the electrode, the solution resistance, the cell volume and the number of electrons transferred.

In addition to diffusion, mass transport can also occur by migration or convection. Migration is the movement of an ion in the presence of an electric field. In voltammetry, the use of a supporting electrolyte at concentrations of 100 times that of the species being determined eliminates the effect of migration. Convection is the movement of the electroactive species by thermal currents, by density gradients present in the solution, or by stirring the solution or rotating the electrode. Convection must be eliminated or controlled accurately so as to provide a controlled transport of the analyte to the electrode.

In polarography the voltammetrie system includes a dropping Hg electrode and the diffusion current in the solution is measured as a function of the applied voltage. The polarographic wave observed when applying a voltage is known as the characteristic of the working electrode [**17**]. The working electrode being a "mercury drop electrode (MDE)" has a polarographic wave where oscillations are imposed on it as a result of variations in the Hg drop size. At the MDE both DC and AC as well as differential pulse polarograms for various metal ions in solution can be obtained. This illustrates the abilities of polarography for qualitative analysis, such as metal species identification and quantitative analysis [**18**].

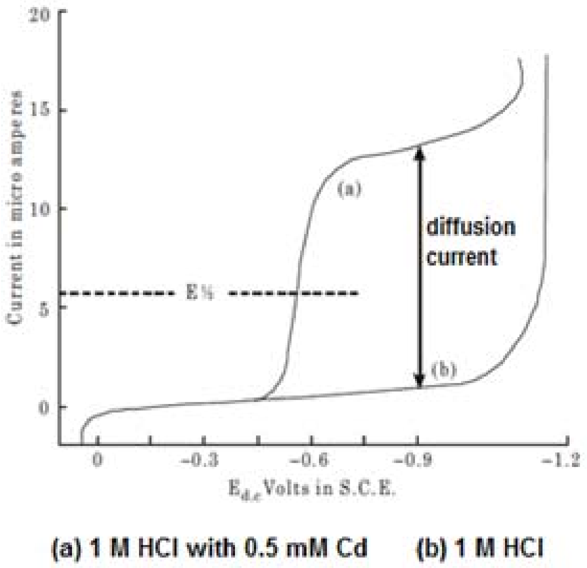


Fig.2 Polarogram (Kamala Zutshi, 2006).

The DME consists of a glass capillary through which Hg flows under gravity to form a series of Hg drops. Each new drop provides a clean surface at which the redox process takes place. This gives rise to a current increase with increasing area as the drop grows, then falling when the drop falls. The potential when the current attains half the value of the plateau current is called the half-wave potential and it is specific to the redox system used. The plateau current is proportional to the concentration of analyte. In Fig. 2 a polarogram is shown for HCl with 0.5 mM of Cd. In this case the peak height is proportional to the analyte concentration [**19**].

1.1.2.3 Inductively coupled plasma optical emission spectrometry (ICP-OES)

The analysis by optical emission spectrometry with the inductively coupled plasma (ICP-OES) in contrast to AAS is an atomic emission method. ICP-OES is based on the use of a high temperature argon plasma to excite the analytes for optical emission. The plasma temperature (~6000-12000 K) of the partially ionized gas that in addition to atoms also contains electrons and ions is reached as a result of the electrodes transmission of high-frequency power from an radio frequency generator to an Ar flow [**20**].

To generate the plasma, Ar gas is supplied through the torch coil. After ignition with a Tesla spark energy transfer via the high frequency electric current occurs at the working coil, which is located at the tip of the torch tube. At the top there are two high quality quartz tubes and an inner alumina injector tube. As a result of the electromagnetic field created in the torch tube by the high frequency current, Ar gas is ionized and a plasma is generated. Free electrons are accelerated, collide with atoms and heat the plasma. This plasma has a high electron density and temperature and this energy is used to excite the sample atoms. The ionization, electron and excitation occur at different locations in the plasma. The aerosol samples introduced into the plasma are atomized and eventually ionized before they are excited above the narrow tube in the center of the torch [**5**,**21**].

The high temperature plasma removes any remaining solvent and causes sample atomization followed by ionization. In addition to being ionized, sample atoms and ions are excited in the plasma. The green parts of the plasma are the locations where more Ar is introduced to the flow. [**8**].

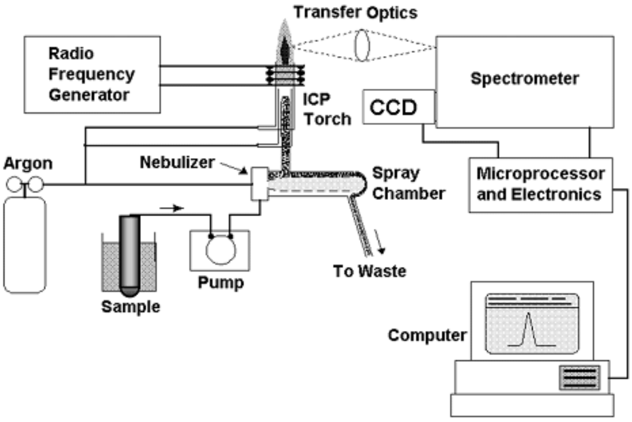


Fig. 3 ICP-OES

The most important components of a spectrometer for ICP-OES are the high-frequency generator, the plasma torch, the nebulizer and the spectrometer itself, which can be a monochromator (sequential) or a polychromator (simultaneous spectrometer). An echelle mounting is typically used for a polychromator so as to realize a high resolution. This is required in OES rather than in line source AAS because of the very large number of lines emitted by the hot plasma [**22**].

1.1.2.4 Inductively coupled plasma mass spectrometry (ICP-MS)

ICP-MS also enables multi-elemental analyses with excellent sensitivity. An ICP-MS instrument uses an inductively coupled plasma (ICP) as ionization source and a mass spectrometer (MS) to detect the ions produced. The principle is illustrated in Fig.4. With ICP-MS both solid as well as liquid samples can be analyzed [**23**,**24**]. With a laser ablation system solid samples can be directly analyzed, with a nebulizer system aqueous sample solutions can be brought in the aerosol form. Therefor the sample solution passes through the nebulizer, small droplets are formed and the aerosol moves into the torch together with Ar gas [**25**].

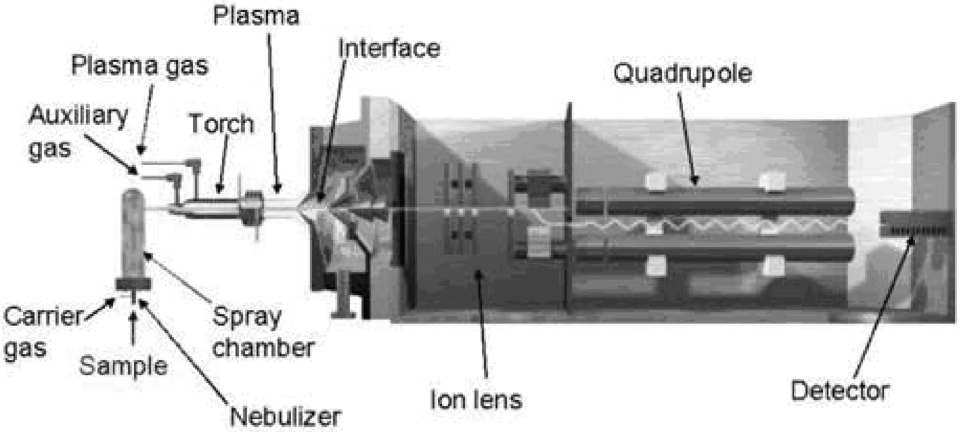


Fig. 4 ICP-MS

The interface between the ICP and MS components is required as atomization or/and ionization take place at atmospheric pressure and the vacuum environment is essential for the MS system. In the interface ions flow through a small orifice which is approximately 1 mm in diameter. The vacuum system is realized by a high displacement rotary pump. Here a supersonic jet is formed, the sample ions pass into the MS system at high speed and the plasma expands in the vacuum. The entire mass spectrometer is at high vacuum conditions realized by turbomolecular pumps, so that the ions are free to move without collisions with air molecules.

The beam is focused further by means of electrostatic lenses. There are different types of mass analyzers which can be employed to separate isotopes based on their mass to charge ratios. Mostly a quadrupole or a sector field system is used. The ions impact on a detector that records the number of ions per mass. This makes quantification of elements possible including isotope determination.

The great advantages of ICP-MS are the extremely low detection limits for a wide variety of elements [**4**,**26**]. Some elements can be determined down to the part per quadrillion ranges while most can be detected at the part per trillion levels. ICP-MS can be applied to the determination of trace, minor and major elements in almost every analytical field. It can be used to perform qualitative, semiquantitative and quantitative analyses and also isotopic ratios can be determined [**27**].

1.2 Fundamentals of atomic absorption spectrometry

1.2.1 Atomic absorption spectrometry instrumentation

Atomic absorption spectrometry (AAS) in analytical chemistry is a method for determining the concentration of a particular element in a wide variety of samples. Basically AAS instrumentation consists of the primary radiation source, an atomization unit, a wavelength selector and a detector. A primary radiation source which sharp by emits the atomic lines of the element to be determined is required. The most widely used source is the hollow cathode lamp. These lamps are designed to emit the atomic spectrum of a particular element, and specific lamps are selected depending on the element to be determined [**28**]. The atomization unit has to produce analyte atoms in the ground state. A flame or a graphite furnace typically are used to atomize the sample. The radiation emitted by the primary radiation source is absorbed upon passing through the atomization unit and conducted into the monochromator. The monochromator consists of an entrance collimator, a dispersive element (diffraction grating), usually several mirrors and an exit collimator. The grating spectrally disperses the radiation that is passing the atomizer. The slit of the exit collimator separates the analytical line from the total spectrum, blocking off the other lines emitted by the radiation source. The detector converts the photon current (radiation flux) received into an electric signal and registers the absorption of the analytical line [**29**].

1.2.2 Primary radiation source

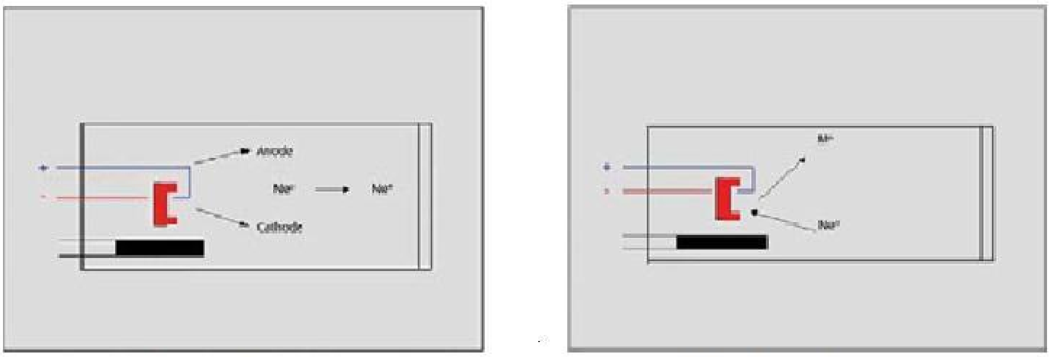
An atom absorbs radiation at discrete wavelengths. In order to measure this narrow absorption of radiation with maximum sensitivity, it is necessary to use a line source, which emits the specific wavelengths which can be absorbed by the atom. The hollow cathode lamp (HCL) and the electrodeless discharge lamp (EDL) are the radiation sources typically used in commercially available line source AAS [**30**].

Hollow cathode lamp (HCL)

The hollow cathode lamp works like a cathode ray tube. In the lamp a cylindrical metal cathode containing the metal for excitation and an anode are mounted. The glass cylinder itself is filled with Ne or Ar at a pressure of a few millibars. The cathode has the shape of a hollow cylinder and either consists of, or is filled with the element of interest. The electrical discharge is used to ionize gaseous atoms and to produce a flow of positive gas ions

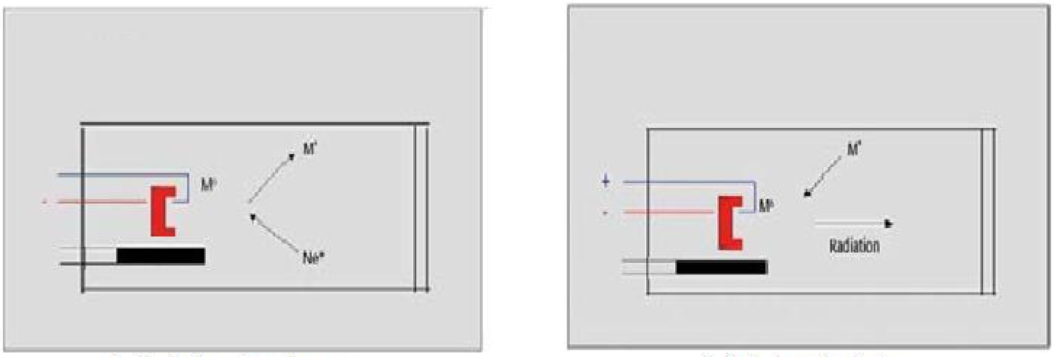
(Ne^+ or Ar^+) which then impact onto a metal cathode. Atoms are sputtered from its surface, they are excited and emit the spectrum of the cathode material. The metal is volatilized and electronically excited and hence emits its characteristic lines when it returns to its ground state. Because of the low pressure and the low temperature in a HCL discharge as compared to that in the atomizer, the width of the lines emitted by the radiation source is significantly lower than that of the absorption lines. Depending on the wavelength of the main analytical line the exit window of the lamp is made of silica or glass. The fill gas is selected in a way that no spectral interferences are encountered between the spectrum of the fill gas and the analytical line and to achieve the highest possible emission intensity of the analyte spectrum [**31**,**32**].

Each HCL will have a particular current for optimum performance. In general, higher currents will produce brighter emission and less baseline noise. As the current is increased, however, the lamp lifetime may shorten and spectral line broadening may occur, resulting in a reduction in sensitivity and linear working range. The recommended current specified for each lamp will usually provide the best combination of lamp lifetime and performance [**33**].



1. Ionization of gas atoms

2. Sputtering of metal atoms



3. Excitation of metal atoms

4. Emission of radiation

Fig. 5 Principle of a hollow cathode lamp (HCL).

The type of HCL depends on the metal being determined. The analyte atoms in the flame can be excited to a higher state of energy by absorbing a quantity of energy named a quantum. This amount of energy is specific to a particular electron transition in a particular element. As the intensity of the radiation lead into the flame is known and the intensity arriving at the detector can be measured, it is possible to get a signal that is proportional to the concentration of the element being determined [**34**].

HCLs have a limited lifetime. Firstly, sputtered atoms are deposited in part on the colder parts of the lamp, e.g. the glass cylinder, where they form a metal film. Secondly, the fill gas is adsorbed slowly by the metal film and the glass. Further, some cathode materials can slowly evolve hydrogen when heated. When the concentration of H in the fill gas increases, a background continuum emission contaminates the purity of the line spectrum of the element, resulting in a reduction of element-specific atomic absorption sensitivity and a poorer linearity of the calibration [**35**].

Electrodeless discharge lamp (EDL)

The HCL is a completely suitable source for many elements in atomic absorption, but especially when handling volatile elements, the quality of the analysis is impaired by limitations of the intensity and a short lifetime of HCL. The determination of these elements in AAS can often be significantly improved by the use of brighter, more stable sources such as the electrodeless discharge lamp (EDL). The EDL is typically much more intense and, in some cases, enables a higher sensitivity than a comparable HCL. They therefore offer the analytical advantages of better precision and lower detection limits where an analysis is limited by the intensity of the primary source. In addition to superior performance, the lifetime of an EDL is typically much longer than that of a HCL for the same element. It should be noted, however, that the optical image for the EDL is considerably larger than that in a HCL. As a result, the performance benefits of the EDL can only be realized in instruments with optical systems designed to be compatible with the larger image [**36**,**37**].

In Fig. 6 the design of the Perkin-Elmer EDL is shown. Here a small amount of the metal or salt of the element for which the source is to be used is sealed inside a quartz bulb. This bulb is placed inside a small, self-contained RF generator or ‘‘driver’’. When power is applied to the driver, an RF field is created.

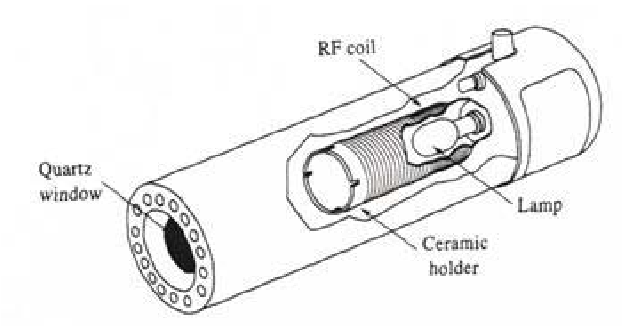


Fig. 6 Electrodeless discharge lamp (EDL).

Excitation of the element vapor is achieved with the aid of a radiofrequency or a microwave powered coil through ionization of Ar. Ionized Ar will hit the metal causing excitation of the atoms of the metal of interest and emission of their characteristic spectrum. A suitable radiofrequency power supply is required to operate an EDL. The intensity output of the EDL is higher than that of the HCL. Nevertheless, compared to HCLs, EDLs are rarely used [**38**], as they are more expensive.

1.2.3 Atom reservoirs

1.2.3.1 Flames

Flame atomic absorption spectrometry (FAAS) is a fast and high sensitivity method for elemental determinations, although problems can arise as a result of chemical and spectral interferences [**39**]. The sample is transferred into the liquid form e.g. by dissolution. The nebulizer aspirates the solution and brings it into a fine aerosol. This is directed onto an impact bead for post-nebulization in order to create an even finer aerosol. Large droplets are separated off in the mixing chamber and the aerosol is mixed with fuel gas and additional oxidant. The aerosol/fuel gas/oxidant mixture is ignited above the burner head and flame temperatures ranging from 2100 to 2800 ºC, depending on the fuel gas used are obtained. During combustion, atoms of the element of interest in the sample are reduced to the atomic state. A radiation beam from a lamp whose cathode is made of the element to be determined is passed through the flame and conducted into a monochromator with a suitable detector.

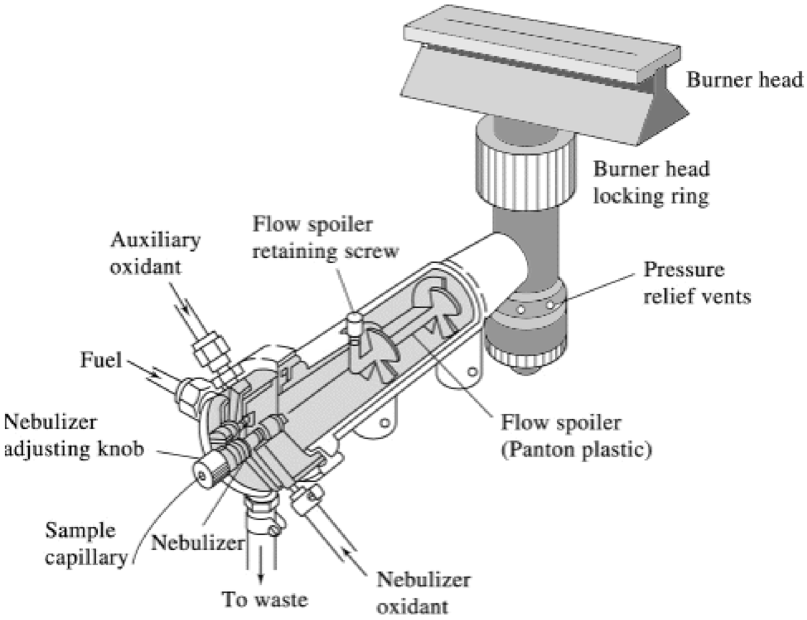


Fig. 7 Premix burner with nebulizer for FAAS.

The amount of absorbed radiation is proportional to the concentration of the element to be determined. Free ground state atoms of the element absorb radiation at characteristic wavelengths. The reduction of the radiation intensity at the analytical wavelength allows it to determine the concentration of the element in the sample [**40**].

The flame gases are supplied by the gas control system at constant pressure, guaranteeing well defined flow rates of fuel gas and oxidant. The most current gas mixtures used are air/acetylene and nitrous-oxide/acetylene. The latter result in higher atomization efficiencies and thus better detection limits for elements like Si, Al, Sc, Ti, V and Zr. The air/acetylene flame can be used for easy atomized elements (e.g. As and Se).

1.2.3.2 Graphite furnace atomizer

The graphite furnace atomizer which is also called an electrothermal atomizer utilizes an electrically heated cup or tube made of graphite. In modern equipment almost uniquely tubes are used. The heated graphite furnace provides the thermal energy to break the chemical bonds of the analyte substances in the sample and to produce free ground state atoms of the analyte.

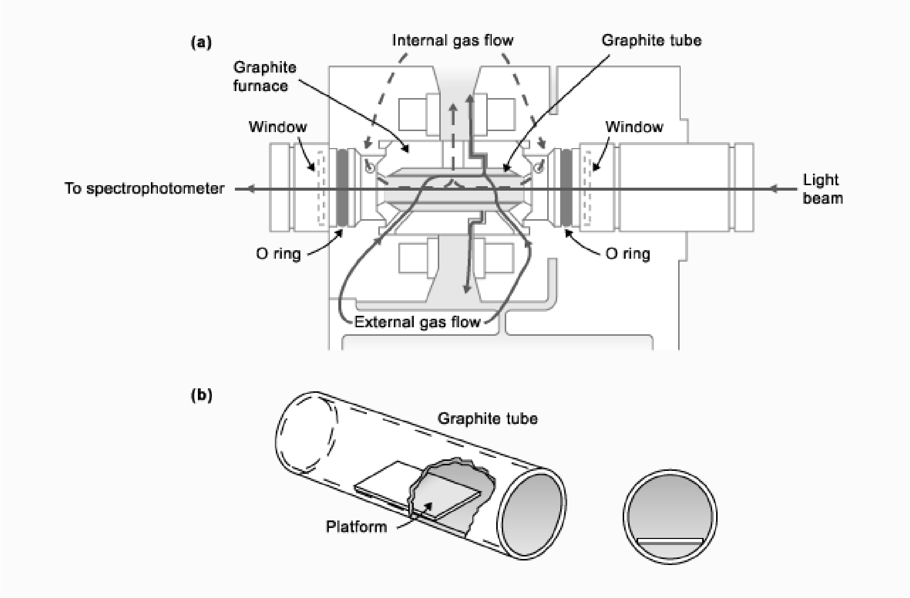


Fig. 8 Cross-sectional view of a graphite furnace atomizer.

Normally the graphite tube is the heating part of the graphite furnace. The cylindrical tube is aligned horizontally in the optical path of the spectrometer and serves as the spectrometer sampling cell. A few microliters (usually 5-50 μL) of sample are used and dispensed through a hole in the center of the tube wall onto the inner tube wall or a graphite platform. The tube is held in place between two graphite contact cylinders, which provide the electrical connections. The electrical potential applied to the contacts causes current to flow through the tube, the effect of which is a heating of the tube and the sample.

The entire assembly is mounted within an enclosed, water-cooled housing. Quartz windows at each end of the housing allow radiation to pass through the tube. The heated graphite is protected from oxidation by air with the end windows and two streams of Ar. An external gas flow surrounds the outside of the tube, and a separately controllable internal gas flow purges the inside of the tube. The system should regulate the internal gas flow so that the internal flow is reduced or preferably, completely interrupted during atomization. This helps to maximize sample residence times in the tube and to increase the measurement signal.

GFAAS is a highly sensitive atomic spectrometric method that provides excellent detection limits for metals in liquid and in solid samples. Routine determinations at the sub-mg/L level for most elements make it ideal for environmental applications. Advances in instrumentation and techniques have made it possible to analyze samples with very complex matrices, such as those frequently found in biological and geological samples. The more sophisticated GFAAS system has turrets for several lamps and therefore is capable of sequential and automatic determinations of more than one element [**41**]. The advantages of GFAAS include a higher sensitivity and lower detection limits than other methods, the possibility for direct analysis of some types of liquid samples, low spectral interferences and the requirement of very small volumes or amounts of sample [**42**,**43**].

1.2.3.3 Hydride generation

The hydride generation technique, which makes use of a separation of the analyte element from the matrix by conversion to its volatile hydride, offers a route to the trace determination of several important elements, which have specific problems when determined by conventional methods. Hydride generation atomic absorption spectrometry is a measurement method which is now applied to the determination of Hg and the elements that are forming volatile hydrides (e.g. Sb, As, Bi, Ge, Pb, Se, Te and Sn) in a wide range of matrices. For example it is used for the determination of traces of these elements in biological samples and it is used in the analysis of alloys and environmental materials [**44**].

Here the sample solution is mixed with a solution of $NaBH_4$ in a suitable flow cell. The generated hydrides are purged out of the solution using a carrier gas flow. Doing so, the analyte can often be separated completely from the matrix. Atomization may be carried out in a heated quartz tube placed in the beam of the spectrometer. Because of the relatively low temperature of the quartz tube, atomization cannot be due to thermal dissociation, but proceeds via free hydrogen radicals formed in the entrance part of the quartz tube [**11**,**45**].

Hydride generation is especially valuable for the determination of trace levels of As and Se because the useful resonance lines of these two elements are below 200 nm, a region where there are very considerable spectral interferences from radicals in flame AAS. Other advantages include the high efficiency of analyte introduction to the atomizer, the ease of preconcentration of the analyte and the possibility of speciation [**46**].

1.2.4 Spectrometer

The optical components of a spectrometer required for AAS may be classified into two major groups:

1. The monochromator, which has the task of dispersing the incoming radiation spectrally and to prevent that any radiation, except the one for the analytical line, reaches the detector.
2. Lenses and mirrors, which focus the radiation of the HCL, at first in the atomization zone (flame, graphite tube, quartz tube) then on the entrance slit of the monochromator and finally on the detector.

In order to isolate the analytical line, it is of advantage to use a small spectral bandwidth. In order to obtain a stable measurement signal with a favorable signal-to-noise ratio it is necessary that as much radiation energy as possible enters the monochromator. This requires a large (geometric) slit width. These two apparently contradictory conditions can be realized by using a monochromator with high dispersive power. In practice a spectral bandwidth in the range of 0.2 nm to 1.2 nm is typically used.

In LS AAS the high resolution that is required for the measurement of atomic absorption is provided by the narrow analyte line emitted by the primary radiation source and the monochromator simply has to resolve this analytical line from other radiation emitted by the lamp with a band pass between 0.2 and 2 nm. Another feature of LS AAS is the possibility to modulate the primary radiation and to use a selective amplifier that is tuned to the same modulation frequency, as already proposed by Alan Walsh. In this way any (unmodulated) radiation emitted for example by the atomizer can be excluded, which is imperative for LS AAS. Simple monochromators of the Littrow or the Czerny-Turner design are typically used for LS AAS. As detectors in LS AAS mostly photomultiplier tubes are used, although more and more solid state detectors might be preferred because of their higher simultaneous inlet capacity and better signal-to-noise ratio [**10**].

Also a continuum radiation source can be used as primary radiation source for AAS. However, here it is indispensable to work with a high-resolution monochromator. The resolution has to be equal to or better than the half-width of an atomic absorption line (about 2 pm) in order to avoid losses of sensitivity and linearity of the calibration curve. The first commercial equipment for HR-CS AAS was introduced by Analytik Jena (Jena, Germany) at the beginning of the 21st century. It has been based on the design proposed by Becker-Ross and Florek [**47**,**48**,**49**] These spectrometers use a compact double monochromator with a prism pre-disperser and an echelle grating monochromator for high resolution. A linear charge coupled device (CCD) array with 200 pixels is used as the detector. The second monochromator does not have an exit slit, hence the spectral environment at both sides of the analytical line becomes visible at high resolution. As typically only 3–5 pixels are used to measure the atomic absorption, the other pixels are available for spectral background correction purposes. A further correction is the one for lamp flicker noise, which is independent of the wavelength and this results in measurements with very low noise level [**49**].

1.2.5 Analytical interferences

An interference is defined as an influence of the matrix components on the analytical result. All solvents, reagents, glassware and other sample processing hardware may cause contamination in sample analyses. So these materials must be demonstrated to be free from contamination under the conditions of the analysis by analyzing blank samples. Specific selection of reagents and purification of solvents by distillation in all-quartz systems may be necessary. The frequently encountered interferences in atomic absorption spectrometry with flames and graphite furnaces are discussed below.

1.2.5.1 Flame atomic absorption spectrometry

Since the concentration of the analyte element is considered to be proportional to the ground state atom population in the flame, any factor that affects the ground state population of the analyte element can lead to interferences. The following interferences are often in FAAS encountered:

1.2.5.1.1 Spectral interferences

The most frequent spectral interference in AAS is background absorption. It is caused by radiation scattering at particles in the atomization unit or by molecular absorption. Spectral interferences may also be caused by direct overlap of the analytical line with the absorption line of a matrix element. Although this interference is rare in AAS, it exists and mostly is due to overlapping with radiation of the primary radiation source. Other spectral interferences occur with radiation from an emission line of another element or compound or general background radiation from the flame, the solvent or the analytical sample. This specially occurs when using organic solvents, but it can also happen e.g. when determining Na in the presence of Mg and Fe in the presence of Cu or Ni.

1.2.5.1.2 Non-Spectral interferences

Non-spectral interferences in FAAS are those which affect the formation of analyte atoms. They are generally classified into:

1. *Transport interferences*

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

2. *Spatial distribution interferences*

   Spatial distribution interferences may be observed in flames when the distribution of the analyte over the width of the flame is influenced by the presence of concomitants. This could result in measurement errors when the radiation absorption is not measured over the entire width of the flame.

3. *Vaporization interferences*

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

4. *Dissociation interferences*

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

5. *Ionization interferences*

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

1.2.5.2 Graphite furnace atomic absorption spectrometry

The interferences associated with the graphite furnace in AAS (GF-AAS) are the same as in the flame AAS. The interferences are divided into two categories, namely spectral and non-spectral interferences. Spectral interferences are those resulting from the absorption of radiation by molecules or by atoms other than those of the analyte element. Non-spectral interferences are those which affect the production or the availability of analyte atoms, which create the measured atomic absorption.

1.2.5.2.1 Spectral interferences

Spectral interferences are the result of an absorption of radiation by an element or molecule that is not the analyte of interest or of black body radiation. Spectral interferences caused by another element are rare in GF-AAS because of the narrow atomic line widths emitted by the primary radiation source lamps and the narrow absorption profiles. Molecular species, however, can produce broadband absorption profiles. The use of matrix modifiers, optimized furnace temperature programs and deuterium lamp as well as Zeeman background correction can help to minimize the effect of this non-specific absorption. Black body emission from the hot graphite tube can also produce spectral interferences. By using atomization temperatures which are not higher than necessary to volatilize the analyte and maintaining proper furnace alignment can minimize this type of interference.

1. Deuterium background correction

The most severe spectral interference problem encountered with graphite furnace analyses is background absorption. In the deuterium background correction technique non-specific absorption is absorbing the same portion of the continuum radiation from the deuterium lamp as from the radiation of the line source. The element-specific absorption, however, in a first approximation only reduces the radiation of the line source, but not that of the deuterium lamp.

2. Zeeman effect background correction

The Zeeman effect is based on the shift of energy levels of atoms and molecules under the influence of a magnetic field.

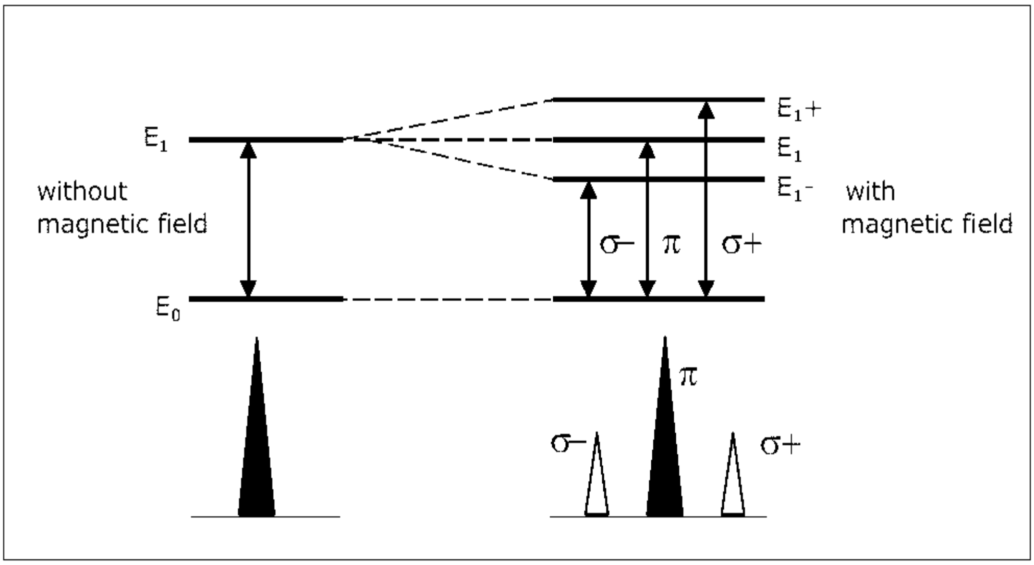


Fig. 9 Zeeman effect.

When a magnetic field is applied across the atomizer (graphite furnace), the absorption lines of the analyte atoms are split into three components. Two of these components (σ-components) are shifted to slightly lower and higher wavelengths, respectively, whereas the third component (π-component) is at the original wavelength. The π-component can be removed from the spectrum by using a polarizer. In background correction using the Zeeman effect, a strong magnetic field also can be turned on and off in rapid sequence. Then the total absorbance (element-specific and non-specific background absorption) is measured with the magnetic field off and the background absorption only with the magnetic field on. The difference of the two values gives the corrected absorption signal [**11**].

3. Background correction in HR-CS AAS

In HR-CS AAS no additional system is required for background correction. The instrument is equipped with a CCD array with 200 pixels, and hence with 200 simultaneously and independently operating detectors. By the software we can automatically select a few of these detectors on both sides of the analytical line for correction purposes. Any change in the radiation intensity that appears equally on all pixels then is corrected automatically. Among these changes are for example fluctuations of lamp emission intensity, but also any continuous background absorption. Discontinuous background absorption, e.g. direct line overlap with a line of a matrix element or molecular absorption with rotational fine structure can be eliminated mathematically by using reference spectra [**49**].

1.2.5.2.2 Non-Spectral interferences

The most frequently observed interference in GF AAS is a premature volatilization of the analyte during the pyrolysis step. This may happen when the analyte forms a compound with a matrix component that is volatile at lower temperatures than the analyte in the calibration solution. For this reason we should record pyrolysis curves not only with pure solutions, but also with at least one representative sample. Another phenomenon that may result in interferences is analyte loss during the pre-atomization. This loss can occur even when using a matrix modifier and a conservative charring temperature. A pre-atomization loss is indicated by the occurrence of an absorbance less than zero at the beginning of the reading cycle and by the termination of the signal with the peak tail dipping below the baseline. Further, analytes at high concentration levels in the analytical solution often are not volatilized completely out of the graphite furnace. This residual analyte may have a memory effect, resulting in errors for the next measurements. The use of a clean-out step of a few seconds at maximum temperature should minimize these problems [**49**,**41**]

1.3 Flame atomic absorption

In flame atomic absorption the sample solution is nebulized by a flow of gaseous oxidant, mixed with a gaseous fuel, and the resulting aerosol is carried into a flame where atomization occurs. The first step is a desolvation, during which the solvent is evaporated and a finely divided solid molecular aerosol is formed. From these molecules finally an atomic gas is formed. Some of the atoms ionize and give cations and electrons. Undoubtly, other molecules and atoms also are produced in the flame as a result of interactions of the fuel gas with the oxidant gas and with various species in the sample.

In flame AAS mostly a pneumatic nebulizer is used, which converts the sample solution into the aerosol, which then is fed into a burner. A common type of nebulizer is the concentric type. Here the liquid sample is sucked through a capillary tube by a high-pressure stream of a gas flowing around the tip of the tube. This liquid accordingly is transported by aspiration. The high velocity gas breaks the liquid into fine droplets of various sizes, which then are carried into the flame. Also cross-flow nebulizers are employed in which the high-pressure gas flows perpendicularly to the liquid capillary. In this type of nebulizer, the liquid normally must be pumped through the capillary. In most nebulizers, such as the high-pressure nebulizer the oxidant is used as nebulizer gas and the aerosol containing the oxidant is mixed subsequently with the fuel [**38**].

1.3.1 Type of flame

The possibilities of FAAS are related to the fuels and oxidants that are used and the temperatures realized with each of these mixtures. These temperatures are in the range of 1700-2400ºC defending on the various fuels when air serves as the oxidant. The burning velocities listed in the last column are of considerable importance because flames are only stable within certain ranges of gas flow rates. When the gas flow rate does not exceed the burning velocity, the flame propagates itself back into the burner, giving flashback. As the flow rate increases, the flame rises until it reaches a point above the burner where the flow velocity and the burning velocity are equal. In this region the flame is stable.

Table 1. Temperature of some flames.

No.	Fuel	Oxidant	Temperature (ºC)	Maximum burning velocity (cm s^{-1})
1.	Natural gas	Air	1700-1900	39-42
2.	Natural gas	Oxygen	2700-2800	370-390
3.	Hydrogen	Air	2000-2100	300-440
4.	Hydrogen	Oxygen	2550-2700	900-1400
5.	Acetylene	Air	2100-2400	158-266
6.	Acetylene	Oxygen	3050-3150	1100-2480
7.	Acetylene	Nitrous oxide	2600-2800	285

1.3.2 Instrumentation

An atomic absorption instrument contains a primary radiation source, a sample container, a wavelength selector and a detector. Both single and double beam instruments are available. A HCL is mostly used as primary radiation source. Here the cathode is made of the element to be determined. The atomization unit has to produce analyte atoms in the ground state. The radiation emitted by the radiation source is attenuated upon passing through the atomization unit and conducted into the monochromator.

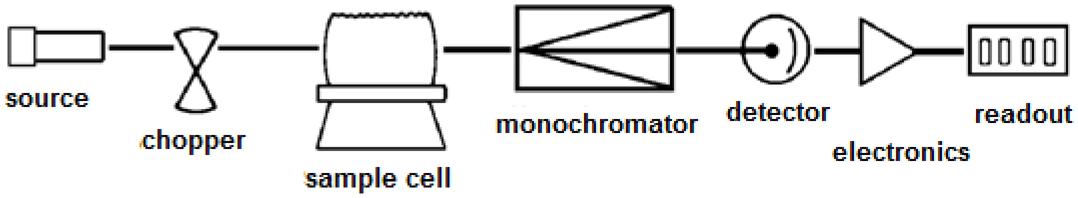


Fig. 10 Single beam atomic absorption spectrometer.

In a single beam instrument (Fig. 10) radiation from the source enters the monochromator through the entrance slit and is directed to the grating where dispersion takes place. The dispersed radiation is directed towards the exit slit. By adjusting the angle of the grating with the incoming radiation beam, a selected emission line from the source can be allowed to pass through the exit slit and fall onto the detector. All other lines then are blocked from exiting. The detector converts the radiation flux into an electric signal and allows it to record the attenuation of the analytical line intensity.

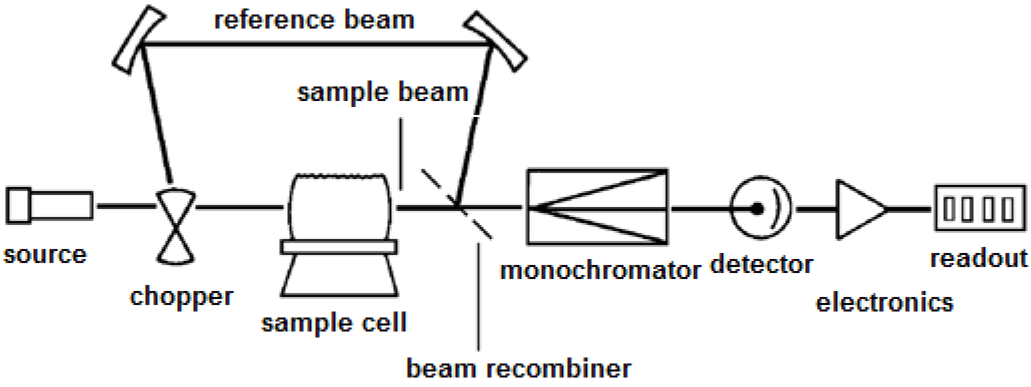


Fig. 11 Double-beam atomic absorption spectrometer.

In a double-beam instrument, the radiation coming from the hollow cathode source is split by mirrors and a chopper, by which one half of the radiation passes through the flame and the other half directly to the monochromator. The two beams are then recombined by a half-silvered mirror and passed into a monochromator. The output from the photomultiplier is fed to a lock-in-amplifier that is synchronized with the chopper drive. The ratio between the intensities of the reference and sample signals is then amplified and fed to a digital meter or a signal recorder [**41**].

1.4 High resolution-continuum source atomic absorption with graphite furnace and flame techniques.

The measuring principle of both High Resolution Continuum Source Atomic Absorption Spectrometry (HR-CS AAS) and classical Line Source Atomic Absorption Spectrometry (LS AAS) is based on the absorption of primary radiation by the analyte atoms in their ground state. The measured absorbance signal is proportional to the concentration of the respective element in the analyzed sample.

In HR-CS AAS, hallow cathode lamps as the element-specific primary radiation source of classical AAS are replaced by a single continuum source, namely a xenon short-arc lamp, which is used for all elements and lines. Due to the special electrode geometry of the xenon short-arc lamp, a hot arc spot is formed that emits a very high radiation density and continuously covers the entire spectral range (190 – 900 nm).

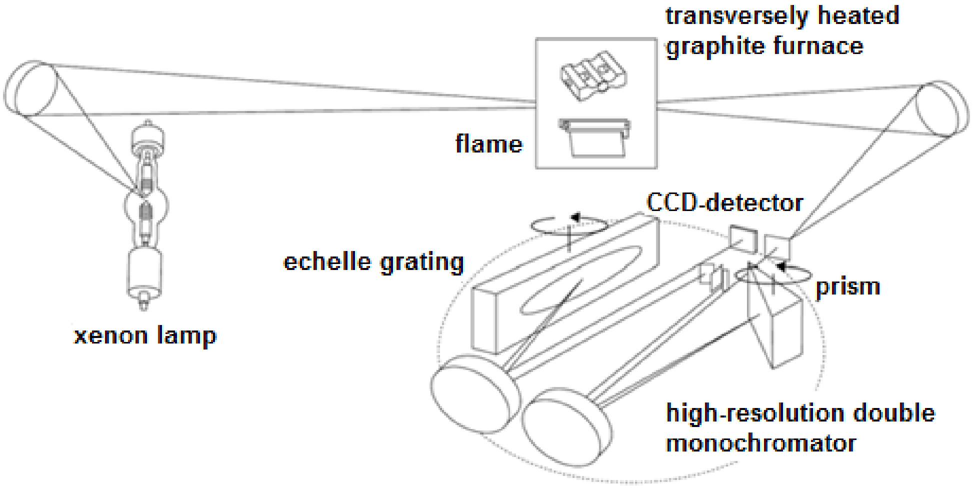


Fig. 12 HR-CS AAS (Analytik Jena, 2008).

In this way, all analytical lines of interest are available without any restrictions and at any time, including both the resonance lines of the elements to be determined and all secondary lines without the technical limitations caused by specific properties of the HCL, such as exit window and emission intensity. In addition, absorption lines or bands of diatomic molecules can be used analytically for elemental determinations [**49**].

During the analysis, the position of the arc spot is monitored and automatically readjusted. In this way, lamp drift by warm-up effects is avoided. All further drifts of the xenon lamp simultaneously are corrected in the whole spectra through the use of correction pixels [**10**].

1.4.1 High resolution continuum source atomic absorption spectrometry with the flame technique (HR-CS FAAS)

Flame atomic absorption spectrometry is used for the determination of trace elements in the concentration range from the mg/L to the µg/L and for the determination of the main components. The technique requires a flame with constant properties. The composition of the flame must be adjusted in dependence on the element to be determined. In the instrument used a motorized vertical adjustment of the nebulizer-mixing chamber-burner unit over 12 mm makes it possible to move the flame zone with the maximum absorption into the beam path. For the determination of the main components, the burner head can be turned by 90° on the burner neck until it is at a right angle with respect to the beam. Herewith, we shorten the absorption path of the radiation through the flame.

The sample solution is aspirated by a pneumatic concentric nebulizer mounted in the mixing chamber. In this mixing chamber, the sample aerosol is mixed with acetylene and auxiliary oxidant before it emerges from the burner slot. The length of the flame is either 5 or 10 cm and the width is of the order of a few millimetres depending on the burner type used. The beam transmits the full length of the flame.

Burner-nebulizer unit

The nebulizer produces an aerosol of the sample solution, which is atomized in the flame. The oxidant is supplied to the nebulizer through a lateral connector. It flows through the central corrosion-proof Pt-Rh tube placed in a Ti tube and connected to a plastic nozzle. The sample solution is expelled from the tube and further sample solution aspirated by the negative pressure produced. The position of the tube end relative to the nozzle determines the aspiration rate and the aerosol output. It can be manually adjusted with the aid of an adjusting screw and a lock nut.

The sample aerosol hits the impact bead, where larger droplets are separated off and drain away through the siphon. The fuel gas flow hits the impact bead perpendicularly. Once generated, the aerosol flows through the mixing chamber into the burner. During its way through the mixing chamber, it reaches equilibrium conditions. Larger droplets are then sorted out as a result of gravitational forces and drain away through the siphon. The aerosol is atomized by the flame. Here, the smaller droplets of the aerosol are evaporated when it enters the flame and the molecules are atomized in the hot zone of the flame. When the solvent evaporates incompletely, the accuracy of the analytical result is negatively affected, as background absorption is increased by unevaporated droplets.

Burner and flame type

The HR-CS FAAS instrument available for our work could be operated with the following types of flames and burners:

- An acetylene/air flame with a 50 mm single-slot burner (standard burner) or a 100 mm single-slot burner for high sensitivity can be used for most of the elements.

- An acetylene/nitrous oxide flame with a 50 mm single-slot burner is required for elements that are difficult to atomize, such as B, Al and Si.

When the range of elements to be determined as in environmental samples includes both elements which are easy to atomize and elements which are difficult to atomize, only the standard 50 mm single-slot burner should be used so as to avoid the need to change the burner between measurements [**50**].

1.4.2 High resolution continuum source atomic absorption spectrometry with the graphite furnace technique (HR-CS GFAAS)

The transversally heated graphite tube with its contact surfaces is pneumatically pressed and held against annular shaped graphite electrodes, which are held by water cooled metal bodies. Between the metal bodies, which carry the electrodes, there is a furnace shroud made of graphite as additional component. Together with the graphite electrodes, it forms a closed inner chamber around the graphite tube, which stabilizes the heating conditions of the graphite tube and also guarantees for chemically inert conditions. For pre-adjustment of the graphite tube when the atomizer is open, the furnace shroud has special supports at the inside. When closing the movable furnace component, the tube is raised to the resting position and pressed into the contacts, without touching the furnace shroud.

Gas channels for a separate supply of the primary gas flow (cleaning gas) and the secondary gas flow (protection gas) are housed in the furnace shroud. Oxidizing or reducing gases (O_2 or H_2) can be added to the primary gas flow when necessary. The primary gas flow has the task of removing all gases which are released in the graphite tube during the drying and charring step. It should prevent condensation of the sample material on the furnace windows and steer the residence time of the analyte atoms in the beam path. During atomization, the primary gas flow is generally interrupted in order to obtain the longest possible residence time for the atoms in the beam path and to maximize the sensitivity of the measurement. The secondary gas flow surrounds the graphite tube and also reaches the outside through the funnel of the dosage opening.

The secondary gas flow is responsible for ensuring that the graphite tube is surrounded by inert gas, even when the primary gas flow has stopped. Accordingly, it provides protection against oxidation by atmospheric oxygen. The thermal flow in the furnace shroud is realized via a cylindrical attachment to the fixed furnace component. The operating temperature of the atomizer is thus increased in the desired steps so that, condensations of the analyte at the inner walls are avoided.

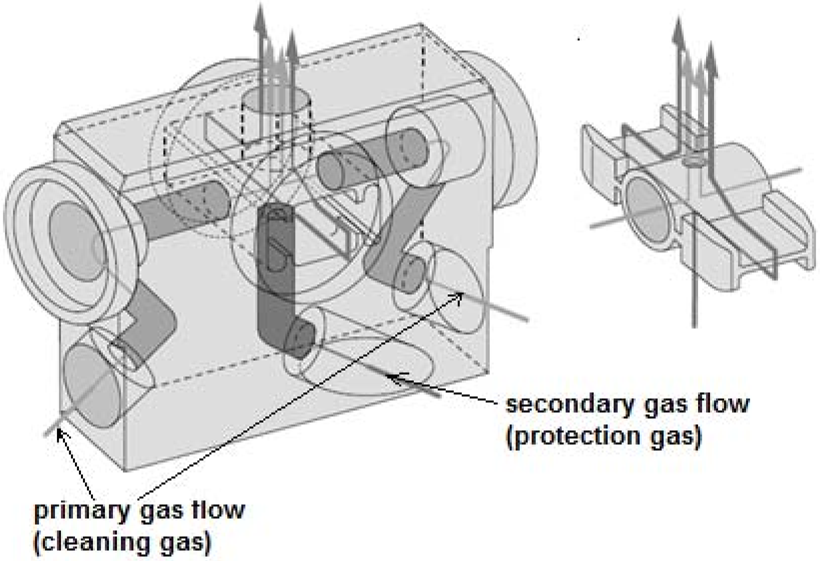


Fig. 13 Primary and secondary gas flows in the graphite tube furnace (Analytik Jena, 2008).

The conical attachment on the opposite side of the furnace shroud, together with the sealing ring in the rotatable furnace component, forms an exactly defined slit and thus guarantees a safe sealing of the cell inner chamber from any penetration of surrounding air. When the tube in the furnace shroud is broken, the sealing ring in the movable furnace component prevents a short circuit between the furnace components. The furnace shroud is bored in the direction of the optical axis, the outer cylinders support the furnace window. These can be pulled off easily for cleaning purposes by a twisting.

1.4.3 Instrumentation

1.4.3.1 Radiation source (xenon-arc lamp)

As radiation source in HR-CS AAS one single radiation source is used for all elements and wavelengths, namely a xenon short-arc lamp. The lamp has a modified electrode configuration and works under high pressure. Under this condition a hot spot is forming that reaches a temperature of about 10 000 K. The emission intensity of the lamp is at least a factor of 10 higher than that of a conventional xenon short-arc lamp, and more than a factor of 100 higher in the far UV range. The more important for AAS is that the emission intensity of this lamp is in average a factor of 100 higher than that of a conventional HCL over the entire spectral range.

Fig. 14 Xenon short-arc lamp for HR-CS AAS.

The basic design of a HR-CS AAS lamp is shown in Fig. 14. One of the big advantages of HR-CS AAS is for surely that only a single radiation source is required for all elements and all wavelengths over the entire spectral range from 190 – 900 nm. Another advantage results from the significantly higher emission intensity of this lamp as compared to HCLs. Although the radiation intensity has no influence on the sensitivity in AAS, it has an influence on the signal to noise ratio. As a result of this, detection limits are in average about a factor of 5 better in HR-CS AAS as compared to line source AAS [**49**].

1.4.3.2 The atomizer

In HR-CS AAS the same atomizers as in the classical line source AAS can be used. The following atomization techniques are used in HR-CS AAS; the flame technique, the graphite furnace technique, the hydride as well as the cold vapor technique and the HydrEA technique (combination of hydride and graphite furnace technique).

Atomization in a flame

In flame atomization the sample has to be brought into the liquid form, e.g. by dissolution, the nebulizers used have been described before.

Atomization in a graphite furnace

When using atomization in a graphite furnace the sample to be analyzed may be a liquid, a slurry or a solid and it is introduced directly into the graphite tube. A voltage is applied across the graphite tube, which is heated rapidly to a high temperature (up to 2600ºC) due to its resistance. Using time-controlled stepwise heating of the graphite tube the sample solution first is dried and then the matrix can be destroyed or removed, until the element of interest is atomized. The graphite tube is permanently flushed with Ar while it is in operation. The protective gas flow efficiently prevents the entrance of air and hence guarantees for a long lifetime of the graphite tube and an undisturbed determination. Integrated water cooling provides rapid cooling of the graphite tube after the operating voltage has been switched off and enables a high sampling frequency. Graphite tube atomization results in detection limits that are up to a factor of 1000 better than those obtained with flame atomization however, occasionally sophisticated temperature programs are required so as to control the matrix effects [**52**].

Atomization using the hydride and cold vapor techniques

Hg and elements which are forming volatile hydrides (e.g. As, Se, Sb, Te, Sn, Bi) can be determined by the cold vapor and the hydride technique, respectively. The detection limits often are comparable or better than those of graphite furnace AAS, depending on the sample volume used. The clear advantage as compared to the graphite furnace is the relative absence of matrix effects as a result of the isolation of the analyte by the chemical reaction during the measurement. It has to be mentioned, however, that in the presence of several transition metals at high concentrations in the measurement solution, these metals may be reduced as well and precipitate in a finely dispersed form. They react with the generated hydrides. These hydrides are obviously lost for the absorption process unless proper action is taken. It has therefore to be decided in each case, which technique should be applied [**49**,**52**].

Atomization using the HydrEA technique

The HydreEA technique is a combination of the graphite furnace and the hydride technique. It is used to obtain even lower detection limits for the hydride-forming elements. For this purpose the hydride is not introduced into a heated quartz tube, but into a heated graphite tube which has been treated with Ir, where it is pre-concentrated. The graphite tube is subjected to a temperature program as usual and the analyte is atomized and determined by AAS [**51**,**52**].

1.4.3.3 The monochromator

The optical system in HR-CS AAS is fundamentally different from the one in conventional AAS, although similar components are used. Classical monochromators as they are used in optical emission spectrometry require a lot of space and have a tendency to exhibit wavelength drift. Both of these characteristics are unacceptable in HR-CS AAS. This problem was solved by the use of a compact double monochromator with active wavelength stabilization. The resolution of this double monochromator is in the range of 140 000, which corresponds to a spectral bandpass of 1.6 pm at 200 nm, a value which is about a factor of 100 better than the resolution of classical AAS monochromators.

The selectivity of the analysis is realized by the high-resolution double monochromator based on a prism and an echelle grating monochromator. In this way, a very compact design and a high spectral resolution of $\lambda/\Delta\lambda$ =145 000 is achieved, which corresponds to a spectral band width of < 2 pm per pixel at 200 nm. The monochromator is wavelength-stabilized by the use of an integrated Ne source. The wavelength accuracy is guaranteed by a calibration of the monochromator of which the wavelength is adjusted to the ones of well defined Ne lines [**10**,**51**,**52**]

1.4.3.4 The detector

A linear CCD array with typically 512 pixels is used as detector in HR-CS AAS and 200 pixels are used for analytical purposes. All individual pixels are evaluated independently. These pixels are illuminated simultaneously (for 1-10 ms) and read out simultaneously. The next illumination can already be carried out during signal evaluation, which makes a very rapid measurement frequency possible [**52**].

1.4.3.5 The evaluation device

The automation of the measurement processes, all aspects of sample preparation and the course of the analytic data evaluation are handled by a computer (PC). An advantage of measuring with a continuum source is that all the pixels in the vicinity of a line become visible at high resolution.

Background correction is done by a polynomial function using selected reference points. The reference points are dynamically selected for every spectrum using a special algorithm, which is based on criteria to ensure an approximation to the actual baseline for the measuring pixels, which is as accurate as possible. When a fine-structured background overlaps with the analytical line, a multivariant method can be applied. To this end, reference spectra of matrix constituents are used for determining the polynomial function by a least-squares fit. When atom lines directly overlap with the analysis line, it is also possible to perform interelement correction (IEC). For this correction spectral lines are used, which are adjacent to the interfering line and measured within the observation width of the detector (e.g. correction of the spectral interference of Fe at the analysis wavelength of Zn at 213 nm or Se at 196 nm).

Lamp drift and all broad-band effects can be instantly eliminated from the spectrum by automatic and simultaneous background correction with the correction pixels. In this way, a simultaneous double-beam system is realized with only one optical path, which results in a clearly higher measurement stability as compared to classical LS AAS. While the sensitivity of this technique is comparable to that of LS AAS, it delivers improved signal-to-noise ratios and thus lower detection limits. These are achieved by the use of a CCD detector in the contrAA 700, which has an extremely low noise as compared to the photomultipliers customary used in LS AAS and by the use of the high-energy xenon short-arc lamp with its very high radiation intensity [**51**].

Chapter 2. Materials and methods

2.1 Sample preparation for elemental determinations in environmental samples

The analytical studies were performed with a HR-CS AAS series ContrAA 700 manufactured by Analytik Jena, Jena, Germany. The instrument is equipped with a xenon short-arc lamp with UV arc in the hot-spot mode. High-purity Ar 5.0 was used as inner gas for furnace AAS. As fuel gas for the flame AAS acetylene 2.6 was used. A line source flame AAS and vapour systems S series spectrometer (Thermo Electron Corporation, Cambridge, United Kingdom) was used as instrument for comparison and validation of the measurements with the dissolved samples. All samples were prepared in duplo and measurements were carried out under optimized conditions with three replicates using an auto sampler Micropipettor unit MPE 60 for the sample solutions in flame AAS. The samples were pipetted manually into the graphite furnace for slurry and direct solids sampling. Here 10 replicate measurements were made and an aqueous solution of the element to be determined was used as standard solution. The organic content was performed with an Elemental Analysis-Isotope Ratio Mass Spectrometry (EA-IRMS) Euro Vector manufactured by IVA Analysentechnik e.K, Düsseldorf, Germany. Microwave assisted digestion system CEM MARS 5 manufactured by CEM Corporation, NC, USA. Shaker machine 2400 rpm manufactured by Heidolph, Germany.

All chemical reagents were of analytical grade, HNO_3 and H_2O_2 from Merck, Germany were used for preparation of the calibration solutions and for sample pretreatment. Bi-distilled H_2O purified by sub-boiling distillation in a quartz distillery was used for the preparation of all solutions. Calibration solutions were prepared with a standard solution of 1000 mg L^{-1} of Fe, Cu, Ni, Cr, Cd and Pb from Merck, Germany. A solution of chemical modifier was prepared from 10 g L^{-1} $Pd(NO_3)_2$ and 10 g L^{-1} $Mg(NO_3)_2$ solutions (Merck, Germany), which were diluted with 0.2 % (v/v) HNO_3 so as to obtain 10 µg of $Mg(NO_3)_2$ and 15 µg of Pd as $Pd(NO_3)_2$ in 10 µL of modifier solution.

2.1.1 Water samples

Two bottles of natural water were sampled from the Alster lake, Hamburg and analyzed for Fe and Cu. The samples were treated by filtration using sterile filter papers Sartorius 0.2 µm and 0.45 µm. After filtration the samples are ready to be analyzed by LS FAAS and HR-CS GFAAS for Cu and Fe. Measurements were carried out at the Fe 248.327

nm and Cu 324.754 nm lines, respectively. Measurements were made with the same sample with and without matrix modifier. The calibration standard solutions for each element were prepared freshly every day of measurement.

2.1.2 Wet chemical sample treatment

For wet chemical treatment each water sample was coded and divided into four bottles, further each bottle was analyzed twice. The samples were collected in pure dark plastic bottles, stored at room temperature and than treated with distilled HNO_3 (Merck, Germany). Another sample was analyzed after adding H_2O_2 48% (Merck, Germany) without further purification. After adding acid in each bottle of sample, the samples were shaken at 2400 rpm for 5 minutes using a shaker machine (Heidolph, Germany). Afterwards the samples were directly analyzed. The duplicate samples obtained after wet digestion were filtered using a sterile filter paper Sartorius 0.2 µm and 0.45 µm and were ready to be analyzed for Cu and Fe by LS FAAS and HR-CS GFAAS. The standard calibration solutions for each element were freshly prepared at the beginning of each measurement day.

2.1.3 Quality Control

For quality control, analytical blanks and a sample with known concentrations of heavy metals were prepared and analyzed using the same procedures and reagents. As groundwater sample, standard reference material 1643e (NIST) was analyzed for trace elements. As sediment standard reference materials IMEP-14, CRM-320 and PACS-1 were used for the determination of trace elements.

2.2 Sample dissolution of sludge samples using microwave digestion

The goal of this procedure was to obtain a complete sample decomposition after an appropriate choice of acids for most matrices. We optimized the selection of the reagents towards the highest possible recoveries for the analytes. All sediment samples were digested under the use of a microwave assisted digestion system CEM MARS 5 (CEM Corporation Matthews, NC, USA). The microwave enhanced system was operated in accordance to the instruction manual and safety precautions. As acid digestion solution HNO_3 and HCl of ultrapure grade (Merck, Germany) were used after a purification by sub-boiling distillation.

As certified reference materials for sediments IMEP-14 (International Measurement Evaluation Programme, European Commission, Joint Research Centre (JRC), Institute for Reference Materials and Measurements (IRMM), Retieseweg, Geel, Belgium), CRM-320 (Trace Elements in River Sediment, Community Bureau of Reference, Geel, Belgium) and PACS-1 (Marine Sediment Reference Material for Metals and Other Constituents, National Research Council, Ottawa, Canada) were analyzed. Further, a total of 12 sediment samples obtained from SETOC, WEPAL (Wageningen Evaluating Programs for Analytical Laboratories, Wageningen, Netherlands) were analyzed. All samples were dried in an oven at 110 ºC for 5 h. The samples were weighed accurately to amounts of 500 mg. These samples were subjected to microwave assisted digestion in closed vessels with 16 mL of a mixture of $HCl:HNO_3$ (12:4). The microwave digestion program shown in **Table 2** was applied to the samples and after the digestion program, the samples solutions were filtered and the filtrate diluted to 50 mL with be-distilled water. The metal determinations were performed by FAAS, HR-CS GFAAS and HR-CS FAAS.

2.2.1 Acid digestion

Matrix destruction based on oxidation with concentrated acids is the most widely used approach for dissolving solid samples. Acid digestions in an oven or in closed pressured vessels are carried out with a wide variety of reagents. The selection of the specific reagent or the preparation of a reagent mixture depends on the sample to be digested. In this work the purpose of the digestion process was to obtain a digestion being as complete as possible while avoiding losses and contamination of the analytes. In this context, wet chemical digestions utilizing various acid solutions HCl, HNO_3, H_2O_2 and other liquid reagents were carried out in a closed vessel microwave assisted decomposition system. The sediment samples were treated by applying a temperature and pressure program aiming at a complete digestion. The general chemical reactions of various acid digestion reagents can be described as follows:

1. HNO_3 / H_2O_2

   Increase of the oxidation potential as a result of the reaction: $2H_2O_2 \rightarrow 2H_2O + O_2$

   Reoxidation of NO_x into NO_3^- by which the formation of the yellow nitrous oxides typical of nitric acid is suppressed. As typical a $HNO_3:H_2O_2$ mixture of 4:1 is used.

2. HNO_3 and HCl: HCl : HNO_3 = 3:1
   The mixture forms NOCl and releases chlorine as active component:
   $2NOCl \rightarrow 2NO_2 + Cl_2$
   The vapour pressure is: ~ 25 bar at ~ 200 ºC

3. HNO_3 oxidizes organic substances as: $(CH_2)_n + 2HNO_3 \rightarrow CO_2 + 2NO + 2H_2O$
   Its boiling point of 122 ºC (HNO_3 65%) and its vapour pressure is ~ 25 bar at ~ 225 ºC. It is frequently mixed with H_2O_2, HCl, HF or H_2SO_4. Soluble nitrates are formed with all elements except: Au, Pt, Al, B, Cr, Ti, Zr

4. HCl is a non-oxidizing agent with a boiling point of 84 ºC (HCl 32%) and a vapour pressure of ~ 25 bar at ~ 205 ºC. It forms soluble chlorides with all elements except: Ag, Hg, Ti. It dissolves the salts of weaker acid (carbonates, phosphates, borates) and can be used to digest iron alloys.

Attention must be paid to contamination when using concentrated acids and from the containers used for the digestion process. Additionally, attention must be paid to the microwave assisted temperature and pressure program in order to achieve complete mineralization of all analytes in the sediment samples.

2.2.2 Digestion program (power, temperature, pressure and hold time)

Microwave assisted sample preparation provides for an efficient and clean sample preparation for multi-element analytical techniques. The digestion programs vary for each element of interest, because each element has different properties and we need to consider the vapor pressure and other physiochemical properties to avoid losses of analyte. The heating profile often must be modified for each procedure. A typical microwave program is shown in Table 2.

Table 2. Microwave assisted digestion program.

Step	Power	%	Time (min.)	P (Bar)	Temperature (ºC)	Hold (min.)
1	600	100	30	10:00	150	10
2	600	100	30	15:00	175	10
3	600	100	30	20:00	200	10

Microwave assisted digestion in closed vessels with the system CEM MARS 5 (CEM Corporation Matthews, NC, USA) typically allows temperatures in the range of 180 – 260 ºC. The vessels should then be heated to at least 180 °C over 5 minutes and then held at 180 °C for at least 10 minutes. Amounts of 0.25 to 0.50 g of sample are weighed out in each reaction vessel and 12 mL of HCl are added to each vessel. Then 4 mL of H_2O_2 and/or HNO_3 are added. Further the vessels are sealed and placed in the rotor of the microwave digestion system. Here, the samples are heated directly by the absorption of microwave radiation. The temperature and pressure during the digestion process are monitored with the aid of temperature and pressure sensors. When the required temperature and pressure are reached and the digestion program is completed the sample vessels are removed from the microwave digestion system and the temperature and pressure inside the vessels were allowed to decrease to about 25-30 ºC and ~5 bar, respectively. Then the vessels can be opened gently because of the safety reasons. The sample solutions are poured into flasks of 50 mL and the sample remaining in the tube was removed by rinsing with bi-distilled H_2O. The rinsing water is mixed with the previous sample in the flask and was used to make up the solution up to the mark of the flask. The sample solution then was filtered using sterile filter paper Sartorius 0.2µm and 0.45 µm and is ready to be analyzed.

2.3 Procedure using an analysis of slurry samples

A slurry is a suspension of insoluble particles, usually in acid solution and/or in another media such as Triton X-100. Here, we have a homogeneous sample and the trace elements up to some extent are liberated into the solution [**53**]. Analyses of slurry samples could produce better results with respect to the elements recovery as compared to sample dissolution, where losses of analyte during sample preparation as a result of evaporation or adhesion to the filter paper may occur. Further, consideration must be given to the safety aspects and to the environmental, economic, time and contamination aspects so as to permit low detection limits. To obtain a good precision and recovery with slurry techniques it is necessary to optimize the influence of the particle size, the slurry concentration and homogeneity. The use of low concentrations of HNO_3 and H_2O_2 or other reagents that enhance the decomposition of residues inside the atomizer may help to improve the analytical performance. In this study slurry sample analyses of CRM and SETOC sediment samples were studied with respect to the heavy metal elements present in the sample. For the optimization of the analyses by slurry techniques there are several aspects to be considered:

2.3.1 Particle size and homogeneity

The particle size plays an important role for the recovery in slurry sampling and only with a homogeneous sample we can obtain low standard deviations. The finer the particle size also the longer the time for particle deposition lasts and that means the slurry is easier to handle. Because of this reason only a sample with very fine particles can be successfully used in slurry techniques. In this study the slurry technique was applied for 3 of the CRMs (IMEP-14, CRM-320, and PACS-1) and 2 of the SETOC samples (F1026 and F2159) with particle sizes of 37-125 µm so as to determine Cd, Cr, Cu, Fe, Ni and Pb. The samples were prepared from the CRM and SETOC samples after drying them at ±110 ºC during 5 hours. After the drying process, the samples were stored in desiccators for minimum 12 hours. An amount of sample of 5 mg is weighed and transferred into 50 mL sterile plastic tubes. After the addition of 20 mL of bi-distilled H_2O, the samples were shaken with a shaker rotor machine (Heidolph, Germany) during 5 hours. Amounts of 10 µL of the samples were aliquoted and pipetted manually into the furnace of the HR-CS GFAAS to determine the elements of interested.

2.3.2 Interferences and acidification

The acids added to the slurry samples could produce interferences in atomic spectrometry. Easily ionized elements are the most commonly present matrices which may produce interferences in elemental determinations by FAAS, GFAAS, ICP-AES and ICP-MS. Acids are often present in the solutions, because they are used for digestion or they are used for sample storage and analyte stabilization. Interferences such as spectral interferences often are due to the presence of polyatomic ions. To study the interferences resulting from acidification in the determination of Cd, Cr, Cu, Fe, Ni and Pb in sediment samples by slurry of HR-CS GFAAS, the acid concentrations in the slurry samples of CRMs were varied. Therefore, amounts of 50 mg of the samples were weighed appropriately and put into the sterile plastics tubes. After the addition of 20 mL of bi-distilled H_2O and 1, 2.5, 5 mL of distilled HNO_3 in addition, the samples were shaken on a shaker rotor machine (Heidolph, Germany) for about 5 hours and shaken again in the same way during 5 minutes each time before being introduced into the graphite furnace.

2.4 Direct solids sampling analysis

Here, the graphite platform is used as sample carrier and inserted into the graphite tube by the so called solid autosampler for manual mode (SSA 6). The solid sampler SSA 6 enables a reproducible placement of the sample platform with the solid sample in the graphite tube. The precision mechanism of the SSA 6 with the contamination-free Ti claw arm, enables the platform to be taken off and replaced in the inside of the graphite tube with exact positioning. The solid sampler SSA 6 is inserted into the sample chamber and, with the help of adjustable stops, its location is adjusted to the furnace position. A simple manual movement of the gripping pliers allows for a fast sample change. The sample weights used are recorded with an external balance before mounting the sampler. For a transport of the platform into and from the balance, a covered tray made of polyethylene was used. Prior to the first analysis run, the platform was cleaned by applying the temperature program. The sample was loaded onto the platform by means of a microspatula. The sample mass applied for an analysis cycle varied from 0.2 to 1 mg for a determination of the elements Cu, Fe, Cr, Ni, Cd and Pb in the sediment CRMs (IMEP-14, CRM-320, PACS-1) and also for the 12 SETOC sediment samples. In determinations with matrix modifier, appropriate amounts of modifier were added to the samples with the aid of a pipette before loading the sample to the furnace. Then the complete temperature program was executed and the measurement started. The instrument settings and the temperature program used are summarized in Appendix 13. These depend on the sample mass applied. After 1–5 sample runs the accumulated matrix residue was tipped out from the platform, followed by a cleaning of the tube and a blank measurement. For the determination of the blank, the complete analytical cycle was performed, including transport to and from the balance, but without using any sample. Calibration was performed by pipetting 10 μL of aqueous standard solutions on a used platform containing the matrix residue from a previous sample run. For signal evaluation, integrated absorbances were used. For direct solids sampling using weight variation, after each measurement the tube and the platform were subjected to the cleaning process.

2.5 Individual elements of interest

In analyses of inorganic samples such as in the case of the determination of heavy metals in environmental samples both the sample preparation and analysis must be optimized. Some metals have a different behaviour and also need a different pretreatment of the sample. Further, one also needs to consider the broadening of the absorption line of the metal, because in a spectrometric method, additional metals present in a complex mixture could lead to analyte interferences. By the width of the line emitted from the radiation source, together with the broad absorption line, the wavelength selector only has to isolate the line of interest from the spectrum emitted by the radiation source.

In elemental analyses by an atomic spectrometry method such as flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) the sample is normally analyzed as a solution. For each sample treatment, however, we have to consider that a minimum loss of analytes should be tolerated and that the interferences should be low. The most common interferences in atomic absorption are chemical interferences and background interferences, which relate to coincidences of spectral background structures with the elemental lines used [**20**]. When the sample to be analyzed contains a thermally stable compound of the analyte which is not totally decomposed by the energy of the flame, a chemical interference exists. Indeed, as a result hereof the number of atoms in the flame capable of absorbing radiation is reduced [**11**].

Particular information on matrix interferences for Cd, Cr, Cu, Fe, Ni and Pb for the individual elements is resumed below.

1. Cadmium (Cd)

Cd is an element of major environmental concern because of its high toxicity, and it has therefore to be determined in a wide variety of matrices at very low concentration levels. The most sensitive Cd line is 228.80 nm. This Cd line is located in the vicinity of strong PO absorption bands [**49**]. Further, spectral interferences arise from the As 228.81 nm line in FES and AAS. Also Na may interfere at this wavelength. When using the

326.11 nm line, the Cu 327.40 nm line interferes when the band pass is 0.64 nm or larger. In AAS the Co 326.1 nm line also might interfere. The pressure of Si may cause chemical interferences [**54**].

2. Chromium (Cr)

The international literature has provided many arguments that trivalent Cr is essential for living organisms and has a very low toxicity. However, hexavalent Cr such as present in chromates is highly toxic under common conditions. Nevertheless in daily praxis, as a result of the fact that the reduction of Cr(V1) to Cr(111) during uptake proceeds very rapidly its toxicity often is not serious [**7**].

Cr can be determined by FAAS or by GFAAS, but the latter determination is much more subject to interferences, which makes it difficult in the case of complex matrices. The main line is Cr 357.868 nm and it often is interfered by strong CN absorption bands. This has to be considered when a nitrous oxide / acetylene flame is used for its determination [**49**].

3. Copper (Cu)

Cu is a metal of major environmental concern because it is one of the essential trace nutrients for plants [**1**]. The resonance line of Cu (Cu 324.754 nm) is interfered by an absorption band of the PO molecule, for which the band head is at 324.62 nm. This has to be considered in GFAAS in the case of the presence of phosphate matrices [**49**].

4. Iron (Fe)

Fe is a most abundant element in the earth’s crust, which contains about 5% of Fe. Accordingly, contaminations in its determination often are an issue. Iron hydroxide and oxide surfaces strongly adsorb some environmentally important anions, such as phosphate, arsenate, selenite and cations like Cu, Pb, Mg and Cr [**55**]. The most sensitive analytical line is the Fe 248.327 nm line and Fe has more than 500 lines with greatly different sensitivity [**49**].

5. Nickel (Ni)

Ni is a heavy metal and its different compounds can be toxic in the environment. Natural pollution by Ni is associated with soils in which it is often present as the mineral serpentine. Serpentine containing soils are toxic for many plants and although large concentrations of Ni are the most significant toxic stressor, sometimes the presence of Co and/or Cr, along with a high pH and a low supply of nutrients also creates a toxic environment [**55**]. The most sensitive analytical line is the Ni 232.003 nm line which is in the spectral vicinity of strong PO absorption bands [**49**].

6. Lead (Pb)

Pb is one of the elements which are most frequently determined by AAS. The most sensitive analytical line is the Pb 217.001 nm line, which is in the vicinity of PO absorption bands [**49**].

Chapter 3. Results and discussion

3.1 Determination of Fe and Cu in natural water samples

Analyses of Alster lake water by HR-CS GFAAS were performed for Fe and Cu with the temperature program as shown in Appendix 1. The limits of detection (LOD) were calculated as the concentration for which the signals are equal to three times the standard deviation for 10 measurements of blanks, divided by the slope of the calibration curve. The figures of merit of the measurements are shown in more details in Appendix 2. Various treatments performed to the natural water samples are given in Table 5 and the measurements were made with 5 replications. The measurement results are presented in Fig. 15 and 16 and in more detail in Appendix 3.

Table 5. Water sample treatments for the determination of Fe and Cu.

Samples code	Treatments
N	Alster Lake sample no. 1 without treatment
S	Alster Lake sample no. 2 without treatment
NF	Sample N with filtration
SF	Sample S with filtration
NFHN	Sample N with filtration and HNO_3 was added to 5% v/v
SFHN	Sample S with filtration and HNO_3 was added to 5% v/v
NFHO	Sample N with filtration and H_2O_2 was added to 5% v/v
SFHO	Sample S with filtration and H_2O_2 was added to 5% v/v
NHN	Sample N without filtration and HNO_3 was added to 5% v/v
SHN	Sample S without filtration and HNO_3 was added to 5% v/v
NHO	Sample N without filtration and H_2O_2 was added to 5% v/v
SHO	Sample S without filtration and H_2O_2 was added to 5% v/v.

A filtration of the natural water samples (NF, SF) did not give any significant differences in the concentrations of Cu in the samples when comparing with the same natural water samples without filtration treatment (N, S). For the case of Fe, however, the result without a filtration and with the addition of modifier was 77.8±1.6 µg L^{-1} of Fe, which is almost 3 times higher than with the other treatment procedures for the same sample. This is due to the fact that the Fe mostly is contained in suspended particles retained on the filter.

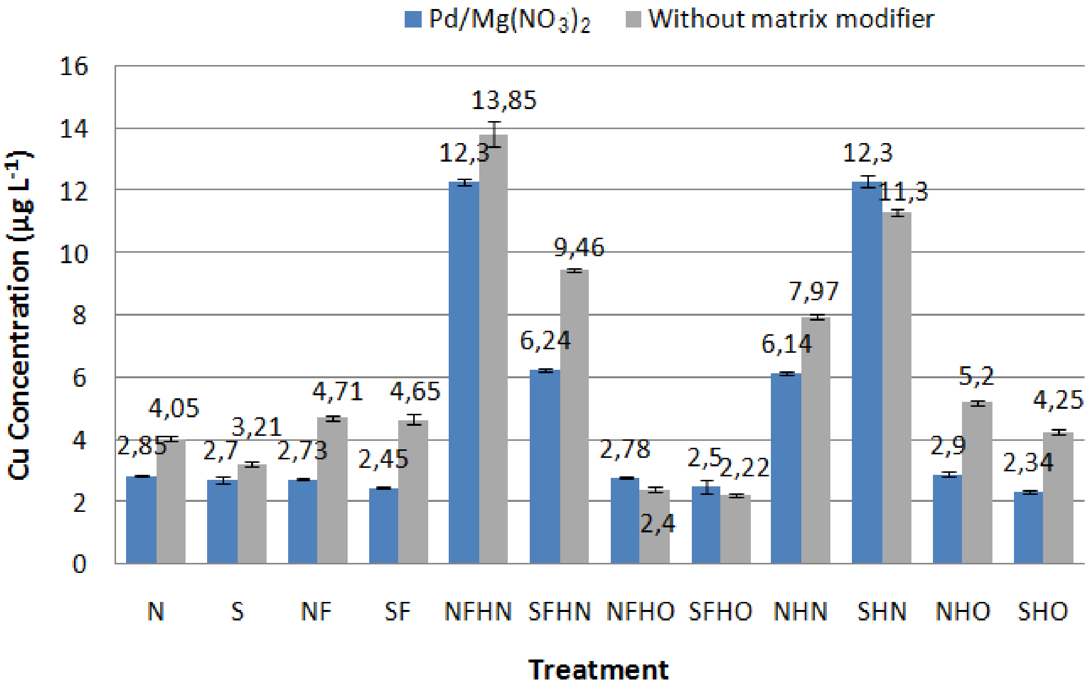


Fig. 15 Analysis results for Cu in Alster water samples obtained by HR-CS GFAAS without matrix modifier and by using Pd/Mg(NO_3)$_2$ as matrix modifier.

For the Cu in the samples there was no significant difference between results obtained without and with a modifier. The results obtained after an addition of 5% v/v of HNO_3 and H_2O_2 to the samples (NFHN) were about six times higher than those obtained after a treatment with HNO_3 only or with H_2O_2 only. The concentrations of Fe obtained with various treatments were the largest when directly adding HNO_3 to the natural water sample without previous filtration. Here a result of 152.9±6.4 µg L^{-1} of Fe was obtained. When analyzing the same sample (NHN) after a direct addition of HNO_3 without filtration by HR-CS GFAAS using a matrix modifier 196.3±5.8 µg L^{-1} of Fe were found. This indicates that the total amount of analyte in an unfiltered sample is the sum of the concentrations of metals in both the dissolved and suspended fractions. With HR-CS GFAAS we can determine the analyte in suspended particles in the natural water sample as the instrument also is capable to perform both slurry and direct solids sampling analyses.

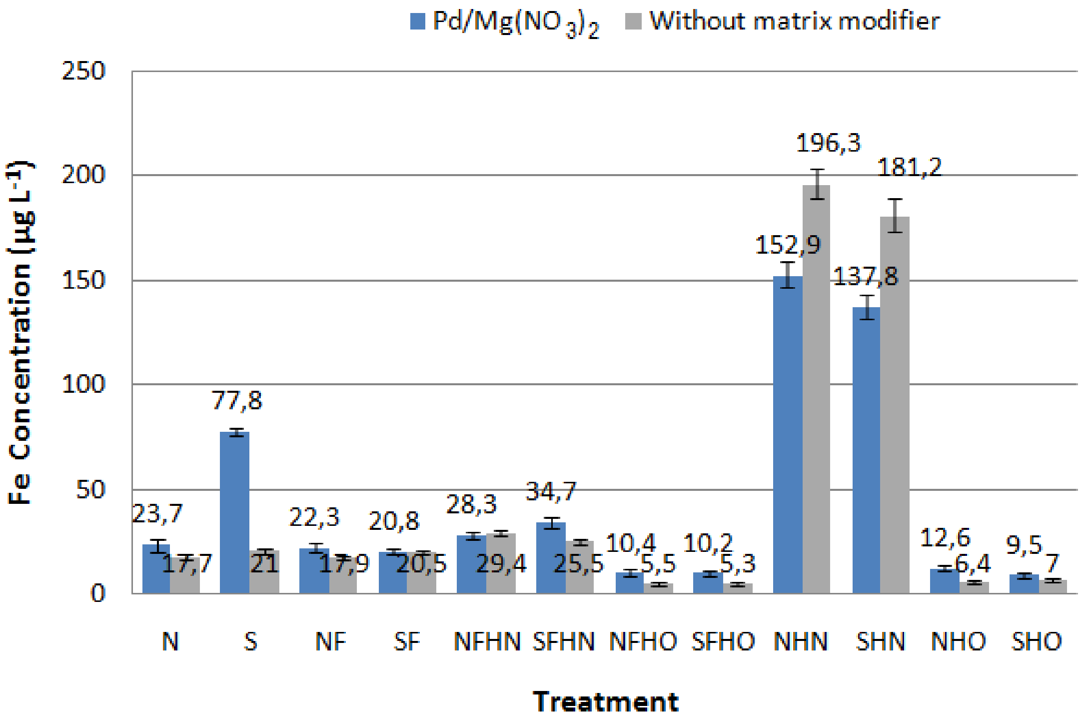
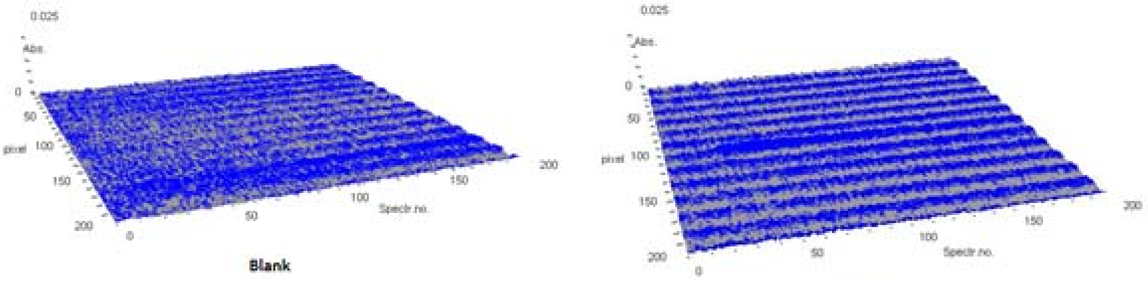


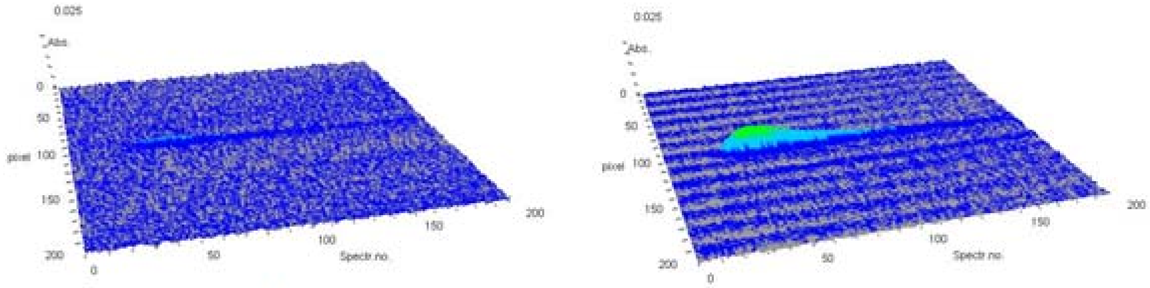
Fig. 16 Analysis results for Fe in natural water obtained by HR-CS GFAAS without matrix modifier and when using Pd/Mg(NO_3)$_2$ as matrix modifier.

Measurments under the use of a matrix modifier tend to give results with higher concentrations than when the samples (NHN, SHN) are treated by adding HNO_3. Treatments of the sample (NHO, SHO) with H_2O_2 usually give lower concentrations than measurements for Fe with a matrix modifier. The spectral interferences encountered during the analyses for Fe and Cu in natural water could always easily be compensated for by polynomial formation through selected reference points and by automatic spectral correction. This means that no special problem has ever been noticed when adding HNO_3 and H_2O_2 to the natural water samples with respect to an interference for the absorption for Cu.

When HNO_3 is used in the sample treatment, the absorbances for Fe and Cu were found to increase. This is confirmed by the blank absorbance spectra of 5% v/v HNO_3, where there is an absorption signal of 0.0056 only. However, when we investigate spectra obtained for HNO_3 (purified by distillation), $HNO_{3(p)}$ itself gives an absorption signal of about 0.0456 while $H_2O_{2(p)}$ did not give an absorbance signal as shown in Fig. 17.



Blank **$H_2O_{2(p)}$**



5% v/v HNO_3 **$HNO_{3(p)}$**

Fig 17. Spectrum of blank H_2O_2 and HNO_3 obtained with platform by HR-CS-GFAAS in the vicinity of Fe 248,327 nm (Pixel no. 101) and Cu 324.754 nm (Pixel no. 101).

The interference from HNO_3 on the analysis will take effect when the water sample is not filtered prior to acid addition [**56**]. The sample which is filtered before the acid addition treatment did not display a significant absorbance. Accordingly, it is clear that the increased absorbance for the Cu and Fe in the sample without filtration does not only stem from a HNO_3 interference. The use of a matrix modifier in the determination of Cu and Fe produces a slightly different result. For Cu the use of $Pd/Mg(NO_3)_2$ as matrix modifier lead to increased concentrations, while for Fe slightly lower concentrations as compared to measurements without matrix modifier with the same sample pretreatment were found [**57**].

3.2 Trace elements determination in water and sediment standard reference materials by LS FAAS and HR-CS GFAAS/FAAS

The determination of heavy metals in sediment and soil samples is important so as to monitor hazardous substances at low concentrations in the environment. Monitoring of the concentrations of metals such as Pb, Cd, Cr, Cu, Ni and Fe in such samples is crucial. The most commonly used methods for these studies are flame atomic absorption spectrometry (FAAS) and electrothermal atomic absorption spectrometry (ETAAS) also called graphite furnace atomic absorption spectrometry (GFAAS) as well as inductively coupled plasma atomic emission spectrometry (ICP-AES) or mass spectrometry (ICP-MS). These methods have recently been compared for the case of the determination of metals in acid digests of solids [**3**,**4**]. Most analytical methods require that the sample is in the liquid form. The conventional wet digestion procedures make use of a heating of the sample for some hours with several mixtures of acids, the addition of oxidizing agents such as HNO_3 or H_2O_2 (EPA method 3050) and eventually also works at high pressure under the use of a microwave digestion system.

When determining trace elements in environmental samples and especially in sediment or soil samples, we must treat the sample also in consideration of the elements of interest. Indeed, we need to consider that different elements need a different treatment to achieve the best result. The treatment must also address the type of sample we have and the concentration of the analyte.

Due to the heterogeneity of the matrices encountered in environmental work, we need to consider the distribution of the elements in the sample, especially in determinations by GFAAS. Because the matrix may hinder a complete atomization of the analyte and thus impact on the accuracy of the determination, several methodologies are practiced to separate the analyte from the matrix. Recent advances in instrumentation now also permit direct solids sampling approaches that remove the necessity for sample preparation. In addition, other aspects have to be taken into account, such as the clean-up and the homogeneity of the samples [**58**].

3.2.1 Determination of Cu, Fe, Cr, Ni, Cd and Pb in water and sediment standard reference materials by LS FAAS and HR-CS GFAAS

The determination of metals by FAAS in most frequently used procedures requires a digestion to dissolve the metal and remove the matrix. Most digestion methods involve dry ashing, the use of wet digestion with aqua regia, HNO_3 or a combination of two or more acids or oxidizing agents. Many procedures have been applied which differ with regard to reagent concentrations, temperature, pressure and/or time. Microwave and acid assisted digestion is claimed to be suitable for a wide variety of matrices [**59**].

3.2.1.1 Optimization of the temperature program for the determination of Cu, Fe, Cr, Ni, Cd and Pb in water and dissolved sludge samples by HR-CS GFAAS

Analyses by HR-CS GFAAS using a graphite tube equipped with or without platform need the use of a temperature program specific for each element. The temperature program is to be optimized while observing the signal generated.

Typical temperature programs are shown in Appendix 4. After dissolution of the sediment sample an aliquot of sample solution and modifier are mixed and introduced into the graphite tube inside the furnace with the aid of the automatic micropipettor unit MPE 60. The first step of a furnace temperature program is the drying step. Here the solution of sample and modifier is dried and during the following pyrolysis step contaminants or matrix constituents often can be removed [**49**]. The pyrolysis and atomization temperatures can vary, depending on the element being determined. In this study for all elements the same drying program is used prior to the pyrolysis. The pyrolysis step begins at 350 °C and the temperature is gradually increased according to the ramp and time of the pyrolysis program. When the temperature reaches the atomization step the temperature is drastically increased until the atomization is complete. After the atomization is completed, the furnace temperature is still increased to the temperature of the cleaning step. This aims at a thorough cleaning of the tube with respect to sample remains which potentially could interfere with the next measurement [**51**].

The temperature program plays an important role in analyses by HR-CS GFAAS. It determines the quality of the analysis results. The first step of a method development in GFAAS usually deals with an optimization of the pyrolysis and atomization temperatures by establishing pyrolysis and atomization curves with a matrix-free analyte solution as well as at least one representative sample or reference material. The pyrolysis curve shows the integrated absorbance signal obtained at a fixed atomization temperature as a function of the pyrolysis temperature [**49**]. The temperature program for each element of interest must be worked out to get the best results of measurement, because each element has a different thermal behavior resulting from the physicochemical properties of the element and its compounds. For instance, when the temperature program used allows atomization at low temperatures the analyte is likely to be partially lost due to early atomization. The atomization time also affects the number of pixels that are to be read by the detector in the instrument used in this work.

In this study the results obtained by LS FAAS and HR-CS GFAAS after such a digestion procedure using microwave digestion given data are shown in Table 9. The detection limits based on 3σ of the blank and the quantification limits based on 10σ of the blank for each analyte in the case of LS FAAS and HR-CS GFAAS are given in Table 6. The results show that the contaminations of the samples during microwave assisted digestion are not a significant problem. Indeed, the levels of blanks were found to be close to the detection limits. The detection limits and the quantification limits for each analyte by HR-CS GFAAS, however, were found to be considerably lower for most elements in HR-CS GFAAS.

Table 6. Analytical characteristics of the LS FAAS and HR-CS GFAAS procedures.

	LS FAAS				**HR-CS GFAAS**			
Element	**R^2**	**Slope (L μg^{-1})**	**LOD (μg L^{-1})**	**LOQ (μg L^{-1})**	**R^2**	**Slope (L μg^{-1})**	**LOD (μg L^{-1})**	**LOQ (μg L^{-1})**
Cr	0.999	0.0402	230	770	0.997	0.0063	0.06	0.19
Fe	0.999	0.0492	190	630	0.999	0.0483	0.05	0.17
Ni	1.000	0.0210	160	530	0.999	0.0633	0.02	0.067
Cu	0.999	0.0019	60	200	0.998	0.1454	0.21	0.71
Cd	0.999	0.0925	100	330	0.998	0.3160	0.012	0.041
Pb	0.999	0.0056	180	600	0.998	0.0296	0.008	0.027

The determination of metals by LS FAAS and HR-CS GFAAS needs to include the sample decomposition and the instrument optimization, in this case mainly the optimization of the temperature program of HR-CS GFAAS. In LS FAAS there are many aspects to consider e.g when the concentration of analyte in the sample is very high it is better to select a less sensitive line. Further, appropriate air and burning gas flows need to be selected so as to optimize the combustion. The optimum conditions found in this study for the determination of each element by LS FAAS using the Thermo S-series system are shown in Table 7.

The Cr 357.9 nm line is suitable for the determination of Cr by LS FAAS and HR-CS GFAAS. The Fe 248.327 nm line and the Ni 232.003 nm line are suitable for the analysis of water and sediment samples after dissolution. Cu has several resonance lines of different sensitivities suitable for LS-FAAS and HR-CS GFAAS determinations.

Table 7. Instrumental parameters used for the analysis of water and sediment samples by LS FAAS.

Parameters	Element					
	Cr	Fe	Ni	Cu	Cd	Pb
λ (nm)	357.9	248.3	232.0	324.8	228.8	217.0
Lamp current (%)	100	75	75	75	50	75
Gas flow (L min^{-1})	1.4	0.9	1.0	1.2	1.2	1.1
Burner high (mm)	8.0	7.0	7.0	7.0	7.0	7.0
Band width (nm)	0.5	0.5	0.2	0.5	0.5	0.5
Calibration range (mg L^{-1})	0.5 – 5.0	1.0 – 8.0	0.5 – 5.0	0.5 – 4.0	0.2 – 2.0	1.0 – 8.0

For determinations of Cu in this study the main resonance line Cu 324.754 nm is used, which has a high sensitivity and is suitable for measurements after sample dissolution. For Cd the most sensitive 228.802 nm line is chosen, because of the low Cd concentrations in the samples. The other lines Cd 226.502 nm and Cd 326.105 nm were of a too low sensitivity, For Pb a different line is used in LS FAAS and HR-CS GFAAS, namely the Pb 217.000 nm for LS FAAS and the Pb 283.306 nm line for HR-CS GFAAS. The latter Pb line has a sensitivity which is 40% of the one of the Pb 217.000 nm line in HR-CS GFAAS and it gives a very good signal for the case of analyses after dissolution of the sample. The resonance line of Pb 205.328 nm was found to have a too low sensitivity and was not suitable for the measurements. More details on the instrumental parameters used for the analysis of water and sediment samples by HR-CS GFAAS are shown in Appendix 4.

Meanwhile the same lines for all elements for LS-FAAS are also used in all measurements by HR-CS GFAAS, except for Pb. In LS-FAAS the Pb line 283.306 nm used in this study gives good signals compared with the Pb 217.0 nm line. This is possibly due to the high concentration of Pb in the sample, as the HR-CS GFAAS is a very sensitive instrument. Accordingly, it requires a less sensitive line as alternative when analyzing samples with high analyte concentrations.

Table 8. Trace element determinations in water standard reference material 1643e (NIST) by HR-CS GFAAS.

Element	Reference value (µg/kg)	LS-FAAS Results (µg/kg)	HR-CS GFAAS Results (µg/kg)	Recovery (%)
Cr	19.90±0.23	< LOD	18.9±0.5	95
Fe	95.7±1.4	< LOD	95.2±0.7	99
Ni	60.89±0.67	< LOD	61.4±4	101
Cu	22.20±0.31	< LOD	21.8±0.5	98
Zn	76.5±2.1	< LOD	76.5±2	100
Cd	6.408±0.071	< LOD	5.5±0.4	86
Pb	19.15±0.2	< LOD	20.6±1.3	107

The analysis results for a water certified reference material (CRM 1643e) obtained by LS-FAAS show that the concentrations of all elements determined are below the detection limits. The analysis of CRM 1643e by HR-CS GFAAS leads to very good results for all elements. The smallest recovery is obtained for Cd (86%) and an overestimate of 107% is obtained for Pb, with mean values and relative standard deviations for Cd of 5.5±0.4 µg/kg and for Pb of 20.6±1.3 µg/kg, respectively. All elements could be obtained with a very good recovery and a relatively small standard deviation.

The results of a statistical comparison of the mean values obtained with the reference values for the water standard reference material 1643e in the case of HR-CS GFAAS are shown in Table 8 and more details are given in Appendix 5. The results show that between the mean value for Cr and Cd and the attested value there is a significant difference, with $| t |$ being 4.47 and 5.08 for Cr and Cd, respectively. The observed values for Cr and Cd are outside the critical value as $t_4 = 2.78$ (P=0.05). However, the methods provide a recovery of 95 and 89 % for both analytes. So the concentrations for all analyte elements in the case of LS FAAS were < LOD, as the detection limits of LS FAAS are at the mg/kg level, while the concentration of trace elements in the sample are in the µg/kg range.

This can be understood from the fact that the sensitivities of both instruments are different and accordingly also the limit of detection. HR-CS GFAAS has lower limits of detection than LS FAAS, but in practice analyses by HR-CS GFAAS require a considerably longer time of analysis because of the temperature program used in HR-CS GFAAS. Especially the fact that in HR-CS GFAAS slurry sampling and even direct solids sampling can be applied is interesting. HR-CS GFAAS with direct solids sampling analysis is very helpful in terms of less needs for sample preparation whereby the risk for losses of analyte during sample preparation are lower [**49**,**60**,**61**].

3.2.1.2 Use of matrix modifiers in the determination of Cu, Fe, Cr, Ni, Cd and Pb by HR-CS GFAAS

The use of a Pd compound as modifier in analyses may be helpful to decrease matrix interferences and it may prevent elements from being lost by vaporization during the pyrolysis step by GF-AAS [**62**]. The mechanism of reaction of Pd compounds as a chemical matrix modifier in GF-AAS has been the subject of intensive investigations over 30 years of application of this method. The mechanisms of analyte retention on Pd during the pyrolysis step are based on three different types of migration: migration onto a Pd modifier, wall to platform migration and migration into the graphite [**63**]. The mechanism includes thermal decomposition during which the sample is dispersed in the beginning of the atomization. The initial sample undergoes a close to unity order reaction during the atomization of the analyte. Futher, a redistribution of solid sample residue over the surface during the pyrolysis step occurs and in particular the sample possibly escapes from the platform onto the tube wall.

Table 9a. Analysis of the sediment certified reference material IMEP-14 by microwave assisted digestion and HR-CS GFAAS with and without matrix modifier (n=5).

Element	**Reference value**	**IMEP-14**			
		Without modifier	**Recovery (%)**	**With modifier**	**Recovery (%)**
Cr(mg/kg)	57.4±1.6	53.6±17	93	60.1±5.4	105
Fe(g/kg)	25.4±2.5	23.4±2.9	92	25.7±0.4	101
Ni(mg/kg)	26.06±0.7	26.9±0.3	103	26.2±0.8	100
Cu(mg/kg)	47.21±4.7	49.8±8.8	105	45.7±2.0	97
Cd(mg/kg)	2.61±0.09	2.3±0.4	88	2.8±0.5	107
Pb(mg/kg)	87.25±1.7	83.9±3.4	96	86.6±3.2	99

Table 9b. Analysis of the sediment certified reference material CRM-320 by microwave assisted digestion and HR-CS GFAAS with and without matrix modifier (n=5).

Element	**Reference value**	**CRM-320**			
		Without modifier	**Recovery (%)**	**With modifier**	**Recovery (%)**
Cr(mg/kg)	138±7	137±6	99	119±24	86
Fe(g/kg)	-	32.2±2	-	39.5±4	-
Ni(mg/kg)	75.2±1.4	82.7±5.6	110	70.1±1.4	93
Cu(mg/kg)	44.1±1.0	47.9±8	109	39±4	88
Cd(mg/kg)	0.533±0.026	0.55±0.3	103	0.53±0.01	99
Pb(mg/kg)	42.3±1.6	44.2±0.7	104	44.8±4	106

Table 9c. Analysis of the sediment certified reference material PACS-1 by microwave assisted digestion and HR-CS GFAAS with and without matrix modifier (n=5).

Element	**Reference value**	**PACS-1**			
		Without modifier	**Recovery (%)**	**With modifier**	**Recovery (%)**
Cr(mg/kg)	113±8	-	-	92±11	81
Fe(g/kg)	48.7±0.8	-	-	48.7±0.8	100
Ni(mg/kg)	44.1±2.0	41.9±4.5	95	42.1±1.5	95
Cu(mg/kg)	452±16	-	-	439±36	97
Cd(mg/kg)	2.38±0.026	2.47±0.8	104	2.41±0.05	101
Pb(mg/kg)	404±20	-	-	-	-

The peak shape and the magnitudes of the background absorption signals were considered in the development of the temperature programs using both the sample and the standard solution. When no modifier is added to the sample, the background signal of the analyte is influenced by the sample matrix. Matrix modifiers in the determination of heavy metals in sediments and soils also significantly contribute to the determination of elements because matrix modifiers may prevent analyte losses that very commonly occur in the analysis of environmental samples. Several matrix modifiers were used in the determination of Cu so as to get the optimum conditions of measurement. The modifier $Pd(NO_3)_2$ 0.1% + $Mg(NO_3)_2$ 0.05% was used in the determination of Cu and gave results which are in good agreement with the certified value. In other cases measurements using the same temperature program and amount of sample did not give good results, because a loss of analyte occurs during the drying or pyrolysis step [**63**,**64**].

A loss of analyte in the pre-atomization step can be minimized by applying a modifier as well. In many reports it is shown that the modifier $Mg(NO_3)_2$ 0.05% can be used to avoid a loss of analyte during the measurement. Mg and Pd compounds are used as modifier in this study and the measurement results are shown in Table 9a to 9c. The *t*-test showed that there was a difference in the case of CRM samples, using in other case eight degrees of freedom for which the critical value is t_8=2.31 at a confidence level of 95%. More detailed results are shown in Appendix 9. Although the value of the *t*-test is not far away from the critical value, it can be stated that measurements with and without modifier give significantly different analytical results.

3.2.2 Determination of Cu, Fe, Cr, Ni, Cd and Pb in sediment standard reference materials by LS FAAS and HR-CS FAAS

The results for three certified reference materials of sediment samples (IMEP-14, CRM-320, PACS-1) obtained by LS FAAS after sample dissolution using microwave assisted digestion are shown in Table 10. The results for IMEP-14, CRM-320 and PACS-1 by HR-CS FAAS are shown in Table 11. The comparison between the mean values of Cr, Fe, Ni, Cu, Cd and Pb in the three CRM sediment samples determined by LS FAAS give the $| t |$ values shown in Appendix 6, which testify that there is a good agreement with the certified values (for four degrees of freedom $t_4 = 2.78$ (P=0.05)) [**65**].

The $| t |$ values for Cr and Cu in IMEP-14 are 13.42 and 10.25, respectively, and more details the statistical evaluation is given in Appendix 6. For both elements the t-values obtained are higher than in the $| t |$ table, so that the results for Cr and Cu have a significant difference with the reference value. However, the analysis result for Cr is 47.8±1.6 mg/kg and for Cu it is 44.0±0.7 mg/kg and for both elements the recovery is 83 and 93%, respectively. This percentage is a pretty good result, as the difference in the standard deviation for Cu in this study is small when compared with the standard deviation of the certified value. This is understandable since the certified value is the average value of various laboratory values and of different instruments. The measurement results for Fe, Ni, Cd and Pb are 24.8±1.38 g/kg, 26.2±0.4 mg/kg, 310±17 mg/kg and 84.4±2.9 mg/kg, respectively. The $| t |$ values calculated for Fe, Ni, Cd and Pb did not differ significantly and the recovery for each element being between 97 and 103% is also very good.

Measurements for CRM-320 gave $| t |$ test values for Cr, Ni, Cu, Zn and Pb of 38.01, 14.91, 0.84, 20.12 and 1.68, respectively, while for Fe and Cd they were not determined as no reference value was available. The $| t |$ test values for the obtained Cr, Ni and Zn values were higher than in the tables, so the results of this analysis are statistically different from the certified values. However, the recovery for these measurements for Cr, Ni, Cu, Zn and Pb with 88, 105, 103, 81, 103 %, respectively, was still very good. The lowest recovery of 81% was obtained for Zn and the highest for Ni (105%). This is possibly due to the loss of analytes during sample preparation or dilution. As reflected by the relative standard deviations of analysis, the precision of this method is high.

For the sediment reference material PACS-1 in the case of the elements Cr, Fe, Ni, Cu, Cd and Pb a good recovery is obtained and only for Cu and Cd the $| t |$ values calculated with 21.2 and 4.5, respectively, considerably differ from the values connected with four degrees of freedom $t_4 = 2.78$ (P=0.05). However, with a recovery of 91% for Cr, 96% for both elements Fe and Cu, 98% for Cd, 99% for Ni, 102% for Pb and 103% for Zn the results are still very good. The recoveries for Pb and Zn are higher than 100% but still within the tolerance given for the reference values for both elements.

A determination of the analytes in the sediment certified materials by HR-CS FAAS gave somewhat better results than in the case of LS FAAS. The measurement results for Cr, Fe, Ni, Cu, Cd and Pb by HR-CS FAAS are shown in Table 11 and more details are given in Appendix 7. The $| t |$ values calculated are below the critical value, except for Cu and Pb in IMEP-14, Cr and Zn in CRM-320 and for Ni and Cu in PACS-1. For Cu in IMEP-14 and PACS-1 the *t*-test gave values of 8.66 and 3.73, respectively. In general the method gave a good agreement between analysis results and reference values and the recoveries are above 81% for all elements determined.

Table 10. Results for elemental determinations in CRM sediment samples obtained with microwave assisted digestion system using HNO_3 and LS-FAAS (n=5).

Element	IMEP-14			CRM-320			PACS-1		
	Reference value	Results	Recovery (%)	Reference value	Results	Recovery (%)	Reference value	Results	Recovery (%)
Cr(mg/kg)	57.4±1.6	47.8±1.6	83	138±7	121±1	88	113±8	103±8.2	91
Fe(g/kg)	25.4±2.5	24.8±1.38	98	-	38.5±1.0	-	48.7±0.8	46.9±1.6	96
Ni(mg/kg)	26.06±0.7	26.2±0.4	101	75.2±1.4	79.2±0.6	105	44.1±2.0	43.7±1.2	99
Cu(mg/kg)	47.21±4.7	44.0±0.7	93	44.1±1.0	43.5±1.6	103	452±16	433±2	96
Zn(mg/kg)	324±32	310±17	96	142±3	115±3	81	824±22	851±30	103
Cd(mg/kg)	2.61±0.09	2.7±0.2	103	0.533±0.026	-	-	2.38±0.026	2.3±0.04	98
Pb(mg/kg)	87.25±1.7	84.4±2.9	97	42.3±1.6	43.5±1.6	103	404±20	414±26	102

Table 11. Results for elemental determinations in CRM sediment samples obtained with microwave assisted digestion system using HNO_3 and HR-CS FAAS (n=5).

Element	IMEP-14			CRM-320			PACS-1		
	Reference value	Results	Recovery (%)	Reference value	Results	Recovery (%)	Reference value	Results	Recovery (%)
Cr(mg/kg)	57.4±1.6	58.7±1.8	102	138±7	121±5	88	113±8	113±7	100
Fe(g/kg)	25.4±2.5	25.0±0.5	99	-	39.0±1.2	-	48.7±0.8	48.0±1.2	99
Ni(mg/kg)	26.06±0.7	25.9±3.5	99	75.2±1.4	74.5±4.0	99	44.1±2.0	39.3±3.3	89
Cu(mg/kg)	47.21±4.7	44.5±0.7	94	44.1±1.0	44.5±1.4	99	452±16	442±6	98
Zn(mg/kg)	324±32	310±17	96	142±3	115±3	81	824±22	851±30	103
Cd(mg/kg)	2.61±0.09	2.6±0.05	100	0.533±0.026	0.53±0.01	97	2.38±0.026	2.3±0.1	98
Pb(mg/kg)	87.25±1.7	84.2±2.9	96	42.3±1.6	42.2±0.4	100	404±20	415±22	103

The results of analysis for each element obtained by LS FAAS and HR-CS FAAS show where there is a significant difference. Indeed, in the case of each method five determinations were made, so that these two methods have mean differences with eight degrees of freedom and a critical value t_8=2.31 for a confidence level of 95% (*P*= 0.05). For the sample IMEP-14 in the case of Cr there is a significant difference for | *t* | (10.12) while for other elements this is not the case. For sample CRM-320 there is a significant difference for Ni with a | *t* | of 2.60. In the case of the sample PACS-1 there is also a significant difference between the | *t* | values of Ni and Cu with | *t* | values of 2.80 and 3.18, respectively. For the other elements the | *t* | values for the results obtained by both methods were below the critical value.

Table 12. Results for SETOC samples obtained by microwave assisted digestion and LS-FAAS (n=5).

Samples	Cr (mg/kg)	Fe (g/kg)	Ni (mg/kg)	Cu (mg/kg)	Cd (mg/kg)	Pb (mg/kg)
F1026	111±5	17.1±0.8	30.9±1.7	50.4±5.0	2.0±0.1	384±22
F1027	142±2	27.8±0.3	42.7±2.3	132±9	1.73±0.03	141.5±0.2
F1028	77.7±2.2	19.3±0.2	25±0.4	38.6±2.5	-	48±2.6
F1029	69.8±0.6	21.4±0.3	43.4±0.6	50.5±2.5	-	317±10
F2159	94.2±0.5	28.0±1.1	42.4±2.6	51.6±4.9	-	108±4
F2160	194±3	35.8±0.3	46.4±1.1	139±1	5.9±0.2	304±2
F2161	88.8±7.6	16.5±1.4	38.0±0.9	54.6±5.2	2.0±0.3	344±29
F2162	71.0±1.0	35.8±0.2	26.2±0.5	103±8	-	176±2
F0454	46.4±0.5	20.47±0.09	30.1±1.5	16.3±0.8	-	26.7±1.2
F0455	146±2	29.9±0.7	38.9±3.6	56.1±6.2	-	147±0.5
F0456	54.8±0.5	19.1±0.5	21.2±0.9	62.5±2.0	-	270±15
F0457	106±1	16.44±0.01	28.7±0.2	54.01±0.09	2.10±0.06	368±12

Table 13. Results for SETOC samples obtained by HR-CS FAAS subsequent to microwave assisted digestion (n=5)

Samples	Cr (mg/kg)	Fe (g/kg)	Ni (mg/kg)	Cu (mg/kg)	Cd (mg/kg)	Pb (mg/kg)
F1026	105±2	18.5±0.1	32.4±2.2	56.6±3.8	2.6±0.2	383±10
F1027	147±2	30.2±0.4	46.9±0.9	137±4	4.1±0.3	148±9
F1028	72.4±2.0	23±1.1	27.1±4.0	43.4±2.9	0.8±0.2	53.8±1.2
F1029	73.8±1.5	24.4±0.5	44.6±0.4	58.9±0.6	1.26±0.07	324±3
F2159	95.0±0.6	30.4±0.7	40.1±2.0	61.4±0.4	1.9±0.3	109±4
F2160	198±4	39.7±1.0	57.2±0.5	146±3	4.8±0.4	312±3.4
F2161	90±0.7	18.6±0.9	38.68±0.01	53.3±6.4	2.8±0.2	341±7.1
F2162	72.3±0.3	34.4±2.4	41.1±1.1	118±2	0.82±0.02	173±4
F0454	50.9±1.1	21.8±0.3	34.5±0.6	18.3±0.6	0.54±0.06	26.4±1.0
F0455	154±7	31.20±0.07	42.1±0.2	60.25±0.04	1.1±0.1	164±7
F0456	56.4±3.4	20.0±0.2	23.8±1.1	63.5±0.9	1.1±0.1	256±7
F0457	95.7±3.2	18.7±0.3	31.16±0.09	52.2±0.3	2.4±0.1	388±26

Measurements by LS-FAAS and HR-CS FAAS subsequent to dissolution using microwave digestion for the SETOCs sample gave good results. With respect to the standard deviations for each element, it can be said that the results of the methods used are still in good agreement. Only for Cd in some of SETOC samples the concentrations were below the detection limit. By comparing the data in Table 12 with those in Table 13, it is understandable why it was not possible to determine the concentrations of analyte in the samples with LS-FAAS, as the concentration of Cd in the samples was below the detection limit.

The t-test for the mean values for the results of analysis of the SETOC samples by LS FAAS and HR-CS FAAS (Table 12 and 13) show that there are significant differences in the results in both cases, where eight degrees of freedom and critical value of t_8=2.31 (confidence level 95%) apply. More details are shown in Appendix 8. It can be concluded that the two methods often give statistically different results. This can be understood from the fact that the sensitivities of both instruments are different and accordingly also the limits of detection. HR-CS FAAS has lower limits of detection than LS FAAS.

3.3 Application of the slurry technique for the determination of Cu, Fe, Cr, Ni, Cd and Pb in sediment samples by HR-CS GFAAS

Slurry analysis has been used for the determination of a variety of elements by flame and graphite furnace AAS. The slurry technique also was applied in the case of the hydride generation, which offers the advantages of a much simpler and faster sample pretreatment [**66**].

In this work the slurry technique was used for the three sediment certified reference materials IMEP-14, CRM-320, PACS-1 and as real samples the two SETOC samples coded F1026 and F2159 were analyzed. Prior to the slurry preparation, the sediment samples were not further grounded and all the CRMs and SETOC samples were used in accordance with the standard conditions. Slurries of the sediments were prepared in 2.5 mL of 7% HNO_3 by weighing 5.00 mg of sediment in the polyethylene vessels. Then the slurries were homogenized in the vessels with the aid of a shaker rotor during 2 hours and additionally shaked for 5 minutes before the slurry sample was introduced into the graphite tube, so as to reduce the error caused by the lack of stability of the slurries. In this study no slurry stabilizer was used.

For the slurry procedure calibration was applied by the standard addition technique using analyte solutions and $Pd/Mg(NO_3)_2$ was used as matrix modifier. Analysis results for the standard references materials and for SETOC samples are shown in Table 14. The results show that the recoveries for the slurry technique in HR-CS GFAAS were between 60% and

125%. The lowest recovery results are obtained for Ni in IMEP-14 and PACS-1, being only 60% and 66 %, respectively.

The determination of Cr in sediment samples in the case of $Mg(NO_3)_2$ as matrix modifier was possible with a good recovery for the sample IMEP-14 and CRM-320, namely 106% and 98%, respectively. For the PACS-1 sample, however, the same procedure and matrix modifier lead only to a recovery of 79%. A similar result was obtained for Fe in PACS-1 where the recovery was 79%.

The recovery for Fe in IMEP-14 was 90%, while for CRM-320 no reference value was available. However, for the analysis result a value of 39.4±0.8 g/kg was obtained. Accordingly, the determination of Fe using $Mg(NO_3)_2$ as matrix modifier had provided a good precision.

The low recoveries for Ni with the slurry technique in IMEP-14 and PACS-1 are somewhat difficult to explain. Also the origin of the sediment in each CRM and SETOC samples is unable to provide an explanation, as IMEP-14 [**67**] and CRM-320 [**68**] are river sediments while PACS-1 is a marine sediment [**69**,**70**,**71**]. Possibly a loss of Ni during the pyrolysis step and incomplete atomization occurred. On the other hand for the reference sample CRM-320 with the same procedure a good recovery (107%) was obtained.

All the determinations of Ni in sediment samples done with the slurry procedure used a matrix modifier, because it is almost impossible to determine Ni because of interferences and significant deviations in the results of the analysis when not using a matrix modifier. The presence of HNO_3 from the slurry preparation has been found to have no significant influence on the absorbance for Ni [**72**]. The recovery of 66% for Ni in PACS-1 was pretty poor, because other studies reported that without matrix modification and background correction it is almost impossible to determine precisely Ni in sea water [**73**].

In the determination of Cu using $Pd/Mg(NO_3)_2$ as matrix modifier for the case of CRM-320 the highest overestimate (129%) was obtained, whereas for Cd in IMEP-14 and PACS-1 the lowest recovery (92%) for both samples was measured. The result for Cd in CRM-320 seems much higher than the reference value, but when viewed from the uncertainty factor of the measurement then the values are still acceptable. Since Cu has several resonance lines it is possible to control if a spectral interference during the measurement [**74**]. The use of other matrix modifiers such as $Mg(NO_3)_2$ and $NH_4H_2PO_4$ did not provide good results for Cu in IMEP-14 and PACS-1 samples.

In the determination of Cd in the CRM-320 sample the use of the matrix modifiers $NH_4H_2PO_4$ and $Pd/Mg(NO_3)_2$ gives significantly different recoveries. With $Pd/Mg(NO_3)_2$ the recovery in CRM-320 was 75% and with $NH_4H_2PO_4$ a recovery of 103% was obtained. $NH_4H_2PO_4$ additionally was used as matrix modifier in the determination of Cd in order to prevent interferences from matrix components [**75**].

The determination of Cd in the IMEP-14, CRM-320 and PACS-1 samples with $NH_4H_2PO_4$ as matrix modifier provided results of 3.0±0.3 mg/kg, 0.55±0.07 mg/kg and 2.3±0.2 mg/kg, respectively. Taking into account the uncertainty for all Cd results in the three CRM samples, it can be concluded that the use of $NH_4H_2PO_4$ as matrix modifier has produced a good recovery in the IMEP-14 and CRM-320, namely 115 % and 103 %, respectively, despite the relatively low concentration of Cd in the samples. With the use of $Pd/Mg(NO_3)_2$ as matrix modifier in the PACS-1 sample a recovery of 97% was obtained and for the CRM-320 sample with $Mg(NO_3)_2$ a recovery of 75% was obtained.

The analysis for Pb in CRM-320 in the case of the two modifiers $Mg(NO_3)_2$ and $Pd/Mg(NO_3)_2$ had a good recovery for both modifiers. However, there are significant differences between both modifiers with respect to the uncertainty: with $Mg(NO_3)_2$ a result of 43.7±9 mg/kg was obtained, whereas with $Pd/Mg(NO_3)_2$ the result was 41.5 ±1.4 mg/kg. The presence of Pd resulted in a better precision in the determination of Pb by HR-CS GFAAS. Small amounts of Pd used in the determination of Pb could significantly change the vaporization and the residence times of the atomic vapors. The vapor removal seemed to be 1.5-1.8 times slower than that predicted by theory for the diffusion of the vapor. An involvement of vapor adsorption by the wall and molecular diffusion in the vapor transport is suggested [**76**]. The determination of Pb in IMEP-14 samples with $Pd/Mg(NO_3)_2$ as matrix modifier has provided a result of 80.9±8 mg/kg, which represents a recovery of 93%. The result for the PACS-1 sample is 426±24 mg/kg with a recovery of 105% with respect to the certified value.

Table 14. Slurry sampling analysis of sediment certified reference materials by HR-CS GFAAS (n=10).

Element	IMEP-14			CRM-320			PACS-1		
	Reference value	Results	Recovery (%)	Reference value	Results	Recovery (%)	Reference value	Results	Recovery (%)
Cr(mg/kg)	57.4±1.6	61±6.7$^{\#}$	106	138±7	135±7$^{\#}$	98	113±8	89.8±5.5$^{\#}$	79
Fe(g/kg)	25.4±2.5	22.8±0.1$^{\#}$	90	-	39.4±0.8$^{\#}$	-	48.7±0.8	38.5±1.2$^{\#}$	79
Ni(mg/kg)	26.06±0.7	15.6±0.1$^{\#}$	60	75.2±1.4	80.6±4.3$^{\#}$	107	44.1±2.0	29.3±1.5$^{\#}$	66
Cu(mg/kg)	47.21±4.7	43.3±3.8^{+}	92	44.1±1.0	52.4±5.5^{+}	129	452±16	417±13^{+}	92
Cd(mg/kg)	2.61±0.09	3.0±0.3*	115	0.533±0.026	0.55±0.07*	103	2.38±0.026	2.3±0.2^{+}	97
					0.4±0.03^{+}	75			
Pb(mg/kg)	87.25±1.7	80.9±8^{+}	93	42.3±1.6	41.5 ±1.4^{+}	98	404±20	426±24*	105
					43.7±9$^{\#}$	103			

* $NH_4H_2PO_4$

\# $Mg(NO_3)_2$

\+ $Pd/Mg(NO_3)_2$

A statistical evaluation of the difference between the mean values of the measurements and the reference values with 8 degrees of freedom and a critical t-value of t_8=2.31 at a confidence level 95% was made. The results for the slurry sampling in the analysis of the sediment by HR-CS GFAAS are shown in Appendix 12. The results of analysis of the slurry technique are quite good. Only for Ni in all of the three CRM samples a low recovery was obtained. The difference between the mean values of the measurements and the reference values also here was shown to be significant. For the other elements Cr, Fe and Cu a good precision and recovery was obtained.

The recovery for each element depends on many factors. For Ni in IMEP-14 and PACS-1 it could be explained by an interference of the matrix elements in the sample, while the line of analysis 232.003 nm was the same as applied in the solution technique. For other elements the recovery results with 79% to 106% were quite acceptable. In terms of the standard deviations the slurry technique also provided good results, so it can be concluded that the slurry sample technique for the samples studied produces good results for routine applications.

Table 15. Analysis results for SETOC sediment samples with slurry sampling and HR-CS GFAAS (n=10).

Element	**SETOC**		**Uncertainty (%)**
	F1026	**F2159**	
Cr(mg/kg)	85.0±7.9	$105\pm13^{\#}$	9.3-12.4
Fe(g/kg)	20.4±0.9	$21.1\pm0.9^{\#}$	4.3-4.4
Ni(mg/kg)	25.5±0.1	$45.9\pm1.8^{\#}$	0.4-3.9
Cu(mg/kg)	41.3±0.6	$42.1\pm3.4^{+}$	1.5-8.1
Cd(mg/kg)	2.9±0.1	1.2±0.3*	3.4-25
Pb(mg/kg)	443±26	$110\pm6^{+}$	5.5-5.9

* $NH_4H_2PO_4$

\# $Mg(NO_3)_2$

\+ $Pd/Mg(NO_3)_2$

The same procedure, which has been used for the analysis of the three standard reference materials (IMEP-14, CRM-320 and PACS-1), also has been used for the analysis of two SETOC sediment samples and the analytical results are shown in Table 15. The determination of Cu, Fe, Cr, Ni, Cd and Pb in the SETOC samples by the HR-CS GFAAS slurry technique made use of the matrix modifiers $NH_4H_2PO_4$, $Mg(NO_3)_2$ and $Pd/Mg(NO_3)_2$. The matrix modifiers are used appropriate to the element measured. For the determination of each element in the SETOC samples the slurry technique gave good results. In view of uncertainty factor, the method has a good precision. Only the result for Cd has an uncertainty which is somewhat larger than for the other elements. This can be understood from the very low concentration of Cd in the sample and the possibility of an inhomogeneous distribution of the analyte in the sample.

3.4 Determination of Cu, Fe, Cr, Ni, Cd and Pb in sediments by direct solids sampling HR-CS GFAAS.

Direct solids analysis HR-CS GFAAS makes use of a calibration with aqueous standard solutions. $Pd/Mg(NO_3)_2$ was used as matrix modifier and gave very good results, as shown in Table 16. All analytes are determined with their optimum line. As shown in Fig. 18 in the determination of Cd the Cd 228.802 nm line is very close to lines of the major elements, namely Fe 228.763 nm and Ni 228.840 nm. Nevertheless, the instrument was able to separate and distinguish the analyte signals properly and to use these characteristic lines.

Accordingly, HR-CS AAS is an extremely valuable tool for the analysis of complex samples. Particularly the direct analysis of solid samples and of samples as slurries is interesting. The system is equipped with a linear charge-coupled device (CCD) array detector, of which 200 pixels are used analytically. This means that the equipment works with 200 independent detectors that are illuminated and read out simultaneously. Pixels which are not needed to measure the atomic absorption can be used to correct for any fluctuation of the measured radiant flux, which is continuous over the spectral range covered by the detector. This includes lamp flickering noise or continuous background absorption. The visibility of the spectral environment within approximately ± 0.25 nm at both sides of the analytical line is another feature, which greatly facilitates method development and optimization. It also shows spectral interferences and makes it much easier to correct for them, when spectral interferences cannot be avoided. HR-CS AAS also offers the possibility to correct for them by using a least-squares algorithm [**77**].

The use of 200 independent detectors also makes a simultaneous determination of more than one element possible, provided the second analyte has an absorption line within the spectral window covered by the CCD array. As this second line almost inevitably is a less sensitive secondary line, it is of particular advantage that due to the use of a high-intensity continuum radiation source in HR-CS AAS, the intensity is essentially the same at all wavelengths, resulting in somewhat improved signal-to-noise (S/N) ratios for all analytical lines. A secondary line can actually be used for analytical purposes when the sensitivity ratio between the two lines is compatible with the concentration ratio of the two analytes in the samples to be analyzed. Another condition, particularly in GFAAS, is that a temperature program can be found that allows the simultaneous determination of both elements without deteriorating too much the performance for one of the analytes. Usually the pyrolysis temperature is determined by the more volatile and the atomization temperature by the less volatile analyte [**49**,**58**,**77**].

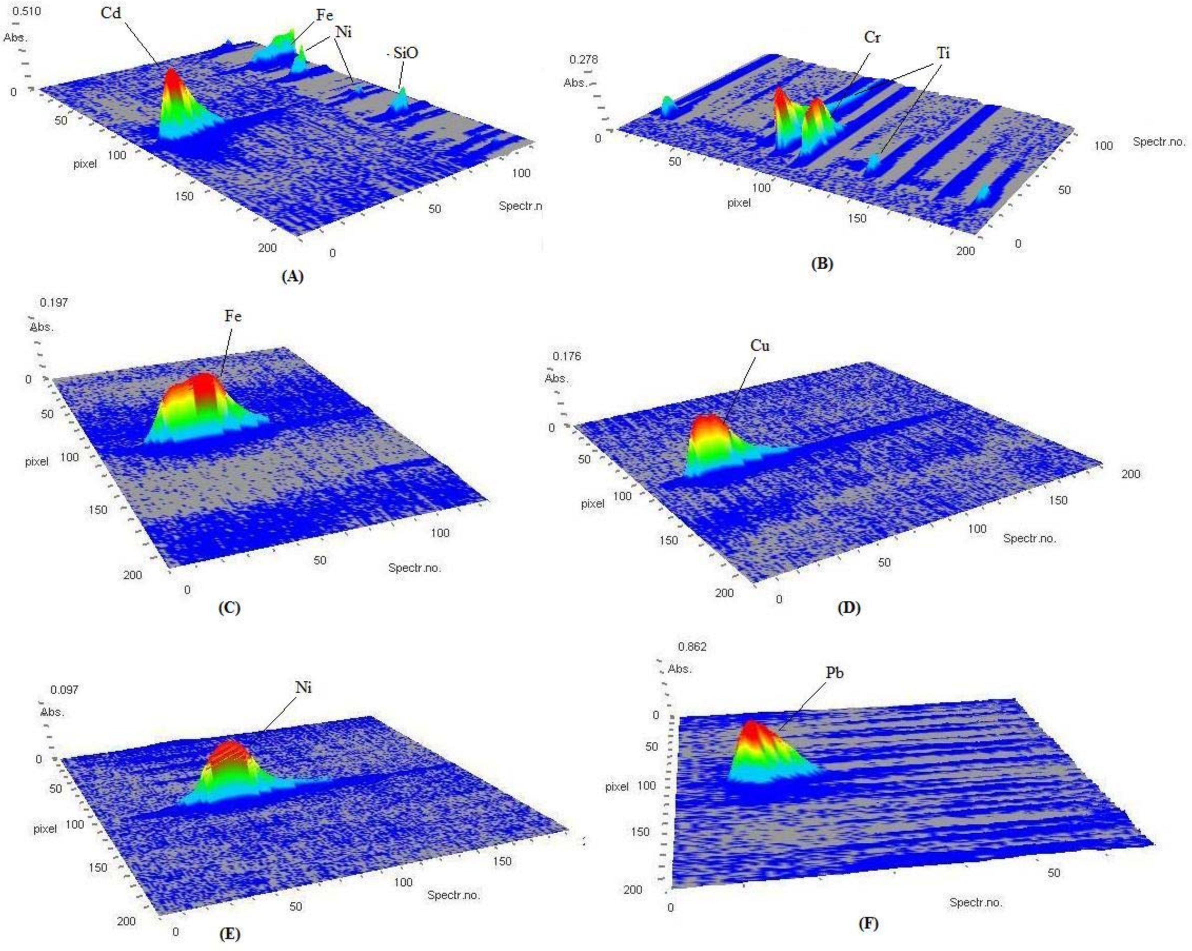


Fig. 18 Spectrum for IMEP-14 sediment certified reference material in direct solids sampling HR-CS GFAAS.

In this study the spectrum in direct solids sampling is shown in Fig. 18. The spectral lines for elements such as Fe, Cu, Ni and Pb can be well measured. There is only a single peak for each element, even despite the analysis is performed at a line that is less sensitive. As shown for the two other elements Cd and Cr the absorption signal of several other elements occur, but they can be separated very clearly. In this analysis for Cd the Cd 228.802 nm line is not interfered by the resonance absorption lines Fe 228.763 nm and Ni 228.840 nm, respectively. For Cr 428.972 nm the signals of the lines Ti 428.907 nm and Ti 428.093 nm can be separated off as well [**78**].

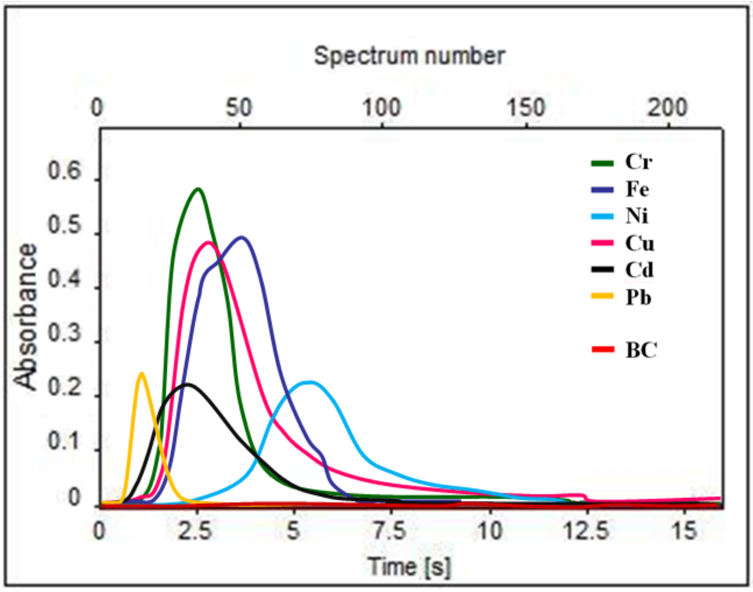


Fig. 19 Absorption vs time curves for the sediment reference material IMEP-14 analysed as solid sample directly by HR-CS GFAAS.

As shown in Fig. 19, the atomization time required for each element is different. It is influenced by several factors, such as the ease for an element to change into the gaseous phase [**79**,**80**,**81**]. The analyte concentration and the amount of sample introduced into the tube graphite furnace also influence the time required. Pb is relative easily atomized as compared with other elements. Indeed, the time required for a complete atomization was only about 2 seconds and the optimum pyrolysis temperature is between 350 ºC and 850 ºC with a hold time of 10 seconds before the atomization at 2000 ºC. For the determination of Cr the line Cr 428.972 nm is used, which is one of the resonant lines. The pyrolysis here is started at

500 ºC and ends at 1200 ºC. The atomization temperature is 2300 ºC and it takes about 4 seconds for a complete atomization. The temperature program for all elements determined is shown in Appendix 13. Direct solids sample analysis can be performed with excellent results with respect to the recovery and uncertainty in the measurements, as shown in Table 16.

A comparison of the measurement results for the reference samples, as obtained by direct solids analysis with the reference values is shown in Appendix 15. In general all methods used gave recoveries of above 81% for all analytes in all reference samples. The data in Table 16 indicate that HR-CS GFAAS with direct solids sampling is a very good method, which is able to overcome the problem of sample preparation in the analysis of sediments. Measurements in direct solids sampling can be performed quickly and avoid losses of analytes during sample preparation, while the results agree well with the reference values. The figures of merit of the procedure are shown more in detail in Appendix 14.

The overall results show that the mean values for all elements in three sediment standard samples did not statistically different from the reference values, except for Ni in the CRM-320, Cr in CRM-320 and IMEP-1 samples. More details are given in Appendix 15. The *t*-test value calculated for Ni in the case of the CRM-320 was 8.15 and for PACS-1 it was 3.13. This value is higher than the critical value with 4 degrees of freedom and a confidence level of 95% (2.78), but with respect to the uncertainty and the recovery for Ni in the case of direct solids sampling excellent results for all CRM samples are obtained. The recoveries for IMEP-14, CRM-320 and IMEP-1 namely are 101%, 93% and 95%, respectively.

The results for Cr in the CRM-320 and IMEP-14 samples lead to a *t*-value above the critical value. The *t*-test values for Cr in both samples are 4.47 and 4.27, respectively. The same method for the IMEP-14 sample give a *t*-value of 1.10, which is below the critical *t*-value of 2.78 in the case of 4 degrees of freedom and a confidence level of 95%. The uncertainty and the recovery for Cr in the case of the samples IMEP-14, CRM-320 and PACS-1 in the case of this method were very good. The recoveries namely were 105%, 91% and 81%, respectively.

Table 16. Analysis of sediment certified reference materials with direct solids sampling HR-CS GFAAS.

Element	IMEP-14			CRM-320			PACS-1		
	Reference value	**Results**	**Recovery (%)**	**Reference value**	**Results**	**Recovery (%)**	**Reference value**	**Results**	**Reccovery (%)**
Cr(mg/kg)	57.4±1.6	60.0±5.3	105	138±7	126±6	91	113±8	92±11	81
Fe(g/kg)	25.4±2.5	25.6±0.4	101	-	39.5±4.1	-	48.7±0.8	45.7±5.1	94
Ni(mg/kg)	26.06±0.7	26.2±0.8	101	75.2±1.4	70.1±1.4	93	44.1±2.0	42.0±1.5	95
Cu(mg/kg)	47.21±4.7	45.7±2.0	96	44.1±1.0	43.3±4.0	98	452±16	453±27	100
Cd(mg/kg)	2.61±0.09	2.8±0.4	107	0.533±0.026	0.53±0.01	99	2.38±0.026	2.4±0.05	101
Pb(mg/kg)	87.25±1.7	86.6±3.2	99	42.3±1.6	44.8±3.6	106	404±20	392±32	93

Table 17. Analysis of SETOC samples with direct solids sampling HR-CS GFAAS.

Samples	Cr (mg/kg)	Fe (g/kg)	Ni (mg/kg)	Cu (mg/kg)	Cd (mg/kg)	Pb (mg/kg)
F1026	115±5	20.8±2.8	32.9±3.8	53.7±3.2	1.6±0.2	389±18
F1027	153±3	24±3.5	51.6±3.0	125±3	5.3±0.5	148±10
F1028	87.3±6.3	24.4±1.6	30.4±4.8	40.1±5.2	0.37±0.03	52.8±3.8
F1029	72.5±2.5	23.1±3.0	44.6±2.4	68.6±2.1	1.6±0.2	319±7
F2159	96.0±3.3	27.5±0.2	46.9±3.0	62.3±3.5	1.9±0.2	109±13
F2160	196±9	37.1±4.8	60.6±1.5	147±2.7	5.2±0.6	326±12
F2161	102±5	18.4±2.4	39.6±2.0	54.8±1.4	2.9±0.7	348±7.8
F2162	71.1±3.0	35.4±4.8	41.6±2.2	120±2	1.10±0.06	176±11
F0454	54.1±5.9	22.2±2.4	37.7±2.3	18.7±0.7	0.18±0.04	25.6±0.4
F0455	148±7	26.5±2.7	45.6±0.2	54.8±2.1	1.9±0.2	149±7
F0456	59.8±4.0	22.3±0.8	20.93±0.08	62.1±2.1	1.0±0.2	258±17
F0457	108±5	19.6±2.0	35.1±1.6	53.7±1.4	3.6±0.2	408±2

The *t*-values obtained for all other elements Cu, Fe, Cd and Pb in IMEP-14, CRM-320 and PACS-1 samples were below the critical *t*-value of 2.78 with 4 degrees of freedom and a confidence level of 95%. It can be said that the analysis of sediment samples with direct solids sampling HR-CS GFAAS has provided excellent results.

The analysis results for the SETOC samples for Cu, Fe, Cr, Ni, Cd and Pb elements and obtained with the same method are shown in Table 17. The data show that HR-CS GFAAS for the analysis of SETOC samples provided a good precision as expressed by the relative standard deviations.

Table 18. Influences of sample drying and of the use of a matrix modifier on elemental determinations in sediment CRMs with direct solids sampling and HR-CS GFAAS.

Element	IMEP-14			CRM-320			PACS-1		
	Without extra drying	5 hours at 110ºC	Reference value	Without extra drying	5 hours at 110ºC	Reference value	Without extra drying	5 hours at 110ºC	Reference value
Cr(mg/kg)	52.7±3.1[a]	60.0±5.3[a]	57.4±1.6	131±7[a]	119±24[a]	138±7	106±7[a]	92±11[a]	113±8
	56.2±3.6[b]	53.6±17[b]		113±12[b]	137±6[b]		-	-	
Fe(g/kg)	22.0±2.4[a]	25.6±0.4[a]	25.4±2.5	33.7±0.9[a]	39.5±4.1[a]	-	-	46.9±1.6	48.7±0.8
	23.9±2.7[b]	23.5±2.9[b]		30.9±2.9[b]	32.2±1.9[b]		-	-	
Ni(mg/kg)	26.4±0.8[a]	26.2±0.8[a]	26.06±0.7	72.5±5.5[a]	70.1±1.4[a]	75.2±1.4	45.5±1.6[a]	42.0±1.5[a]	44.1±2.0
	22.6±0.9[b]	26.9±0.3[b]		74.6±3.2[b]	82.7±5.6[b]		43.4±9.8[b]	42.0±4.9[b]	
Cu(mg/kg)	47.4±3.2[a]	45.7±2.0[a]	47.21±4.7	40.8±3.4[a]	39±4[a]	44.1±1.0	447±44[a]	439±36[a]	452±16
	47.9±6[b]	49.8±8.8[b]		37.0±8.4[b]	47.9±8[b]		-	-	
Cd(mg/kg)	2.78±0.05[a]	2.8±0.4[a]	2.61±0.09	0.52±0.17[a]	0.53±0.01[a]	0.533±0.026	2.2±0.2[a]	2.4±0.05[a]	2.38±0.026
	2.17±0.15[b]	2.3±0.4[b]		0.49±0.62[b]	0.55±0.3[b]		2.2±0.3[b]	2.5±0.8[b]	
Pb(mg/kg)	-	86.6±3.2[a]	87.25±1.7	36.5±3.6[a]	44.8±3.6[a]	42.3±1.6	394±18[a]	392±32[a]	404±20
	83.1±14[b]	83.9±3.4[b]		43.6±12[b]	44.2±0.7[b]		-	-	

a with modifier

b without modifier

3.4.1 Influences of the sample drying and the use of a matrix modifier for elemental determinations by direct solids sampling HR-CS GFAAS

Analytical errors of determinations of trace elements in samples with high water content often occur as shown in results of direct solids sampling atomic absorption spectrometry with Zeeman effect background correction [**82**]. In this study we also conducted analyses after an additional drying of the CRMs for 5 hours at a temperature of 110ºC. A comparison of the analysis results with and without drying the samples before they are introduced into the graphite furnace as solid sample is shown in Table 18.

Statistical errors after drying the sediment CRMs were found for Cd to range from 2 to 8% in the CRM-320 sample and from 5 to 7% in the case of the IMEP-14 sample. In the case of the CRM-320 sample statistical errors were found to be in the range of 5 to 18% without drying, and 1 to 14% in the dried sample. For PACS-1 they range from 6 to 19%. For other elements in all CRMs the error percentage is slightly larger without drying and it was found to range from 1 to 17%. From the point of view of recoveries for all elements an excellent recovery was found, as shown in Appendix 16, 17 and 18.

3.4.2 Influences of the sample mass on metal determinations by direct solids sampling HR-CS GFAAS

In measurements by HRCS-GFAAS using direct solids sampling, we need to consider the weight or the sample amount used [**83**,**84**]. In practical analysis, the amount of sample which is introduced into the furnace must be constant. In direct solids sampling GFAAS we optimized the sampled amounts for the determination of traces of Cd in sediment samples within the range of 1.0-5.0 mg. The recovery values obtained for the CRMs with amounts of sample of 0.05-0.25 mg are shown in Table 16. The results are a very good. The recoveries for Cd and Cr were 107% and accordingly, there is a very good agreement with the certified value.

In the determination of metals by direct solids sampling GFAAS, it was found that the use of too large or too small amounts of sample may lead to erroneous results, even when the absolute amounts of analyte present lie within the linear dynamic range. Measurements performed on a total of 293 samples for Cu in a vitamin complex proved that sample masses smaller than 0.3 mg or larger than 1.1 mg give overestimated and/or underestimated results [**83**].

The elemental determinations using direct solids sampling in HR-CS GFAAS are easy to handle and give a good recovery, however, there are some very important things to consider, such as the amount of the samples used. It must be quite small but also represent a homogeneous sample as a whole [**48**]. Indeed, measurements by direct solids sampling HR-CS GFAAS must be done with a homogeneous sample and a mass of sample so that the amount of analyte present is above the detection limit [**85**].

With a small amount of sample introduced we also intend to avoid incomplete atomization because the atomization time must be as short as possible. When the sample amount introduced into the furnace is too large, there will not be enough time for an atomization of the entire amount of sample. An increase of the amount of sample used requires a longer atomization time or higher atomization temperatures, both of which will lead to memory effects and also will reduce the lifetime of the tube. When the tube is working at high temperature during the atomization step the tube coating will easily be damaged and when the tube coating is damaged further interferences will easily occur during the measurements.

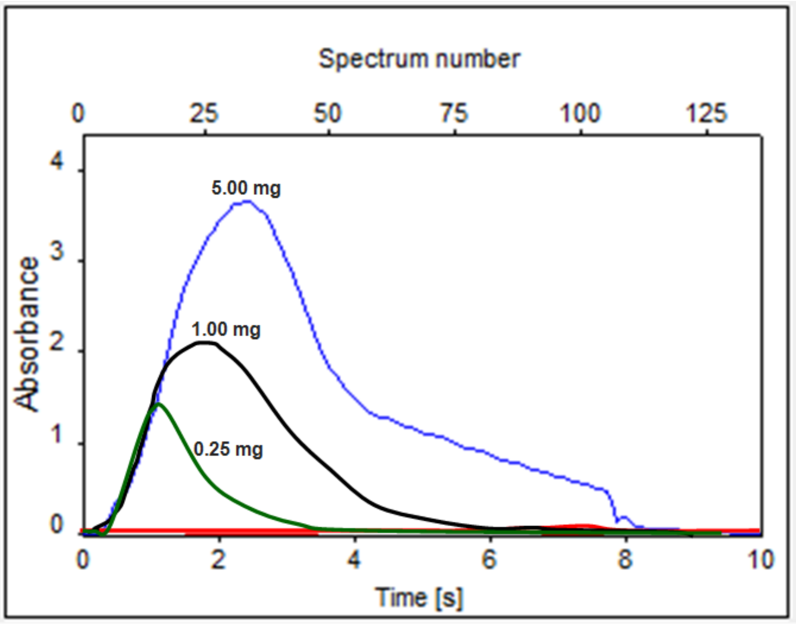


Fig. 20 Spectral interferences for Cd 228.802 nm as a function of the sample amounts for PACS-1 in HR-CS GFAAS.

As shown in Fig. 20, a sample amount of 0.25 mg of PACS-1 requires about 3 seconds to be atomized completely, while for an amount of 1.00 mg about 6 seconds and for a sample amount of 5.00 mg even a longer time, namely 8 seconds (the maximum atomization time in the temperature program of the instrument used here) is required. Even then not the entire sample is successfully atomized. It is clearly visible from the absorption vs. time curves, where there is a drastic tailing over 8 seconds of atomization time. This means that the sample is incompletely atomized after the preset atomization time is ended. The atomization time required is longer at higher amounts of samples. The background signal during the measurement (shown in red color) did not significantly change as the system is continuously corrected through the use of the correction pixels.

Table 19. Direct solids sampling HR-CS GFAAS with various amounts of sample.

	IMEP-14				**PACS-1**			
Element	**Reference value (mg/kg)**	**N**	**Sampled amount (mg)**	**Results (mg/kg)**	**Reference value (mg/kg)**	**N**	**Sampled amount (mg)**	**Results (mg/kg)**
Cr	57.4±1.61	5	0.5	90.9±14	113±8	5	0.2	150±28
		5	1.0	56.6±4				
Fe	25.35±2.5	5	1.0	-	48.7±0.8	5	1.0	-
Ni	26.06±0.7	10	1.0	21.0±8	44.1±2.0	10	1.0	156±12
		5	2.0	41.8±6		5	2.0	80±10
		5	3.0	65.5±10		5	3.0	41.6±14
Cu	47.21±4.7	5	1.0	69.3±11	452±16	10	1.0	-
Cd	2.61±0.09	9	1.0	4.2±0.8	2.38±0.026	10	1.0	5.0±1.5
		10	2.0	4.5±0.6		10	2.0	4.7±0.6
		10	3.0	3.9±0.4		10	3.0	4.6±0.4
		10	4.0	3.6±0.3		10	4.0	3.2±1.0
		10	5.0	3.5±0.5		10	5.0	3.7±0.6
Pb	87.25±1.74	10	0.1	68.5±19.1	404±20	10	1.0	833.8±154.5
		10	2.0	52.6±18.2		10	2.0	648±142.5
		5	3.0	44.2±25		10	3.0	372.8±342.7

N number of analysis

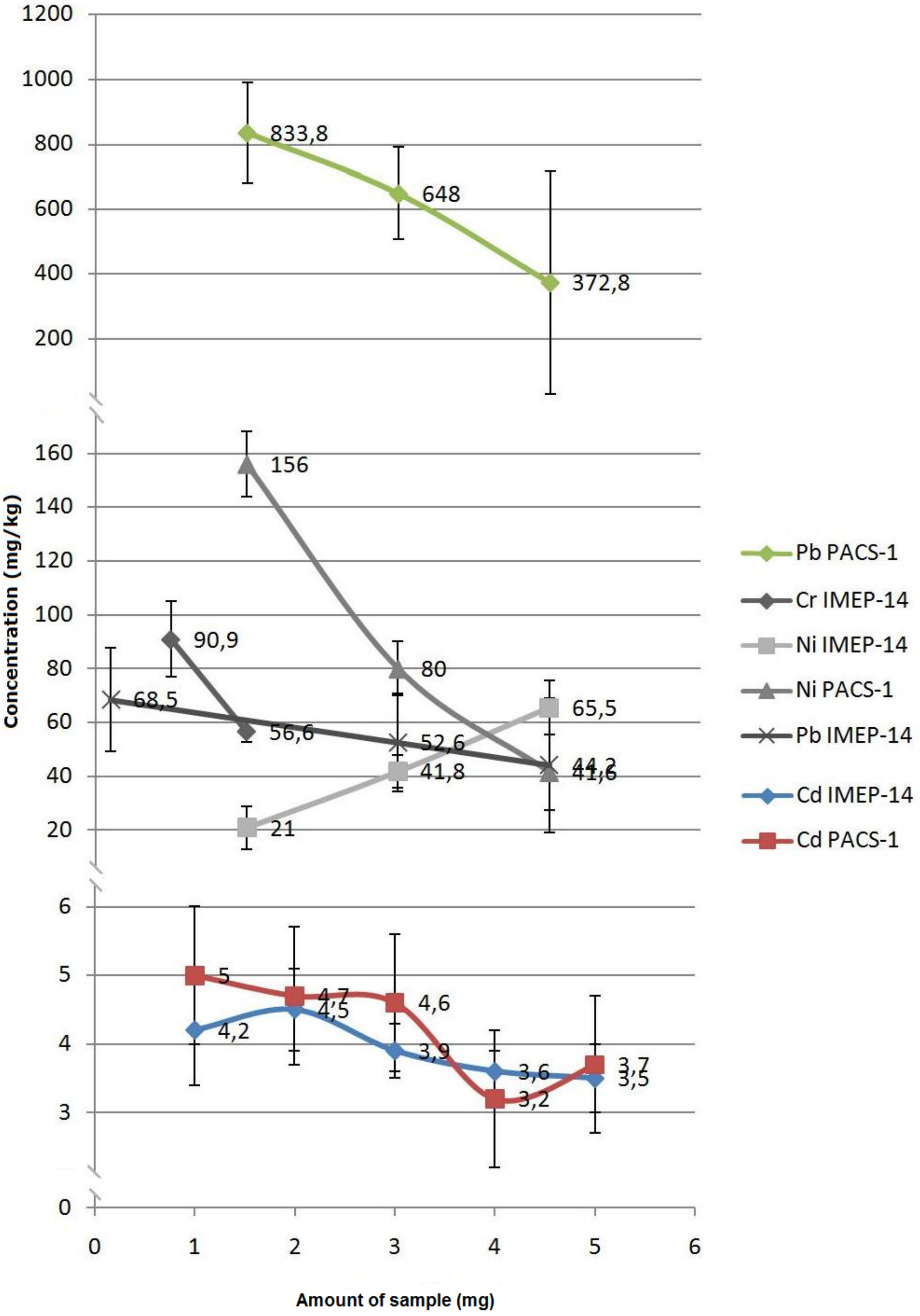


Fig. 21 Influence of the sample amount on the analytical results in direct solids sampling for the analysis of sediments by HR-CS GFAAS.

HR-CS GFAAS with direct solid sampling in the case of various amounts of sample introduced into the furnace give the results shown in Table 19. The results show that the amounts of sample analyzed may greatly influence the results of the analysis. This influence, however, may differ from element to element and depend on the sample matrix as well. This is shown for Ni, where for two different samples the influence on the recovery even is opposite. For volatile elements like Cd, however, the results seem to be better at larger sampling amounts. For less volatile elements the statistical errors tend to increase with the sampled amounts, which might relate to an incomplete sample volatilization as well. The sample weights also influence the performance of the platform that is used to locate the sample. With small amounts of sample it will be possible to maintain the platform more durable, so that it can be used repeatedly before giving memory effects.

In recent years, other authors also have found that the results in direct solids sampling GF-AAS depend on the amount of sample used. Most of them obtained underestimated analyte concentrations from sample amounts that were too large. According to Nakamura, as cited by Bellara et al. [**48**], amounts of sample larger than 1.5 mg are useless for determining various metals in silicates because an increase in the amount of sample inhibits the diffusion of the atomic vapor.

Characteristic masses were on the average three times lower for the state-of-the-art transversely heated graphite atomizers (THGA). By de-coupling the processes of analyte vaporization and atomization the dynamic working range could be increased by 3 to 6 times with respect to conventional measurements in atomic absorption spectrometry [**86**].

The measurement results shown in Fig. 21 demonstrate that the analyte concentrations found decrease with increasing sample amounts, except for Ni in IMEP-1. The Ni concentrations found in IMEP-1 samples increased, although they still deviate from the reference value. This suggests that Ni has its own difficulties in GF-AAS. To overcome the memory effect of Ni, researchers were using a special tube with different designs and it seemed to be necessary to delay the read out so as to obtain maximum absorbance and to avoid memory effects [**87**].

Direct solids sampling with large amounts of sample, however, have the risk that the tube is easily damaged or the coating layer is peeled off. This can influence the measurement results and also leads to high costs as a result of the consumption of tubes.

3.5 Comparison of precision and recoveries in the determination of Cu, Ni, Cr, Ni, Cd and Pb in sediment samples by flame as well as by graphite furnace HR-CS AAS

The measurement results for three sediment certified reference materials (IMEP-14, CRM-320 and PACS-1) and the SETOC sediment samples in the case of LS FAAS and HR-CS GFAAS/FAAS with sample dissolution, slurry sampling and direct solids sampling are given in Table 20 and 21. In general all methods after optimization produced good results of analysis, namely a good recovery and a good precision. The recovery for Cu in the IMEP-14 sample was found to be in the range of 92 to 96%, in CRM-320 it was 96 to 129% and in PACS-1 between 92 to 101%. The recovery for Fe for the case of all samples and methods was high, with recovery values between 90 and 101%. For Cr, Ni, Cd and Pb the recovery was between 79 and 107%.

The recoveries for Cu, Ni, Cr, Ni, Cd and Pb for the CRM samples are good. With respect to the uncertainty, the measurements for samples using dissolution and subsequent LS FAAS and HR-CS FAAS are more precise than the measurements with slurry sampling or direct solids sampling.

The slurry and direct solids sampling tend to have a higher uncertainty than procedures with dissolved samples, but we should remember that dissolution requires a relatively long time for sample preparation and also includes the possibility of losses of analyte during sample digestion. Even though it often has a higher uncertainty or a lower precision the recoveries of the slurry technique and the direct solids sampling are good.

For analyses with slurry and direct solids sampling the samples should have a high homogeneity, so that the analyte is well homogeneously distributed in every part of the slurry sample. The homogeneity is also related to the particle size. Indeed, the powders must have a very fine particle size also so as to avoid a rapid deposition of slurry sample during introduction into the furnace.

The absence of any sample handling makes direct solids sampling HR-CS GFAAS ideally suited for fast screening purposes. HR-CS GFAAS has the additional advantage of a simplified optimization of the furnace programs and the visibility of the spectral environment, which makes it easy to avoid spectral interferences. Further, direct solids sampling analysis is an important contribution to green chemistry, as practically no reagents are used [**88**].

Table 20. Determination of Cu, Fe, Ni, Cr, Ni, Cd and Pb in sediment certified reference materials by LS FAAS, HR-CS GFAAS and HR-CS FAAS.

Samples	Element	Certified Value	LS FAAS		HR-CS GFAAS						HR-CS FAAS	
			dissolution of samples		direct solids sampling		slurry sampling		dissolution of samples		dissolution of samples	
			results	recovery (%)	results	recovery (%)	results	recovery (%)	results	recovery (%)	results	recovery (%)
IMEP-14	Cu (mg/kg)	47.21±4.7	44.0±0.7	93	45.7±2.0	96	43.3±3.8	92	45.0±0.7	95	44.5±0.7	94
	Fe (g/kg)	25.35±2.5	24.8±1.38	98	25.6±0.4	101	22.8±0.1	90	25.7±1.3	101	25.0±0.5	99
	Cr (mg/kg)	57,4±1.6	47.8±1.6	83	60.0±5.3	105	61.0±6.7	106	47.8±1.6	83	58.7±1.8	102
	Ni (mg/kg)	26.06±0.7	26.2±0.4	101	26.2±0.8	101	15.6±0.1	60	25.9±0.4	99	25.9±3.5	99
	Cd (mg/kg)	2.61±0.09	2.7±0.2	103	2.8±0.4	107	3.0±0.3	115	2.4±0.1	92	2.6±0.05	100
	Pb (mg/kg)	87.25±1.7	84.4±2.9	97	86.6±3.2	99	80.9±7.6	93	82.0±3.2	94	84.2±2.9	96
CRM-320	Cu mg/kg)	44.1±1.0	43.5±1.4	99	43.3±4.0	98	52.4±5.5	129	44.5±1.4	101	42.5±1.5	96
	Fe (g/kg)	-	38.5±1.0	-	39.5±4.1	-	39.4±0.8	-	38.5±1.4	-	39.0±1.2	-
	Cr mg/kg)	138±7	121±1	88	126±6	91	135 ±7	98	112±8	81	121±5	88
	Ni (mg/kg)	75.2±1.4	79.2±0.6	105	70.1±1.4	93	80.6±4.3	107	78.8±0.6	105	74.5±4.0	99
	Cd mg/kg)	0.53±0.026	-	-	0.53±0.01	99	0.55±0.07	103	0.53±0.01	100	0.52±0.01	97
	Pb mg/kg)	42.3±1.6	43.5±1.6	103	44.8±3.6	106	43.7±8.7	103	41.5±1.4	98	42.2±0.4	100

,...continued

Samples	Element	Certified Value	LS FAAS		HR-CS GFAAS						HR-CS FAAS	
			dissolution of samples		direct solids sampling		slurry sampling		dissolution of samples		dissolution of samples	
			results	recovery (%)	results	recovery (%)	results	recovery (%)	results	recovery (%)	results	recovery (%)
PACS-1	Cu mg/kg)	452±16	433±2	96	453±27	100	417±13	92	455±12	101	442±6	98
	Fe (g/kg)	48.7±0.8	46.9±1.6	96	45.7±5.1	94	38.5±1.2	79	48.0±1.6	99	48.0±1.2	99
	Cr mg/kg)	113±8	103±8.2	91	92±11	81	89.8±5.5	79	103±2	91	113±7	100
	Ni (mg/kg)	44.1±2.0	43.7±1.2	99	42.0±1.5	95	29.3±1.5	66	43.7±1.2	99	39.3±3.3	89
	Cd mg/kg)	2.38±0.026	2.3±0.04	98	2.4±0.05	101	2.3±0.2	97	2.4±0.1	100	2.3±0.1	96
	Pb mg/kg)	404±20	414±26	102	392±32	93	426±24	105	385±2	95	415±22	103

Table 21. Determination of Cu, Fe, Ni, Cr, Ni, Cd and Pb in sediment SETOC samples by LS-FAAS, HR-CS GFAAS and HR-CS FAAS.

Samples	Element	LS-FAAS	HR-CS GFAAS			HR-CS FAAS
		dissolution of samples	direct solids sampling	slurry sampling	dissolution of samples	dissolution of samples
F1026	Cu (mg/kg)	50.4±5.0	53.7±3.2	41.3±0.6	55.4±3.0	56.6±3.8
	Fe (g/kg)	17.1±0.8	20.8±2.8	20.4±0.9	20.0±0.8	18.5±0.1
	Cr (mg/kg)	111±5	115±5	85.0±7.9	103±6	105±2
	Ni (mg/kg)	30.9±1.7	32.9±3.8	25.5±0.1	32.5±1.2	32.4±2.2
	Cd (mg/kg)	2.0±0.1	1.6±0.2	2.9±0.1	2.1±0.2	2.6±0.2
	Pb (mg/kg)	384±22	389±18	443±26	386±10	383±10
F1027	Cu (mg/kg)	132±9	125±3	-	130±3	137±4
	Fe (g/kg)	27.8±0.3	24±3.5	-	34.6±1.2	30.2±0.4
	Cr (mg/kg)	142±2	153±5	-	150±6	147±2
	Ni (mg/kg)	42.7±2.3	51.6±3.0	-	51.1±1.4	46.9±0.9
	Cd (mg/kg)	1.73±0.03	5.3±0.5	-	2.31±0.01	4.1±0.3
	Pb (mg/kg)	141.5±0.2	148±10	-	150±6	148±9
F1028	Cu (mg/kg)	38.6±2.5	40.1±5.2	-	45.9±2.9	43.4±2.9
	Fe (g/kg)	19.3±0.2	24.4±1.6	-	23.2±1.5	23±1.1
	Cr (mg/kg)	77.7±2.2	87.3±6.2	-	70.1±4.0	72.4±2.0
	Ni (mg/kg)	25±0.4	30.4±4.8	-	31.2±1.2	27.1±4.0
	Cd (mg/kg)	-	0.37±0.03	-	0.27±0.01	0.8±0.2
	Pb (mg/kg)	48±2.6	52.8±3.8	-	49. 6±7.4	53. 8±1.2
F1029	Cu (mg/kg)	50.5±2.5	68.6±2.1	-	63.7±1.4	58.9±0.6
	Fe (g/kg)	21.4±0.3	23.1±3.0	-	26. 6±0.6	24.4±0.5
	Cr (mg/kg)	69.8±0.6	72.5±2.5	-	67.4±3.4	73.8±1.5
	Ni (mg/kg)	43.4±0.6	44.6±2.4	-	46.3±4.1	44.6±0.4
	Cd (mg/kg)	-	1.6±0.2	-	0.5±0.04	1.26±0.07
	Pb (mg/kg)	317±10	319±7	-	330±11	324±3

,...continued

Samples	Element	LS-FAAS	HR-CS GFAAS			HR-CS FAAS
		dissolution of samples	direct solids sampling	slurry sampling	dissolution of samples	dissolution of samples
F2159	Cu (mg/kg)	51.6±4.9	62.3±3.5	42.1±3.4	62.5±0.9	61.4±0.4
	Fe (g/kg)	28.0±1.1	27.5±0.2	21.1±0.9	30.9±0.4	30.4±0.7
	Cr (mg/kg)	94.2±0.5	96.0±3.3	105±13	94.0±0.8	95.0±0.6
	Ni (mg/kg)	42.4±2.6	46.9±3.0	45.9±1.8	46.6±4.0	40.1±2.0
	Cd (mg/kg)	-	1.9±0.2	1.2±0.3	1.42±0.07	1.9±0.3
	Pb (mg/kg)	108±4	109±13	110±6	116±3.6	109±4
F2160	Cu (mg/kg)	139±1	147±2.7	-	146±3	146±3
	Fe (g/kg)	35.8±0.3	37.1±4.8	-	42.6±1.1	39.7±1.0
	Cr (mg/kg)	194±3	196±9	-	203±4	198±4
	Ni (mg/kg)	46.4±1.1	60.6±1.5	-	60.5±0.1	57.2±0.5
	Cd (mg/kg)	5.9±0.2	5.2±0.6	-	4.5±0.2	4.8±0.4
	Pb (mg/kg)	304±2	326±12	-	317±15	312±3.4
F2161	Cu (mg/kg)	54.6±5.2	54.8±1.4	-	50.6±4.6	53.3±6.4
	Fe (g/kg)	16.5±1.4	18.4±2.4	-	19.3±1.2	18.6±0.9
	Cr (mg/kg)	88.8±7.6	102±5	-	100±19	90±0.7
	Ni (mg/kg)	38.0±0.9	39.6±2.0	-	43.9±3.5	38.68±0.01
	Cd (mg/kg)	2.0±0.3	2.9±0.7	-	2.0±0.3	2.8±0.2
	Pb (mg/kg)	344±29	348±7.8	-	352±8	341±7.1
F2162	Cu (mg/kg)	103±8	120±2	-	118±1	118±2
	Fe (g/kg)	35.8±0.2	35.4±4.8	-	39.9±0.9	34.4±2.4
	Cr (mg/kg)	71.0±1.0	71.1±3.0	-	67.0±2.0	72.3±0.3
	Ni (mg/kg)	26.2±0.5	41.6±2.2	-	39.5±0.2	31.1±1.1
	Cd (mg/kg)	-	1.10±0.06	-	0.70±0.01	0.82±0.02
	Pb (mg/kg)	176±2	176±11	-	167±4	173±4

,...continued

Samples	**Element**	**LS-FAAS**	**HR-CS GFAAS**			**HR-CS FAAS**
		dissolution of samples	**direct solids sampling**	**slurry sampling**	**dissolution of samples**	**dissolution of samples**
F0454	Cu (mg/kg)	16.3±0.8	18.7±0.7	-	19.4±0.4	18.3±0.6
	Fe (g/kg)	20.5±0.1	22.2±2.4	-	22.8±0.9	21.8±0.3
	Cr (mg/kg)	46.4±0.5	54.1±5.9	-	62.5±2.1	50.9±1.1
	Ni (mg/kg)	30.1±1.5	37.7±2.3	-	33.3±0.5	34.5±0.6
	Cd (mg/kg)	-	0.18±0.04	-	0.14±0.01	0.54±0.06
	Pb (mg/kg)	26.7±1.2	25.6±0.4	-	26.1±0.5	26.4±1.0
F0455	Cu (mg/kg)	56.1±6.2	54.8±2.1	-	63.6±3.3	60.25±0.04
	Fe (g/kg)	29.9±0.7	26.5±2.7	-	30.5±1.5	31.20±0.07
	Cr (mg/kg)	146±2	148±7	-	153±1	154±7
	Ni (mg/kg)	38.9±3.6	45.6±0.2	-	44.5±2.2	42.1±0.2
	Cd (mg/kg)	-	1.9±0.2	-	0.49±0.005	1.1±0.1
	Pb (mg/kg)	147±0.5	149±7	-	169±12	164±7
F0456	Cu (mg/kg)	62.5±2.0	62.1±2.1	-	61.0±2.4	63.5±0.9
	Fe (g/kg)	19.1±0.5	22.3±0.8	-	23.4±0.7	20.0±0.2
	Cr (mg/kg)	54.8±0.5	59.8±4.0	-	61.6±1.5	56.4±3.4
	Ni (mg/kg)	21.2±0.9	20.9±0.1	-	22.4±0.6	23.8±1.1
	Cd (mg/kg)	-	1.0±0.2	-	0.26±0.002	1.1±0.1
	Pb (mg/kg)	270±15	258±17	-	279.4±12.5	256±7
F0457	Cu (mg/kg)	54±0.1	53.7±1.4	-	55.2±1.6	52.2±0.3
	Fe (g/kg)	16.4±0.1	19.6±2.0	-	20±0.2	18.7±0.3
	Cr (mg/kg)	106±1	108±5	-	97.9±1.4	95.7±3.2
	Ni (mg/kg)	28.7±0.2	35.1±1.6	-	33.5±2.4	31.2±0.1
	Cd (mg/kg)	2.10±0.06	3.6±0.2	-	1.89±0.05	2.4±0.1
	Pb (mg/kg)	368±12	408±2	-	384±21	388±26

For all analytes in CRMs the recovery was above 80%, except for Ni in the slurry technique. Although the same method was used for each CRM sample, in the case of the recovery for Ni different results were obtained. For Ni in IMEP-14 and PACS-1 a recovery of 60 and 66% was obtained, whereas, for CRM-320 a recovery of 101% was found. In this case the organic content in each CRM and SETOC samples likely to provide useful information, as shown in Table 22. The organic content 0.86% of C and <0.2% of N are obtained for CRM-320 much lower than for the IMEP-14 and the PACS-1 samples. High organic content provide losses of analyte by volatilization in slurry technique so that decrease the recovery for Ni in the IMEP-14 and the PACS-1 samples.

Table 22. Organic content of sediment CRM and SETOC samples determined by EA-IRMS.

Samples	Element			
	N (%)	C (%)	H (%)	S (%)
IMEP-14	0.47	7.88	1.03	1.22
CRM-320	< 0.2	0.86	0.45	-
PACS-1	0.34	3.62	0.82	1.11
F01026	0.21	3.86	0.58	< 0.2
F02159	0.48	6.08	1.01	0.36

Analytical results for 12 sediment SETOC samples are shown in Table 21. The measurements gave results with a low uncertainty and good precision. The results including sample dissolution well agree with those of the slurry technique or direct solids sampling, which is easier and faster. As seen from the measurement results for the SETOC samples, only 2 SETOC samples which have a very fine particle size could be analyzed by the slurry technique. Indeed, for powder samples with larger particles deposition occurs more quickly [**89**,**90**], which results in erroneous analyses.

Chapter 4. Conclusions

The analysis of natural water samples using LS-FAAS and HR-CS AAS graphite and flame techniques in this study gave very good results for both instruments used. However, the high resolution continuum radiation source is much more capable in terms of detection limits and to overcome the interferences from other elements and organic compounds, which is important for environmental samples that usually have a very complex matrix. Determinations of Cu and Fe with a matrix modifier and without matrix modifier in natural lake water samples treated by filtration and after acidification could be made by HR-CS GFAAS. The use of matrix modifiers proved to be very helpful for eliminating interferences caused by the matrix. Sample filtration did not produce significant differences in general but the addition of HNO_3 to the sample often lead to a significant increase of the analyte absorbance. The addition of H_2O_2 to water samples without prior filtration was not increasing the analyte absorbances.

The measurement results of LS FAAS for the certified reference material water CRM 1643e have shown that the concentrations of all elements found in the water CRM 1643e were below the detection limit of LS FAAS. For CRM 1643e HR-CS GFAAS gave very good results and the recovery for Cr, Fe, Ni, Cu, Zn, Cd and Pb was high.

Determinations of Cu, Fe, Cr, Ni, Cd and Pb in the sediment standard reference material and in SETOC samples using microwave assisted dissolution and LS FAAS and HR-CS AAS with flame and graphite furnace methods gave good results with respect to analytical precision and recovery. However, HR-CS GFAAS/FAAS has better limits of detection and is more powerfull in precision as compared to LS-FAAS. Practically, HR-CS GFAAS requires a relatively long time of analysis depending on the temperature program.

The temperature program plays an important role in analyses by HRCS-GFAAS, in terms of the quality of the analysis results. The temperature program for each element of interest must be optimized so as to get the best results of measurement, because each element has different thermo-chemical properties. When the temperature program used performs an atomization at too low temperatures the analyte will be partially lost. The atomization time also influences the number of pixels that must be read out on the detector. Another important factor is the use of chemical matrix modifiers. Analyte lost during the pre-atomization step can be minimized by using a modifier. $Mg(NO_3)_2$ 0,05%, $Pd(NO_3)_2$ 0,1% + $Mg(NO_3)_2$ 0,05% and $NH_4H_2PO_4$ have been used as modifier in this study. It was found that in a number of cases the use of $Mg(NO_3)_2$ 0,05% can significantly reduce losses of analyte during the measurements.

Analyses by slurry techniques were also performed in this work for the case of the three sediment certified reference materials IMEP-14, CRM-320 and PACS-1. As real samples two SETOC samples coded F1026 and F2159 were used because the slurry technique only can be applied for samples with a very fine particle size. The results of the slurry technique in the case of sediment samples and HR-CS GFAAS were in good agreement with the reference values for Cu, Fe, Cr, Cd and Pb.

The determination of Ni in IMEP-14, CRM-320 and PACS-1 samples by the slurry technique produced a lower recovery. Indeed, the mean value of the analysis results for Ni was significantly different from the reference value. Determinations of Ni in sediment samples with the slurry technique were all done with a matrix modifier. The presence of HNO_3 from the slurry preparation, however, was found to have no significant influence on the absorbance for Ni. For other elements such as Cr, Fe and Cu, statistically significant differences between the mean values and the reference values were found but the measurements still had a good precision and recovery.

In two SETOC sediment samples Cu, Fe, Cr, Ni, Cd and Pb were determined with slurry sampling HR-CS GFAAS using the matrix modifiers $NH_4H_2PO_4$, $Mg(NO_3)_2$ and $Pd/Mg(NO_3)_2$. The appropriate matrix modifiers for the different elements were determined. After this each element in the SETOC samples could be well determined by the slurry technique from the point of view of uncertainty and precision.

Direct solids sampling could be used to determine of metals in sediment samples by HR-CS GFAAS, while using aqueous standard solutions for calibration and $Pd/Mg(NO_3)_2$ as matrix modifier. The results for Fe, Cu, Ni and Pb were positive. There is only one signal, even though the analysis is performed with lines of lower sensitivity. For the elements Cd and Cr absorption signals from several other elements were found, but they could be separated very clearly.

Increases of the amounts of sample introduced into the graphite furnace tube were found to increase the pyrolysis and atomization times required. Direct solids sampling HR-CS GFAAS gave very good results and helped to overcome problems with sample preparation or prior sample treatments. Measurements with direct solids sampling HR-CS GFAAS can be performed quickly and avoid losses of analytes during sample preparation, as it could be shown for the sediment reference materials IMEP-14, CRM-320 and PACS-1.

Analyses of SETOC sediment samples by HR-CS GFAAS with the same technique also gave good results in terms of precision.

The influence of an additional sample drying prior to direct solids sampling HR-CS GFAAS was studied. For Cd the standard deviations of the absorption signals were of the order of 2 to 8% without drying and of 5 to 7% in the case of drying for the IMEP-14. In the case of the CRM-320 sample standard deviations of 5 to 18% were found without drying and 1 to 14% with drying. For PACS-1 the values were 6 to 19%. For all other elements in all CRM samples the standard deviations are slightly higher in the absence of drying.

Analyses by HR-CS GFAAS using direct solids sampling need to consider the sample amount that is introduced to the furnace. Indeed, the amounts of sample introduced into the furnace must be consistent. When analyzing solid samples by using the manual technique, the sample should be weighed very carefully and brought completely at the same spot in the furnace. It was found that the use of a too large or a too small amount of sample may lead to erroneous results, even when the absolute amount of analyte still lies within the linear dynamic range.

Further, it is important in the analysis of solid samples by HR-CS GFAAS that the amounts of sample introduced into the furnace are quite small but also representative for the sample and that the amount of sample is within the linear range. Increasing amounts of sample will produce higher measurement errors. These errors stem from memory effects and incomplete atomization of the sample.

The distinguished features of HR-CS GFAAS promote it to a powerful method for the analysis of environmental samples. The performance in terms of the analytical figures of merit such as limits of detection is obvious. Compared with LS-FAAS and GFAAS after sample dissolution, direct solids sampling HR-CS GFAAS avoids a digestion under clean conditions and does not require the use of a variety of high-purity chemical reagents. Further, direct solids sampling HR-CS GFAAS reduces the analysis time from hours to some minutes. Furthermore, it improves the limits of detection and allows it to overcome a number of interferences during the measurement, especially in the case of environmental samples that often have a very complex matrix.

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Appendix 1. Temperature program for the determination of Fe and Cu in Alster Lake water by HR-CS GFAAS (n=5)

Step	Temperature (ºC)	Ramp (ºC s^{-1})	Hold time (s)	Ar flow (mL min^{-1})
Drying	90	8	10	300
Drying	130	8	4	300
Pyrolysis	1100	50	10	300
Atomization	2000	1500	auto	auto
Cleaning	2450	500	4	300

Appendix 2. Analytical figures of merit for the determination of Fe and Cu in water samples by HR-CS GFAAS.

Analyte line (nm)	**Slope (L µg^{-1})**	**R^2**	**LOD (µg L^{-1})**	**Calibration range (µg L^{-1})**
Fe 248.327	0.007986	0.993	0.8	5.0-60.0
Cu 324.754	0.013724	0.992	0.7	2.5-20.0
Fe 248.327*	0.011798	0.988	1.0	5.0-60.0
Cu 324.754*	0.015178	0.995	0.1	1.0-20.0

(* without matrix modifier)

Appendix 3. Results obtained by HR-CS GFAAS for the determination of Cu and Fe in natural water samples using variouns sample treatment and matrix modifiers.

Samples code	with matrix modifier		without matrix modifier	
	Cu ($\mu g\ L^{-1}$)	Fe ($\mu g\ L^{-1}$)	Cu ($\mu g\ L^{-1}$)	Fe ($\mu g\ L^{-1}$)
N	2.85±0.02	23.7±3.2	4.05±0.09	17. 7±1.3
S	2.7±0.11	77.8±1.6	3.21±0.08	21.0±1.4
NF	2.73±0.01	22.3±2.1	4.71±0.09	17.9±0.9
SF	2.45±0.02	20.8±1.5	4.65±0.17	20.5±0.9
NFHN	12.3±0.1	28.3±1.8	13.85±0.42	29.4±1.1
SFHN	6.24±0.07	34.7±2.8	9.46±0.08	25.5±1.4
NFHO	2.78±0.04	10.4±1.7	2.40±0.09	5.5±0.8
SFHO	2.5±0.2	10.2±1.2	2.22±0.06	5.3±0.9
NHN	6.14±0.04	152.9±6.4	7.97±0.07	196.3±6.9
SHN	12.3±0.2	137.8±5.8	11.3±0.1	181.2±8.1
NHO	2.9±0.1	12.6±1.5	5.2±0.07	6.4±0.9
SHO	2.34±0.04	9.5±1.2	4.25±0.08	7.0±1.0

Samples code	Treatments
N	Alster Lake sample no. 1 without treatment
S	Alster Lake sample no. 2 without treatment
NF	Sample N with filtration
SF	Sample S with filtration
NFHN	Sample N with filtration and HNO_3 was added to 5% v/v
SFHN	Sample S with filtration and HNO_3 was added to 5% v/v
NFHO	Sample N with filtration and H_2O_2 was added to 5% v/v
SFHO	Sample S with filtration and H_2O_2 was added to 5% v/v
NHN	Sample N without filtration and HNO_3 was added to 5% v/v
SHN	Sample S without filtration and HNO_3 was added to 5% v/v
NHO	Sample N without filtration and H_2O_2 was added to 5% v/v
SHO	Sample S without filtration and H_2O_2 was added to 5% v/v.

Appendix 4. Instrumental parameters and temperature program used for the analysis of water and sediment samples by HR-CS GFAAS

Parameters	**Element**					
	Cr	**Fe**	**Ni**	**Cu**	**Cd**	**Pb**
λ (nm)	357.868	248.327	232.003	324.754	228.802	283.306
Heating program						
Pyrolysis						
Temperature (ºC)	350/1300	350/1100	350/1050	350/1100	350/600	350/800
Ramp (ºC s^{-1})	50/300	50/300	50/300	50/300	50/300	50/300
Hold (s)	20/10	20/10	20/10	20/10	20/10	20/10
Atomization						
Temperature (ºC)	2300	2000	2300	2000	1200	1500
Ramp (ºC s^{-1})	1500	1500	1500	1500	1400	1500
Hold (s)	4	4	5	4	3	4
Modifier	$Mg(NO_3)_2$	$Mg(NO_3)_2$	$Mg(NO_3)_2$	$Pd/Mg(NO_3)_2$	$Pd/Mg(NO_3)_2$	$Pd/Mg(NO_3)_2$, $NH_4H_2PO_4$
Linear range (µg)	0.5-20	1-60	1-60	1-50	1.5-10	1-40

Appendix 5. Reference values for water reference material 1643e (NIST) and mean values from measurements by HR-CS GFAAS (n=5)

Element	Reference value (µg/kg)	HR-CS GFAAS			
		Results (µg/kg)	**Recovery (%)**	**sdev results**	**t-test | *t* |**
Cr	19.90±0.23	18.9±0.5	95	0.5	4.47
Fe	95.7±1.4	95.2±0.7	99	0.7	1.60
Ni	60.89±0.67	61.4±4	101	4	0.29
Cu	22.20±0.31	21.8±0.5	98	0.5	1.79
Zn	76.5±2.1	76.5±2	100	2	0
Cd	6.408±0.071	5.5±0.4	86	0.4	5.08
Pb	19.15±0.2	20.6±1.3	107	1.3	2.49

The critical value | *t* | is 2.78 (P=0.05). Since the value of | *t* | for the measurement is below the critical value of | *t* |, there is no evidence for a systematic error.

Appendix 6. Certified values and mean values for CRM sediment samples obtained by dissolution and determined by LS FAAS. Critical value: t_4=2.78 (confidence level 95%)

Element	IMEP-14		CRM-320		PACS-1	
	Reference value	Measurement value	Reference value	Measurement value	Reference value	Measurement value
Cr(mg/kg)	57.4	47.8	138	121	113	103
Fe(g/kg)	25.4	24.8	-	-	48.7	46.9
Ni(mg/kg)	26.06	26.2	75.2	79.2	44.1	43.7
Cu(mg/kg)	47.21	44	44.1	43.5	452	433
Zn(mg/kg)	324	310	142	115	824	851
Cd(mg/kg)	2.61	2.7	-	-	2.38	2.3
Pb(mg/kg)	87.25	84.4	42.3	43.5	404	414

Element	IMEP-14		CRM-320		PACS-1	
	sdev results	Calculated $\lvert t \rvert$	sdev results	Calculated $\lvert t \rvert$	sdev results	Calculated $\lvert t \rvert$
Cr	1.6	13.42	1	38.01	8.2	2.73
Fe	1.38	0.97	-	-	1.6	2.52
Ni	0.4	0.78	0.6	14.91	1.2	0.75
Cu	0.7	10.25	1.6	0.84	2	21.24
Zn	17	1.84	3	20.12	30	2.01
Cd	0.2	1.01	-	-	0.04	4.47
Pb	2.9	2.20	1.6	1.68	26	0.86

Appendix 7. Certified values and mean values for CRM sediment samples obtained by dissolution and determined by HR-CS GFAAS. Critical value: t_4=2.78 (confidence level 95%).

Element	**IMEP-14**		**CRM-320**		**PACS-1**	
	Reference value	**Measurement value**	**Reference value**	**Measurement value**	**Reference value**	**Measurement value**
Cr(mg/kg)	57.4	58.7	138	121	113	113
Fe(g/kg)	25.4	25	-	-	48.7	48
Ni(mg/kg)	26.06	25.9	75.2	74.5	44.1	39.3
Cu(mg/kg)	47.21	44.5	44.1	44.5	452	442
Zn(mg/kg)	324	310	142	115	824	851
Cd(mg/kg)	2.61	2.6	0.533	0.53	2.38	2.3
Pb(mg/kg)	87.25	84.2	42.3	42.2	404	415

Element	**IMEP-14**		**CRM-320**		**PACS-1**	
	sdev results	**Calculated | *t* |**	**sdev results**	**Calculated | *t* |**	**sdev results**	**Calculationed | *t* |**
Cr	1.8	1.61	5	7.60	7	0
Fe	0.5	1.79	-	-	1.2	1.30
Ni	3.5	0.10	4	0.39	3.3	3.25
Cu	0.7	8.66	1.4	0.64	6	3.73
Zn	17	1.84	3	20.12	30	2.01
Cd	0.05	0.45	0.01	0.67	0.1	1.79
Pb	2.9	2.35	0.4	0.56	22	1.12

Appendix 8. Mean values for SETOC sediment samples obtained by LS FAAS and HR-CS GFAAS, critical value t_8=2.31 (confidence level 95%)

Element	**F1026**			**F1027**			**F1028**		
	s^2	**s**	**calculated $\lvert t \rvert$**	**s^2**	**s**	**calculated $\lvert t \rvert$**	**s^2**	**s**	**calculated $\lvert t \rvert$**
Cr	14.5	3.808	2.491	14.5	3.808	2.076	4.42	2.102	3.986
Fe	0.05	0.224	4.950	0.125	0.354	10.733	0.625	0.790	7.4
Ni	3.86	1.966	1.206	3.05	1.746	3.803	8.08	2.843	1.168
Cu	19.72	4.441	2.208	48.5	6.964	1.135	7.33	2.707	2.803
Cd	0.025	0.158	6.000	0.045	0.213	17.577	0.02	0.141	8.944
Pb	292	17.088	0.093	40.52	6.366	1.615	4.1	2.025	4.529

Element	**F1029**			**F2159**			**F2160**		
	s^2	**s**	**calculated $\lvert t \rvert$**	**s^2**	**s**	**calculated $\lvert t \rvert$**	**s^2**	**s**	**calculated $\lvert t \rvert$**
Cr	1.305	1.142	5.536	0.305	0.552	2.290	12.5	3.536	1.789
Fe	0.17	0.412	11.504	0.85	0.922	4.116	0.545	0.738	8.353
Ni	0.26	0.510	3.721	5.38	2.319	1.568	0.73	0.854	19.986
Cu	3.305	1.818	7.306	12.085	3.476	4.457	5	2.236	4.950
Cd	0.002	0.049	40.249	0.045	0.212	14.162	0.1	0.316	5.5
Pb	54.5	7.382	1.499	16	4	0.395	7.78	2.789	4.535

,... continued

Appendix 8. Mean values for SETOC sediment samples obtained by LS FAAS and HR-CS GFAAS, critical value t_8=2.31 (confidence level 95%)

Element	F2161			F2162			F0454		
	s^2	s	calculated $\lvert t \rvert$	s^2	s	calculated $\lvert t \rvert$	s^2	s	calculated $\lvert t \rvert$
Cr	53.38	7.306	0.259	0.545	0.738	2.78	0.73	0.854	8.328
Fe	1.385	1.177	2.821	2.9	1.703	1.30	0.049	0.221	9.495
Ni	0.405	0.636	1.689	0.73	0.854	27.574	1.305	1.142	6.09
Cu	34	5.831	0.353	34	5.831	4.067	0.5	0.707	4.472
Cd	0.065	0.255	4.961	0.0002	0.014	91.679	0.0018	0.042	20.125
Pb	445.705	21.112	0.225	10	3.162	1.5	1.22	1.105	0.429

Element	F0455			F0456			F0457		
	s^2	s	calculated $\lvert t \rvert$	s^2	s	calculated $\lvert t \rvert$	s^2	s	calculated $\lvert t \rvert$
Cr	26.5	5.148	2.457	5.905	2.430	1.041	5.62	2.371	6.870
Fe	0.247	0.497	4.132	0.145	0.381	3.737	0.045	0.212	16.836
Ni	6.5	2.549	1.985	1.01	1.005	4.091	0.024	0.155	25.081
Cu	19.221	4.384	1.497	2.405	1.551	1.02	0.049	0.221	12.922
Cd	0.005	0.071	24.597	0.005	0.071	24.597	0.007	0.082	5.752
Pb	24.625	4.962	5.417	137	11.705	1.891	410	20.248	1.562

Appendix 9. Mean values for CRM sediment samples obtained by dissolution and determined with and without use of matrix modifier by HR-CS GFAAS, critical value t_8=2.31 (confidence level 95%)

Element	IMEP-14		CRM-320		PACS-1	
	With modifier	Without modifier	With modifier	Without modifier	With modifier	Without modifier
Cr(mg/kg)	53.6	60.1	137	119	-	-
Fe(g/kg)	23.4	25.7	32.2	39.5	-	-
Ni(mg/kg)	26.9	26.2	82.7	70.1	41.9	42.1
Cu(mg/kg)	49.8	45.7	47.9	39	-	-
Cd(mg/kg)	2.3	2.8	0.55	0.53	2.47	2.41
Pb(mg/kg)	83.9	86.6	44.2	44.8	-	-

Element	IMEP-14		CRM-320		PACS-1	
	sdev. results	calculated $\lvert t \rvert$	sdev results	calculated $\lvert t \rvert$	sdev results	calculated $\lvert t \rvert$
Cr	4.6	3.16	12.7	3.17	-	-
Fe	1.6	3.21	5.2	3.14	-	-
Ni	0.5	3.13	8.9	3.17	0.1	4.47
Cu	2.9	3.16	6.3	3.17	-	-
Cd	0.4	2.80	0.01	4.47	0.04	3.35
Pb	1.9	3.18	0.4	3.35	-	-

Appendix 10. Instrumental parameters and temperature program used for the analysis of sediment samples by slurry sampling HR-CS GFAAS

Parameters	**Element**					
	Cr	**Fe**	**Ni**	**Cu**	**Cd**	**Pb**
λ (nm)	357.868 359.348	248.327 302.064	232.003	327.396	326.105 228.802	283.306
Drying program						
Drying 1						
temperature. (ºC)	80	80	80	80	80	80
Ramp (ºC s^{-1})	6	6	6	6	6	6
Hold (s)	20	20	20	20	20	20
Drying 2						
temperature (ºC)	90	90	90	90	90	90
Ramp (ºC s^{-1})	3	3	3	3	3	3
Hold (s)	20	20	20	20	20	20
Drying 3						
temperature (ºC)	110	110	110	110	110	110
Ramp (ºC s^{-1})	5	5	5	5	5	5
Hold (s)	10	10	10	10	10	10
Heating program						
Pyrolysis						
temperature (ºC)	350/1300	350/1100	350/1050	350/1100	350/600	350/800
Ramp (ºC s^{-1})	50/300	50/300	50/300	50/300	50/300	50/300
Hold (s)	20/10	20/10	20/10	20/10	20/10	20/10
Atomization						
temperature (ºC)	2300	2000	2300	2000	1200	1500
Ramp (ºC s^{-1})	1500	1500	1500	1500	1400	1500
Hold (s)	4	4	5	4	3	4
Modifier	$Mg(NO_3)_2$	$Mg(NO_3)_2$	$Mg(NO_3)_2$	Pd+ $Mg(NO_3)_2$	Pd+ $Mg(NO_3)_2$, $NH_4H_2PO_4$	Pd+ $Mg(NO_3)_2$, $NH_4H_2PO_4$
Linear range (µg)	10-100	5-100	5-100	5-20	0.5-15	5-60

Appendix 11. Analytical figures of merit of HR-CS GFAAS using slurry sampling

Element	**R**	**Slope**	**LOD (μg L^{-1})**	**LOQ (μg L^{-1})**
Cr	0.998	0.0076	1.7	5.6
Fe	0.998	0.0082	2.0	6.6
Ni	0.997	0.0017	0.6	2.0
Cu	0.999	0.0063	1.4	4.5
Cd	0.998	0.0061	0.14	0.46
Pb	0.999	0.0021	1.1	3.5

Appendix 12. Certified values and mean values for CRM sediment samples obtained by slurry sampling and determined by LS FAAS. Critical value: t_{48}=2.31 (confidence level 95%)

Element	IMEP-14		CRM-320		PACS-1	
	Reference value	**Measurement value**	**Reference value**	**Measurement value**	**Reference value**	**Measurement value**
Cr(mg/kg)	57.4	61	138	135	113	89.8
Fe(g/kg)	25.4	22.8	-	-	48.7	38.5
Ni(mg/kg)	26.06	15.6	75.2	80.6	44.1	29.3
Cu(mg/kg)	47.21	43.3	44.1	52.4	452	417
Cd(mg/kg)	2.61	3	0.53	0.55	2.38	2.3
Pb(mg/kg)	87.25	80.9	42.3	41.5	404	426

Element	IMEP-14		CRM-320		PACS-1	
	sdev results	**Calculated | t |**	**sdev results**	**Calculated | t |**	**sdev results**	**Calculated | t |**
Cr	6.7	1.20	7	0.96	5.5	9.43
Fe	0.1	58.14	-	-	1.2	19.01
Ni	0.1	233.89	4.3	2.81	1.5	22.06
Cu	3.8	2.30	5.5	3.37	13	6.02
Cd	0.3	2.91	0.07	0.54	0.2	0.89
Pb	8	1.77	1.4	1.28	24	2.05

Appendix 13. Instrumental and temperature program parameters used for the analysis of sediments by direct solids sampling HR-CS GFAAS

Parameters	Element					
	Cr	**Fe**	**Ni**	**Cu**	**Cd**	**Pb**
λ (nm)	428.972	392.026	341.477	327.396	228.802	205.328
Heating program						
Pyrolysis temperature (ºC)	500/1500	350/1000	400/1200	400/900	300/600	350/850
Ramp (ºC s^{-1})	50/300	50/300	50/300	50/300	50/300	50/300
Hold (s)	20/10	20/10	20/10	20/15	20/10	20/10
Atomization temperature (ºC)	2300	2100	2400	2300	2000	2200
Ramp (ºC s^{-1})	1500	1500	1200	1250	1200	1200
Hold (s)	8	12	6	10	5	4
Modifier	$Mg(NO_3)_2$	$Mg(NO_3)_2$	$Mg(NO_3)_2$	Pd + $Mg(NO_3)_2$, NH_4F	Pd + $Mg(NO_3)_2$	Pd + $Mg(NO_3)_2$
Linear range (ng)	1-100	10-600	2.5-100	5-40	0.1-10	10-100

Appendix 14. Analytical figures of merit of HR-CS GFAAS with direct solids sampling

Element	**R**	**LOD (µg/g)**	**LOQ (µg/g)**
Cr 359	0.999	1.3	4.2
Cr 428	0.998	0.11	0.37
Fe 392	0.998	2.8	9.1
Ni 341	0.999	0.67	2.2
Cu 324	0.999	1.2	4.0
Cd 228	0.998	0.0039	0.013
Pb 205	0.999	1.8	6.0

Appendix 15. Certified values and mean values for CRM sediment samples obtained by direct solids sampling HR-CS GFAAS. Critical value: t_4=2.78 (confidence level 95%).

Element	IMEP-14		CRM-320		PACS-1	
	Reference value	Measurement value	Reference value	Measurement Value	Reference value	Measurement value
Cr(mg/kg)	57.4	60	138	126	113	92
Fe(g/kg)	25.4	25.6	-	-	48.7	45.7
Ni(mg/kg)	26.06	26.2	75.2	70.1	44.1	42
Cu(mg/kg)	47.21	45.7	44.1	43.3	452	453
Cd(mg/kg)	2.61	2.8	0.53	0.53	2.38	2.4
Pb(mg/kg)	87.25	86.6	42.3	44.8	404	392

Element	IMEP-14		CRM-320		PACS-1	
	sdev results	Calculated $\lvert t \rvert$	sdev results	Calculated $\lvert t \rvert$	sdev results	Calculated $\lvert t \rvert$
Cr	5.3	1.10	6	4.47	11	4.27
Fe	0.4	1.12	-	-	5.1	1.32
Ni	0.8	0.39	1.4	8.15	1.5	3.13
Cu	2	1.69	4	0.45	27	0.08
Cd	0.4	1.06	0.01	0.67	0.05	0.89
Pb	3.2	0.45	3.6	1.55	32	0.84

Appendix 16. Influences of drying and use of a matrix modifier on elemental determinations in sediment reference sample IMEP-14 with direct solids sampling HR-CS GFAAS

Element	Reference value	Without drying			Drying at ±110ºC during 5 hours		
		Results	Recovery (%)	% error	Results	Recovery (%)	% error
Cr(mg/kg)	57.4±1.6	52.7±3.1[a]	92	8	60.0±5.3[a]	105	5
		56.2±3.6[b]	98	2	53.6±17[b]	93	7
Fe(g/kg)	25.4±2.5	22.0±2.4[a]	87	13	25.6±0.4[a]	101	1
		23.9±2.7[b]	94	6	23.5±2.9[b]	93	7
Ni(mg/kg)	26.06±0.7	26.4±0.8[a]	101	1	26.2±0.8[a]	101	1
		22.6±0.9[b]	87	13	26.9±0.3[b]	103	3
Cu(mg/kg)	47.21±4.7	47.4±3.2[a]	100	0	45.7±2.0[a]	97	3
		47.9±6[b]	101	1	49.8±8.8[b]	105	5
Cd(mg/kg)	2.61±0.09	2.78±0.05[a]	107	7	2.8±0.4[a]	107	7
		2.17±0.15[b]	83	17	2.3±0.4[b]	88	12
Pb(mg/kg)	87.25±1.7	-	-	-	86.6±3.2[a]	99	1
		83.1±14[b]	95	5	83.9±3.4[b]	96	4

a with matrix modifier

b without matrix modifier

Appendix 17. Influences of drying and use of a matrix modifier on elemental determinations in sediment reference sample CRM-320 with direct solids sampling HR-CS GFAAS

Element	Reference value	Without drying			Drying at ±110°C during 5 hours		
		Results	Recovery (%)	% error	Results	Recovery (%)	% error
Cr(mg/kg)	138±7	131±7[a]	95	5	119±24[a]	86	14
		113±12[b]	82	8	137±6[b]	99	1
Fe(g/kg)	-	33.7±0.9[a]	-	-	39.5±4.1[a]	-	-
	-	30.9±2.9[b]	-	-	32.2±1.9[b]	-	-
Ni(mg/kg)	75.2±1.4	72.5±5.5[a]	96	4	70.1±1.4[a]	93	7
		74.6±3.2[b]	99	1	82.7±5.6[b]	110	10
Cu(mg/kg)	44.1±1.0	40.8±3.4[a]	93	7	39±4[a]	88	12
		37.0±8.4[b]	84	6	47.9±8[b]	109	9
Cd(mg/kg)	0.533±0.026	0.52±0.17[a]	98	2	0.53±0.01[a]	100	0
		0.49±0.62[b]	92	8	0.55±0.3[b]	104	4
Pb(mg/kg)	42.3±1.6	36.5±3.6[a]	86	14	44.8±3.6[a]	106	6
		43.6±12[b]	103	3	44.2±0.7[b]	104	4

a with matrix modifier

b without matrix modifier

Appendix 18. Influences of drying and use of a matrix modifier to elemental determinations in sediment reference sample PACS-1 with direct solids sampling HR-CS GFAAS

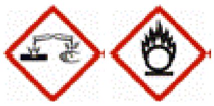
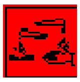
Element	Reference value	Without drying			Drying at ±110°C during 5 hours		
		Results	Recovery (%)	% error	Results	Recovery (%)	% error
Cr(mg/kg)	113±8	106±7[a]	94	6	92±11[a]	81	19
		-	-	-	-	-	-
Fe(g/kg)	48.7±0.8	-	-	-	46.9±1.6	96	4
		-	-	-	-	-	-
Ni(mg/kg)	44.1±2.0	45.5±1.6[a]	103	3	42.0±1.5[a]	95	5
		43.4±9.8[b]	98	2	42.0±4.9[b]	95	5
Cu(mg/kg)	452±16	447±44[a]	99	1	439±36[a]	97	3
		-	-	-	-	-	-
Cd(mg/kg)	2.38±0.026	2.2±0.2[a]	92	8	2.4±0.05[a]	101	1
		2.2±0.3[b]	92	8	2.5±0.8[b]	105	5
Pb(mg/kg)	404±20	394±18[a]	98	2	392±32[a]	97	3
		-	-	-	-	-	-

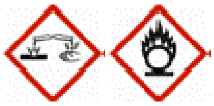
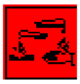
a with matrix modifier

b without matrix modifier

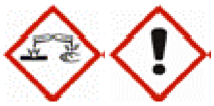
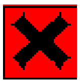
Appendix 19. Risks and Safety Statements:

Chemicals

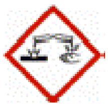
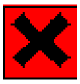
1. Nitric acid 65%	**HNO_3**
Safety information according to GHS	
Signal Word	Danger
Hazard Pictogram(s)	
Storage class	5.1B Oxidizing hazardous materials
WGK	WGK 1 slightly water endangering
Safety information	
R Phrase	R 35
S Phrase	S 23-26-36/37/39-45
Categories of danger	Corrosive
Hazard Symbol	 Corrosive

2. Hydrochloric acid 37%	HCl
Safety information according to GHS	
Signal Word	Danger
Hazard Pictogram(s)	
Storage class	8B Non-combustible, corrosive hazardous materials
WGK	WGK 1 slightly water endangering
Disposal	12
Safety information	
R Phrase	R 34-37
S Phrase	S 26-36/37/39-45
Categories of danger	Corrosive
Hazard Symbol	 Corrosive

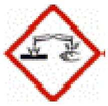
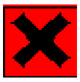
3. Hydrogen peroxide 30% H_2O_2

Safety information according to GHS	
Signal Word	Danger
Hazard Pictogram(s)	
Storage class	5.1B Oxidizing hazardous materials
WGK	WGK 1 slightly water endangering
Safety information	
R Phrase	R 22-41
S Phrase	S 26-39
Categories of danger	harmful, irritant
Hazard Symbol	 Harmful

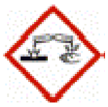
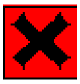
4. Chromium standard 1000 mg Cr, ($CrCl_3$ in 4.2% HCl)

Safety information according to GHS	
Signal Word	Warning
Hazard Pictogram(s)	
Storage class	8B Non-combustible, corrosive hazardous materials
WGK	WGK 1 slightly water endangering
Disposal	28 Aqueous solutions: Container D.
Safety information	
R Phrase	R 22-41
S Phrase	S 26-39
Categories of danger	harmful, irritant
Hazard Symbol	 harmful

5. Cadmium standard solution
$Cd(NO_3)_2$ in HNO_3 0.5 mol/l 1000 mg/l Cd

Safety information according to GHS	
Signal Word	Warning
Hazard Pictogram(s)	
Storage class	8B Non-combustible, corrosive hazardous materials
WGK	WGK 1 slightly water endangering
Disposal	15
Safety information	
R Phrase	R 36/38-52/53
S Phrase	S 61
Categories of danger	irritant, harmful, dangerous for the environment
Hazard Symbol	 irritant

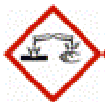
6. Copper standard solution
$Cu(NO_3)_2$ in HNO_3 0.5 mol/l 1000 mg/l Cu

Safety information according to GHS	
Signal Word	Warning
Hazard Pictogram(s)	
Storage class	8B Non-combustible, corrosive hazardous materials
WGK	WGK 2 water endangering
Disposal	28 Aqueous solutions: Container D.
Safety information	
R Phrase	R 36/38-52/53
S Phrase	S 61
Categories of danger	irritant, dangerous for the environment
Hazard Symbol	 irritant

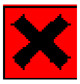
7. Iron standard solution

$Fe(NO_3)_3$ in HNO_3 0.5 mol/l 1000 mg/l Fe

Safety information according to GHS

Signal Word	Warning
Hazard Pictogram(s)	
Storage class	8B Non-combustible, corrosive hazardous materials
WGK	NWG not water endangering
Disposal	28

Safety information

R Phrase	R 36/38
S Phrase	S 26
Categories of danger	irritant
Hazard Symbol	 irritant

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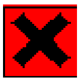
8. Nickel standard solution

$Ni(NO_3)_2$ in HNO_3 0.5 mol/l 1000 mg/l Ni

Safety information according to GHS

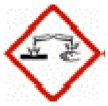
Signal Word	Danger
Hazard Pictogram(s)	
Storage class	6.1B Non combustible substances, toxic
WGK	WGK 2 water endangering
Disposal	28 Aqueous solutions: Container D.

Safety information

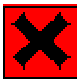
R Phrase	R 36/38
S Phrase	S 26
Categories of danger	irritant
Hazard Symbol	 irritant

9. Lead standard solution
$Pb(NO_3)_2$ in HNO_3 0.5 mol/l 1000 mg/l Pb

Safety information according to GHS

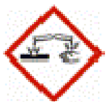
Signal Word	Warning
Hazard Pictogram(s)	
Storage class	8B Non-combustible, corrosive hazardous materials
WGK	NWG not water endangering
Disposal	15

Safety information

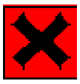
R Phrase	R 36/38-52/53
S Phrase	S 61
Categories of danger	irritant, dangerous for the environment
Hazard Symbol	 irritant

10. Zinc standard solution
$Zn(NO_3)_2$ in HNO_3 0.5 mol/l 1000 mg/l Zn

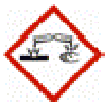
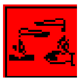
Safety information according to GHS

Signal Word	Warning
Hazard Pictogram(s)	
Storage class	8 B Non-combustible corrosive substances
WGK	WGK 2 water endangering
Disposal	28 Aqueous solutions: Container D.

Safety information

R Phrase	R 36/38-52/53
S Phrase	S 61
Categories of danger	irritant, dangerous for the environment
Hazard Symbol	 irritant

11. Palladium Matrix modifier for graphite furnace AAS

Safety information according to GHS	
Signal Word	Danger
Hazard Pictogram(s)	
Storage class	8B Non-combustible, corrosive hazardous materials
WGK	WGK 1 slightly water endangering
Disposal	12
Safety information	
R Phrase	R 34
S Phrase	S 26-36/37/39-45
Categories of danger	corrosive
Hazard Symbol	 Corrosive

12. Magnesium nitrate hexahydrate

$Mg(NO_3)_2 \ 6 \ H_2O$

Safety information according to GHS	
Precautionary Statement(s)	P262: Do not get in eyes, on skin, or on clothing.
Storage class	10 - 13 Other liquids and solids
WGK	WGK 1 slightly water endangering Disposal
Disposal	14 Inorganic salts: Container I. Neutral solutions of the these salts: Container D. Before placing in Container D, check the pH with pH-Universal indicator strips (Item No. 109535).
Safety information	
S Phrase	S 24/25

13. *Ammonium* dihydrogen *phosphate*

$(NH_4)H_2PO_4$

Safety information according to GHS

Storage class	10 - 13 Other liquids and solids
WGK	WGK 1 slightly water endangering Disposal
Disposal	14

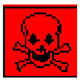
14. **Ammoniumfluorid**

NH_4F

Safety information according to GHS

Signal Word	Danger
Hazard Pictogram(s)	
Storage class	6.1B Non-flammable toxic substances
WGK	WGK 1 1 hazardous for water
Disposal	23

Safety information

R Phrase	R 23/24/25
S Phrase	S 26-45
Categories of danger	Toxic
Hazard Symbol	 Toxic

Risk Information (R Phrases)

R 1	Explosive when dry.

R 2	Risk of explosion by shock, friction, fire or other sources of ignition.
R 3	Extreme risk of explosion by shock, friction, fire or other sources of ignition.
R 4	Forms very sensitive explosive metallic compounds.
R 5	Heating may cause an explosion.
R 6	Explosive with or without contact with air.
R 7	May cause fire.
R 8	Contact with combustible material may cause fire.
R 9	Explosive when mixed with combustible material.
R 10	Flammable.
R 11	Highly flammable.
R 12	Extremely flammable.
R 14	Reacts violently with water.
R 15	Contact with water liberates extremely flammable gases.
R 16	Explosive when mixed with oxidizing substances.
R 17	Spontaneously flammable in air.
R 18	In use, may form flammable / explosive vapour-air mixture.
R 19	May form explosive peroxides.
R 20	Harmful by inhalation.
R 21	Harmful in contact with skin.
R 22	Harmful if swallowed.
R 23	Toxic by inhalation.
R 24	Toxic in contact with skin.
R 25	Toxic if swallowed.
R 26	Very toxic by inhalation.
R 27	Very toxic in contact with skin.
R 28	Very toxic if swallowed.
R 29	Contact with water liberates toxic gas.
R 30	Can become highly flammable in use.
R 31	Contact with acids liberates toxic gas.
R 32	Contact with acids liberates very toxic gas.
R 33	Danger of cumulative effects.
R 34	Causes burns.
R 35	Causes severe burns.

R 36	Irritating to eyes.
R 37	Irritating to respiratory system.
R 38	Irritating to skin.
R 39	Danger of very serious irreversible effects.
R 40	Limited evidence of a carcinogenic effect.
R 41	Risk of serious damage to eyes.
R 42	May cause sensitization by inhalation.
R 43	May cause sensitization by skin contact.
R 44	Risk of explosion if heated under confinement.
R 45	May cause cancer.
R 46	May cause heritable genetic damage.
R 48	Danger of serious damage to health by prolonged exposure.
R 49	May cause cancer by inhalation.
R 50	Very toxic to aquatic organisms.
R 51	Toxic to aquatic organisms.
R 52	Harmful to aquatic organisms.
R 53	May cause long-term adverse effects in the aquatic environment.
R 54	Toxic to flora.
R 55	Toxic to fauna.
R 56	Toxic to soil organisms.
R 57	Toxic to bees.
R 58	May cause long-term adverse effects in the environment.
R 59	Dangerous for the ozone layer.
R 60	May impair fertility.
R 61	May cause harm to the unborn child.
R 62	Possible risk of impaired fertility.
R 63	Possible risk of harm to the unborn child.
R 64	May cause harm to breastfed babies.
R 65	Harmful: May cause lung damage if swallowed.
R 66	Repeated exposure may cause skin dryness or cracking.
R 67	Vapours may cause drowsiness and dizziness.
R 68	Possible risks of irreversible effects.

Combination of R Phrases

R 14/15	Reacts violently with water, liberating extremely flammable gas.
R 15/29	Contact with water liberates toxic, extremely flammable gas.
R 20/21	Harmful by inhalation and in contact with skin.
R 20/21/22	Harmful by inhalation, in contact with skin and if swallowed.
R 20/22	Harmful by inhalation and if swallowed.
R 21/22	Harmful in contact with skin and if swallowed.
R 23/24	Toxic by inhalation and in contact with skin.
R 23/24/25	Toxic by inhalation, in contact with skin and if swallowed.
R 23/25	Toxic by inhalation and if swallowed.
R 24/25	Toxic in contact with skin and if swallowed.
R 26/27	Very toxic by inhalation and in contact with skin.
R 26/27/28	Very toxic by inhalation, in contact with skin and if swallowed.
R 26/28	Very toxic by inhalation and if swallowed.
R 27/28	Very toxic in contact with skin and if swallowed.
R 36/37	Irritating to eyes and respiratory system.
R 36/37/38	Irritating to eyes, respiratory system and skin.
R 36/38	Irritating to eyes and skin.
R 37/38	Irritating to respiratory system and skin.
R 39/23	Toxic: danger of very serious irreversible effects through inhalation.
R 39/23/24	Toxic: danger of very serious irreversible effects through inhalation and in contact with skin.
R 39/23/24/25	Toxic: danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed.
R 39/23/25	Toxic: danger of very serious irreversible effects through inhalation and if swallowed.
R 39/24	Toxic: danger of very serious irreversible effects in contact with skin.
R 39/24/25	Toxic: danger of very serious irreversible effects in contact with skin and if swallowed.
R 39/25	Toxic: danger of very serious irreversible effects if swallowed.
R 39/26	Very toxic: danger of very serious irreversible effects through inhalation.

R 39/26/27	Very toxic: danger of very serious irreversible effects through inhalation and in contact with skin.
R 39/26/27/28	Very toxic: danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed.
R 39/26/28	Very toxic: danger of very serious irreversible effects through inhalation and if swallowed.
R 39/27	Very toxic: danger of very serious irreversible effects in contact with skin.
R 39/27/28	Very toxic: danger of very serious irreversible effects in contact with skin and if swallowed.
R 39/28	Very toxic: danger of very serious irreversible effects if swallowed.
R 42/43	May cause sensitization by inhalation and skin contact.
R 48/20	Harmful: danger of serious damage to health by prolonged exposure through inhalation.
R 48/20/21	Harmful: danger of serious damage to health by prolonged exposure through inhalation and in contact with skin.
R 48/20/21/22	Harmful: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed.
R 48/20/22	Harmful: danger of serious damage to health by prolonged exposure through inhalation and if swallowed.
R 48/21	Harmful: danger of serious damage to health by prolonged exposure in contact with skin.
R 48/21/22	Harmful: danger of serious damage to health by prolonged exposure in contact with skin and if swallowed.
R 48/22	Harmful: danger of serious damage to health by prolonged exposure if swallowed.
R 48/23	Toxic: danger of serious damage to health by prolonged exposure through inhalation.
R 48/23/24	Toxic: danger of serious damage to health by prolonged exposure through inhalation and in contact with skin.
R 48/23/24/25	Toxic: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed.
R 48/23/25	Toxic: danger of serious damage to health by prolonged exposure through inhalation and if swallowed.

R 48/24	Toxic: danger of serious damage to health by prolonged exposure in contact with skin.
R 48/24/25	Toxic: danger of serious damage to health by prolonged exposure in contact with skin and if swallowed.
R 48/25	Toxic: danger of serious damage to health by prolonged exposure if swallowed.
R 50/53	Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
R 51/53	Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
R 52/53	Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
R 68/20	Harmful: possible risk of irreversible effects through inhalation.
R 68/20/21	Harmful: possible risk of irreversible effects through inhalation and in contact with skin.
R 68/20/21/22	Harmful: possible risk of irreversible effects through inhalation, in contact with skin and if swallowed.
R 68/20/22	Harmful: possible risk of irreversible effects through inhalation and if swallowed.
R 68/21	Harmful: possible risk of irreversible effects in contact with skin.
R 68/21/22	Harmful: possible risk of irreversible effects in contact with skin and if swallowed.
R 68/22	Harmful: possible risk of irreversible effects if swallowed.

Safety Information (S Phrases)

S 1	Keep locked up.
S 2	Keep out of reach of children.
S 3	Keep in a cool place.
S 4	Keep away from living quarters.
S 5	Keep contents under ... (appropriate liquid to be specified by the manufacturer).
S 5.1	Keep contents under water.
S 5.2	Keep contents under petroleum.
S 5.3	Keep contents under paraffin oil.
S 6	Keep under ...(inert gas to be specified by the manufacturer).
S 6.1	Keep under nitrogen.
S 6.2	Keep under argon.
S 6.3	Keep under protective gas.
S 7	Keep container tightly closed.
S 8	Keep container dry.
S 9	Keep container in a well-ventilated place.
S 12	Do not keep the container sealed.
S 13	Keep away from food, drink and animal feeding stuffs.
S 14	Keep away from ... (incompatible materials to be indicated by the manufacturer).
S 14.1	Keep away from reducing agents, heavy-metal compounds, acids and alkalis.
S 14.10	Keep away from acids, reducing agents and flammable materials.
S 14.11	Keep away from flammable material.
S 14.12	Keep away from alcalines and basic substances.
S 14.2	Keep away from oxidizing and acidic substances as well as heavy-metal compounds.
S 14.3	Keep away from iron.
S 14.4	Keep away from water and alkalis.
S 14.5	Keep away from acids.
S 14.6	Keep away from alkalis.
S 14.7	Keep away from metals.
S 14.8	Keep away from oxidizing and acidic substances.
S 14.9	Keep away from flammable organic substances.
S 15	Keep away from heat.
S 16	Keep away from sources of ignition - No smoking.

S 17	Keep away from combustible material.
S 18	Handle and open container with care.
S 20	When using do not eat or drink.
S 21	When using do not smoke.
S 22	Do not breathe dust.
S 23	Do not breathe gas/fumes/vapour/spray (appropriate wording to be specified by the manufacturer).
S 23.1	Do not breathe gas.
S 23.2	Do not breathe vapour.
S 23.3	Do not breathe spray.
S 23.4	Do not breathe fumes.
S 23.5	Do not breathe fumes/spray.
S 24	Avoid contact with skin.
S 25	Avoid contact with eyes.
S 26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S 27	Take off immediately all contaminated clothing.
S 28	After contact with skin, wash immediately with plenty of ...(to be specified by the manufacturer).
S 28.1	After contact with skin, wash immediately with plenty of water.
S 28.2	After contact with skin, wash immediately with plenty of soap and water.
S 28.3	After contact with skin, wash immediately with plenty of soap and water, if possible also with polyethylene glycol 400.
S 28.4	After contact with skin, wash immediately with plenty of polyethylene glycol 300 and ethanol (2:1) followed by plenty of soap and water.
S 28.5	After contact with skin, wash immediately with plenty of polyethylene glycol 400.
S 28.6	After contact with skin, wash immediately with plenty of polyethylene glycol 400 then rinse with plenty of water.
S 28.7	After contact with skin, wash immediately with plenty of acidic soap and water.
S 29	Do not empty into drains.
S 30	Never add water to this product.
S 33	Take precautionary measures against static discharges.
S 35	This material and its container must be disposed of in a safe way.

S 36	Wear suitable protective clothing.
S 37	Wear suitable gloves.
S 38	In case of insufficient ventilation, wear suitable respiratory equipment.
S 39	Wear eye/face protection.
S 40	To clean the floor and all objects contaminated by this material, use .... (to be specified by the manufacturer).
S 40.1	To clean the floor and all objects contaminated by this material use plenty of water.
S 41	In case of fire and/or explosion do not breathe fumes.
S 42	During fumigation/spraying wear suitable respiratory equipment (appropriate wording to be specified by the manufacturer).
S 43	In case of fire, use ... (indicate the precise type of fire-fighting equipment) Never use water.
S 43.1	In case of fire, use water.
S 43.2	In case of fire, use water or powder extinguisher.
S 43.3	In case of fire, use powder extinguisher - never use water.
S 43.4	In case of fire, use carbon dioxide - never use water.
S 43.6	In case of fire, use sand - never use water.
S 43.7	In case of fire, use metal fire powder - never use water.
S 43.8	In case of fire, use sand, carbon dioxide or powder extinguisher - never use water.
S 45	In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).
S 46	If swallowed, seek medical advice immediately and show this container or label.
S 47	Keep at temperature not exceeding ... °C (to be specified by the manufacturer).
S 47.1	Keep at temperature not exceeding 25 °C.
S 48	Keep wet with ... (appropriate material to be specified by the manufacturer).
S 48.1	Keep wet with water.
S 49	Keep only in the original container.
S 50	Do not mix with ... (to be specified by the manufacturer).
S 50.1	Do not mix with acids.
S 50.2	Do not mix with alkalis.
S 50.3	Do not mix with strong acids, strong bases, non-ferrous metals or their salts.
S 51	Use only in well-ventilated areas.

S 52	Not recommended for interior use on large surface areas.
S 53	Avoid exposure - obtain special instructions before use.
S 56	Dispose of this material and its container to hazardous or special waste collection point.
S 57	Use appropriate container to avoid environmental contamination.
S 59	Refer to manufacturer/supplier for information on recovery/recycling.
S 60	This material and its container must be disposed of as hazardous waste.
S 61	Avoid release to the environment. Refer to special instructions/Safety data sheets.
S 62	If swallowed, do not induce vomiting: seek medical advice immediately and show this container or label.
S 63	In case of accident by inhalation: remove casualty to fresh air and keep at rest.
S 64	If swallowed, rinse mouth with water (only if the person is conscious).

Combination of S Phrases

S 1/2	Keep locked up and out of reach of children.
S 3/7	Keep container tightly closed in a cool place.
S 3/9/14	Keep in a cool, well-ventilated place away from ... (incompatible materials to be indicated by the manufacturer).
S 3/9/14.1	Keep in a cool, well-ventilated place away from reducing agents, heavy-metal compounds, acids and alkalis.
S 3/9/14.1/49	Keep only in the original container in a cool, well-ventilated place away from reducing agents, heavy metal compounds, acids and alkalis.
S 3/9/14.2	Keep in a cool, well-ventilated place away from oxidizing and acidic substances as well as heavy-metal compounds.
S 3/9/14.2/49	Keep only in the original container in a cool, well-ventilated place away from oxidizing and acidic substances as well as heavy-metal compounds.
S 3/9/14.3	Keep in a cool, well-ventilated place away from iron.
S 3/9/14.3/49	Keep only in the original container in a cool, well-ventilated place away from iron.
S 3/9/14.4	Keep in a cool, well-ventilated place away from water and alkalis.

S 3/9/14.4/49	Keep only in the original container in a cool, well-ventilated place away from water and alkalis.
S 3/9/14.5	Keep in a cool, well-ventilated place away from acids.
S 3/9/14.5/49	Keep only in the original container in a cool, well-ventilated place away from acids.
S 3/9/14.6	Keep in a cool, well-ventilated place away from alkalis.
S 3/9/14.6/49	Keep only in the original container in a cool, well-ventilated place away from alkalis.
S 3/9/14.7	Keep in a cool, well-ventilated place away from metals.
S 3/9/14.7/49	Keep only in the original container in a cool well-ventilated place away from metals.
S 3/9/14.8	Keep in a cool, well-ventilated place away from oxidizing and acidic substances.
S 3/9/14.8/49	Keep only in the original container in a cool well-ventilated place away from oxidizing and acidic substances.
S 3/9/14/49	Keep only in the original container in a cool, well-ventilated place away from ... (incompatible materials to be indicated by the manufacturer).
S 3/9/49	Keep only in the original container in a cool well-ventilated place.
S 3/14	Keep in a cool place away from ... (incompatible materials to be indicated by the manufacturer).
S 3/14.1	Keep in a cool place away from reducing agents, heavy-metal compounds, acids and alkalis.
S 3/14.2	Keep in a cool place away from oxidizing and acidic substances as well as heavy-metal compounds.
S 3/14.3	Keep in a cool place away from iron.
S 3/14.4	Keep in a cool place away from water and alkalis.
S 3/14.5	Keep in a cool place away from acids.
S 3/14.6	Keep in a cool place away from alkalis.
S 3/14.7	Keep in a cool place away from metals.
S 3/14.8	Keep in a cool place away from oxidizing and acidic substances.
S 7/8	Keep container tightly closed and dry.
S 7/9	Keep container tightly closed and in a well-ventilated place.

S 7/47	Keep container tightly closed and at a temperature not exceeding ... °C (to be specified by the manufacturer).
S 20/21	When using do not eat, drink or smoke.
S 24/25	Avoid contact with skin and eyes.
S 27/28	After contact with skin, take off immediately all contaminated clothing, and wash immediately with plenty of . . . (to be specified by the manufacturer).
S 29/35	Do not empty into drains; dispose of this material and its container in a safe way.
S 29/56	Do not empty into drains, dispose of this material and its container at hazardous or special waste collection point.
S 36/37	Wear suitable protective clothing and gloves.
S 36/37/39	Wear suitable protective clothing, gloves and eye/face protection.
S 36/39	Wear suitable protective clothing and eye/face protection.
S 37/39	Wear suitable gloves and eye/face protection.
S 47/49	Keep only in the original container at a temperature not exceeding ... °C (to be specified by the manufacturer).

Curriculum Vitae:

First name : Risfidian
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2002 - 2004	Master of Science: Environmental chemistry, Graduate Program of Gadjah Mada University. Yogyakarta, Indonesia. Research topic: Immobilization of humic acid on chitin and its application for the adsorption of Ag(I) in aqueous medium.
1997 - 2001	Bachelor of Science: Inorganic chemistry. Department of Chemistry, Faculty of Mathematic and Natural Sciences, University of Sriwijaya. Palembang, Indonesia. Research topic: Binding mechanism of Cu(II) and Cd(II) by soil organic materials isolated from peat soil of South Sumatra.

Primary and secondary education

1994 - 1997	Senior high school: SMU Negeri 5 Bengkulu, Indonesia
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Professional jobs:

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2001-2002	Quality control on main laboratory, Lontar Papyrus Pulp and Paper Industry. Jambi, Indonesia.

Course and training

2003	Environmental impact assessment, Office of Indonesian Environmental Ministry, Yogyakarta, Indonesia.
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Publications:

R. Mohadi, Design and synthesis of hybrid inorganic-organic microstructures V_2O_5-PST containing N-functional groups toward toxic metal on aqueous medium, International Conference on Advances in Wastewater Treatment and Reuse. Tehran, Iran, 2009.

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Declaration

I declare that there was no previous attempt made towards the acquiring of a doctorate degree and that this thesis has not been previously submitted to another academic institution.

Hamburg, August , 2012 ……………………………………..

Risfidian Mohadi

I affirm that the above thesis was independently completed by me and that materials herein taken directly or indirectly from external sources were properly marked as such.

Hamburg, August , 2012 ……………………………………..

Risfidian Mohadi

Hiermit erkläre ich, dass vorher keine weiteren Promotionsversuche unternommen worden sind, oder an einer anderen Stelle vorgelegt wurden.

Hamburg, August, 2012 ……………………………………..

Risfidian Mohadi

Eidesstattliche Versicherung
Hiermit erkläre ich an Eides Statt, dass die vorliegende Dissertationsschrift selbständig und allein von mir unter den angegebenen Hilfsmitteln angefertigt wurde.

Hamburg, August, 2012 ……………………………………..

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