

Development of a calibration approach for the analysis of the passive sampler Chemcatcher with the use of Laser Ablation-Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS)

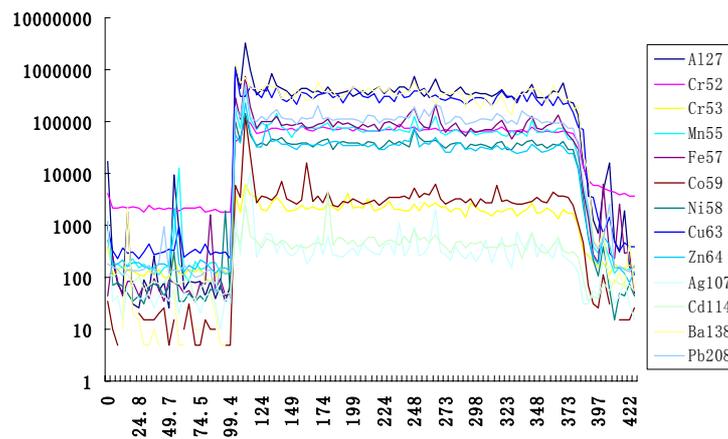
Master's Thesis in the International Master's Programme "Applied Environmental Measurement Techniques"

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 Göteborg, Sweden 2006
 Master's thesis 2006:79

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Abstract

Passive sampling is an increasing used technique for monitoring pollutants levels in the aquatic environment. This thesis presents a study on the analysis of the passive sampler Chemcatcher by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). Aim of the thesis was to calibrate the above samplers using LA-ICP-MS. Calibration of passive samplers requires the determination of sampling rates R_s for each element under the control of defined environmental conditions. Sampling rate (R_s) of 5 elements (lead, zinc, copper, nickel and cadmium) were determined in controlled tank using reference samplers installed in a filtering apparatus. The R_s values were calculated and compared to the corresponding standards, provided by the conventional method of ICP-MS, revealing similar trends of the values and validating in this way the use of LA-ICP-MS. In addition, strong associations between buffer concentration, temperature, turbulence and metal uptake from samplers were found. The overall results allowed a first assessment of the performance and sensitivity of Chemcatcher in the tank. The control of metal uptake appears to be the principal objective, for the determination of time averaged concentrations of the analytes. Further investigations and longer period of exposure will need to determine how different environmental factors like temperature, turbulence and biofouling affect the diffusion rate of metals across the sampler.

Keywords: Passive sampling, Chemcatcher, Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)

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1. Introduction

Detection of metals in aquatic environments leads often to difficulties in analysis but also in evaluation of results. An analytical process includes several steps like sampling, preservation and preparation of sample, qualitative and quantitative analysis.¹ The importance of reliable and right completion of these steps is very high while achievement of high precision results can give information about their ambient levels.

In surface water metals are found in different chemical forms ranging from free hydrated metal ions to weak complexes with organic or inorganic compounds (See Appendix A). However physicochemical forms do not remain stable and they are continuously altered. Redox potential, pH, concentration and the nature of ligands in the surrounding environment are some of the main factors influencing their speciation form. Nowadays it is well established that speciation determination is essential for understanding the toxicity, bioaccumulation and bioavailability of metals.

Currently, water monitoring is based on spot sampling. This technique is limited to the capture of total concentrations of pollutants in water, and thus appear difficulties in the detection of specific physicochemical forms since speciation changes take place during transport and storage. In an effort to overcome these difficulties various techniques have been developed and applied internationally to complement spot sampling. Passive sampling is the examined method which is continuously developing. It is a low cost technique with capability to cover long sampling periods and indicate time average concentration values of metals. Minimisation of speciation changes due to the design of passive samplers, and the attribute of a receiving membrane to retain analytes in the interior material, provide reliability and precision in the sampling of trace metals.²

In addition, the determination of metals requires accurate and sensitive techniques due to their extremely low levels. ICP-MS is relatively a new instrumental method with clear advantages in comparison to other spectrometric techniques due to a number of features. Low detection limits, possibility of multielement analysis and unique possibility of measuring element isotopic ratios are the main characteristics. However this method is limited to direct analysis of solid materials. Sample preparation is essential step in analysis and includes dissolution methods in order to obtain the analytes of interest in liquid form. The choice of reagents and method is often complicated and depends on a number of criteria such as the matrix components in the sample, the elements to be analyzed and the types of interferences anticipated.³ Compared to above conventional dissolution

technique, laser ablation appears many advantages. Laser ablation system was developed as a sampling accessory for ICP-MS aiming at the direct analysis of solid materials, deterring in this way likely contamination or elemental loss through incomplete dissolution steps. Nowadays it finds application in a wide range of fields while its application is gaining more acceptance. However a major problem of LA-ICP-MS refers to the lack of matrix specific calibration standards making quantitative analysis a difficult issue.

1.1 Aims and Objectives

Aim of this thesis was to develop a calibration approach for the analysis of passive samplers known as Chemcatcher using LA-ICP-MS. The sampler is composed of two membranes in a sealed device. The exposed membrane is used to diffuse metals, while the enclosed adsorbs and retains the metals when it is exposed in contaminated sites. Analysis is normally done after extraction of adsorbed compounds into a solution and subsequent analysis with ICP-MS. Direct analysis of the passive samplers using a laser beam could have some advantages. However the use of Laser ablation system implies the optimization of the laser operating conditions (spot size, energy, laser speed). In order to investigate these parameters, experiments on ablation characteristics of the membrane were carried out. In addition, analyses of passive samplers require calibration of the device. This was achieved by determining the sampling rate (R_s) of 5 elements (lead, zinc, copper, nickel and cadmium) under defined environmental conditions in controlled tank. The R_s values were calculated using as reference material samplers installed in a filtering apparatus. Finally uptake rates were compared with results obtained by conventional passive sampler.

This master thesis includes and focuses on the following objectives:

- Introduction to the Passive Sampler concept and Chemcatcher
- Description of Laser Ablation ICP-MS instrumentation
- Preparation of calibration for Cd, Cu, Pb, Zn, Cr, using the filtration equipment
- Calibration of passive sampler in controlled tank studies
- Optimization of laser parameters (beam size, energy, spot/scanning)
- Distribution of metals on chelating membranes
- Analysis of samples and comparison with conventional extraction.
- Assessment of the use of LA-ICP-MS for analyzing passive samplers

2. Background

2.1 Aquatic sampling

Correct sampling is a critical process in environmental studies. Accurate estimates in this step are needed to ensure valid results for subsequent analysis by instrumental techniques. However this step is often underestimated by analysts and sample contamination constitutes a common practice which affects to achieve detection of ambient concentrations.⁴ Moreover metals present at trace levels in the aquatic systems thus the extent of capture of their true concentration is very difficult. Spot sampling is reported as the widespread technique used in monitoring programmes for the determination of metals. Its wide application is due to the low cost of the procedure and the simplicity that it offers. This method refers to the collection of samples with the use of plastic containers (high density polyethylene or propylene) while next important step constitutes the transport of sample to the laboratory. This method is commonly used to evaluate the total concentration of pollutants at the moment of sampling. Detection of dissolved metals requires filtration through 0.45 μm membrane filters in order to separate dissolved metals from colloidal form. It is suitable for aquatic systems where concentrations do not present fluctuations and it can be used to investigate short term exposures for specific events. If variations are to be assessed with this technique, samples are taken frequently. However this technique is time consuming and disadvantageous economically.⁵

A number of problems associated with this method are related to the handling and preservation of samples. If the necessary precautions are not implemented, erroneous results may be obtained. Firstly, non representative results will be obtained if concentrations fluctuate. Preservation of samples is another important consideration. Physical, chemical and biological reactions take place during transport and storage. Dissolved metals tend to bind to colloids and suspended particles in the sample affecting in this way their detection. Relatively it is pointed out the precipitation of metallic compounds such as $\text{Al}(\text{OH})_3$ and $\text{Mg}_3(\text{PO}_4)_2$ while other common example that is often observed constitutes the absorption of pollutants on the surface of containers. In order to avoid loss of analytes water samples are typically stabilized by acidification with 1% acid. However stability in sample's integrity is still critical since it results in a change in speciation. As it is mentioned before, handling of samples by analysts is an other important issue. All the equipment needed for sampling, must be prepared thoroughly and maintained cleaned, while actions must always follow the standards. Likely neglect of any step such as immediate cooling of the samples after sampling, proper packaging for protection of samples by external contamination or even wrong type of containers used in sampling lead to modification of the final results. Serious contamination that also results with this method, originates from minor items such as bottle cap seals, metallic equipment, deionized water, reagents and human contact.⁶

3 Passive Sampling

Passive sampling refers to methods applied over long periods of time to measure pollutants. The period of sampling varies from several weeks to months and results from analysis indicate average concentration values. These techniques involve the collection and isolation of contaminants in the interior structure of a sorbent material for subsequent chemical analysis. Such type of material usually constitute filter membranes. The accumulated mass of analytes on the membrane provides information on the pollutant levels to which the device has been exposed. Therefore this feature permits an overall assessment of water quality.⁷

Passive sampling gained wide recognition in the mid 70's for measuring atmospheric pollutants. This method was used for the first time in 1973 for determination of NO₂ and SO₂ in air. However this technique was not limited in the examination of gases. Research was followed in the mid 80's for the measurement of inorganic and organic compounds in the aquatic ecosystems. Södergren was the first used a passive sampling system by hydrophilic dialysis bag to monitor nonpolar water contaminants. Nowadays a number of passive samplers have been developed and deployed in various environments including stormwater, effluents, pore water, freshwater and marine environments (See Appendix B). The most developed and at the same time most promising for the detection of trace metals are the following: Chemcatcher, DGT (Diffusion Gradient in Thin Film Technique), and SLM (Supported Liquid Membrane), all presenting different function and design.⁸

The sampler design plays a crucial role in passive sampling and determines the sensitivity to the particular analytes of interest. Despite the broad scale of designs referred in bibliography, they all present the same properties. They typically consist of a receiving phase, with high affinity for interested analytes, separated from the aquatic environment by a diffusion limiting barrier. The role of a diffusion barrier is to control the uptake rate of pollutants. This achieved by defining a controlled area above the receiving phase. Different samplers use diffusion barrier, thick membranes or tubes. In practice, barrier serves as a protector from suspended particles, colloids and micro-organisms, main parameters that affect or even prevent the sorption of metals to the receiving phase.⁹

3.1 Chemcatcher

The passive sampler used in this thesis is the mentioned Chemcatcher. The design was developed within a project run by Chalmers University and the University of Portsmouth, based on the model

that Kingston et al. provided¹⁰. The sampler is composed of two filter membranes in a sealed device. The exposed membrane is used to diffuse metals while the enclosed retains the metals. The choice of these two membranes has been taken due to the research provided by Bjorklund and Runeberg. The receiving phase is a chelating filter (3M Empore™ Chelating disc 47 mm diameter). The material that characterizes these membranes is Poly (Styrene-divinylbenzene) while the functional group is sodium salt of iminodiacetic acid. Basic trait of iminodiacetate groups is the capability of reaction with metals and the formation of constant complexes in the interior structure of the membrane, which allows retaining of analytes during deployment. The exposed membrane is a Sartorius cellulose acetate with pore size of 0.45 μm, acting as diffusion limiting barrier of metals at a controlled rate.

The material that characterizes the main body of the device is polypropylene. Polypropylene is suitable to minimize the adsorption of metals onto the body when it is exposed to contaminated aquatic systems. The device is composed of 4 parts. The first piece is used to receipt the examined membranes while the other 3 screw together in order to hold the receiving phase and the limiting membrane and avoid likely contamination or flow of water during transport and storage. The membranes are positioned in passive samplers by placing the diffusion limiting membrane directly to the surface of the receiving membrane. The samplers are accompanied by a screw cap in order to keep wet the membranes during their transport. The following diagram represents the basic parts of the passive sampler.

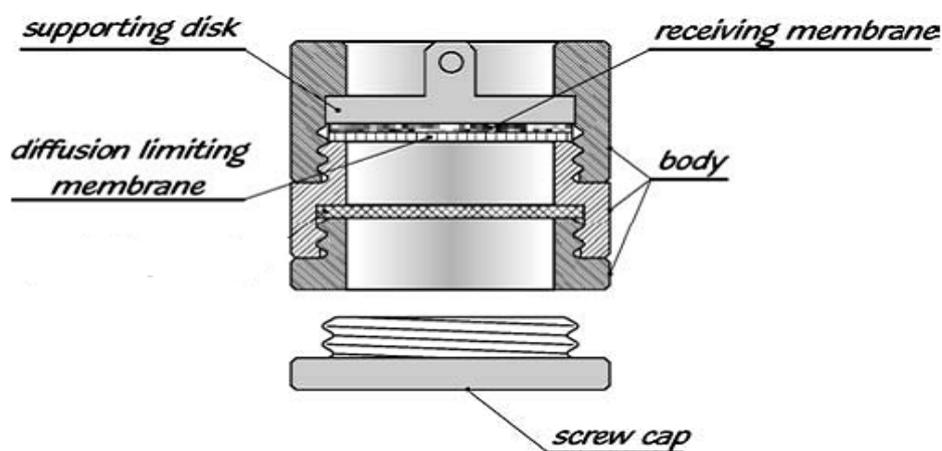


Figure 1: Basic parts of the passive sampler device, Chemcatcher

3.2 Principle of Chemcatcher

The principle that passive sample collection of Chemcatcher relies, is based on Fick's first law. According to this theory the accumulation of contaminants into the sampler is due to the difference in concentration between the water column and the receiving phase. Collection of the analytes operates

until equal concentration exists on both media. During this process, pollutants in water phase diffuse through a well-defined area that cellulose acetate membrane provides and accumulate in the chelating membrane. The following diagram address this phenomenon while the mathematical equation above the figure, describes the theoretical calculated mass accumulation on the receiving phase. In addition the calculation of the following equation allows the determination of time averaged concentration of pollutants at the duration of exposure.⁵

$$M = - D * dc/dx \text{ (Equation 1)}$$

where

M: mass flux of analyte (gcm⁻²/sec)

D: diffusion coefficient (cm²/sec)

C: concentration of the compound (gcm⁻³)

L: distance (cm)

dc/ dx: concentration gradient across distance L

(-): indicates the direction of the concentration gradient

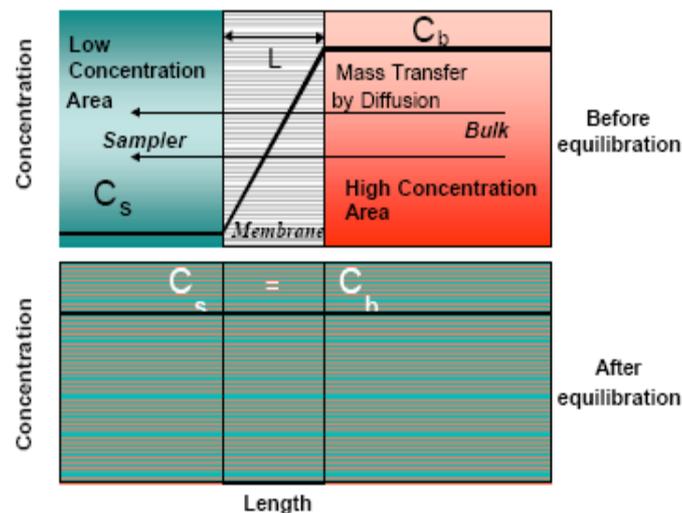


Figure 2: Diffusion route and equilibration for analytes from the bulk aqueous phase to the surface of the receiving phase

4. Metal measurements in natural aqueous systems

4.1 Inductively Coupled Plasma Mass Spectrometry

The determination of metal species requires precise and sensitive analytical techniques due to their extremely ultratrace levels in the environment. Nowadays the most widespread applied measurement techniques include Flame Atomic Absorption Spectrometry (FAAS), Anodic Stripping Voltammetry (ASV), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma Mass-Spectrometry (ICP-MS). ICP-MS appears clear advantages in comparison to other spectrometric techniques due to a number of features. Low detection limits in the sub parts per trillion (ppt) range, quantitation in the range of parts per million (ppm), specificity and isotopic capability classify this method as the dominant trace element technique.^{9,3}

However all the above mentioned methods including ICP-MS, require the analysis of sample in liquid form. For the analysis of solid samples a sample pretreatment step precedes. This step involves removal of the interested analytes from the solid matrix to an aqueous solution by using dillution methods. However this step is associated with many considerations. First, sample preparation process prevents rapid analysis. The time required for the preparation of samples is the most time consuming part in the analysis, especially in cases of complex matrices such as minerals for geology studies. In addition, the use of reagents to extract metals from the examined material disposes large volumes of solvents and chemicals and thus appears additional expenses in the analysis. Moreover, the preparation of sample solutions implies the loss of the solid sample and thus does not allow repetition of the process¹⁴. This refers mainly to matrices such as filter membranes. After wetting with solvents, the membrane is not recommended to dry out because drying alters the pore size. Finally, the analysis of solutions with the obtained analytes, resulting from dillution step, does not always represent the analytes in the solid phase. Loss of elements due to incomplete dissolution, wrong selectivity of reagents due to the polyatomic spectral interferences anticipated and contamination from the glassware (beakers, volumetric flasks and autosampler tubes) are common practices.^{9,3} Many studies applied on filter membranes and analysis with conventional extraction have shown the disability of some elements to be identified. Extraction results for chelating membranes containing metal species, reported by Runeberg, mention difficulty for the detection of lead (Pb).

4.2 Instrumentation of Inductively Coupled Plasma Spectrometry

Schematic diagram of a typical ICP-MS apparatus is shown in Figure 3. The basic departments that compose the instrument are plasma torch, interface, vacuum system, mass spectrometer and detector.

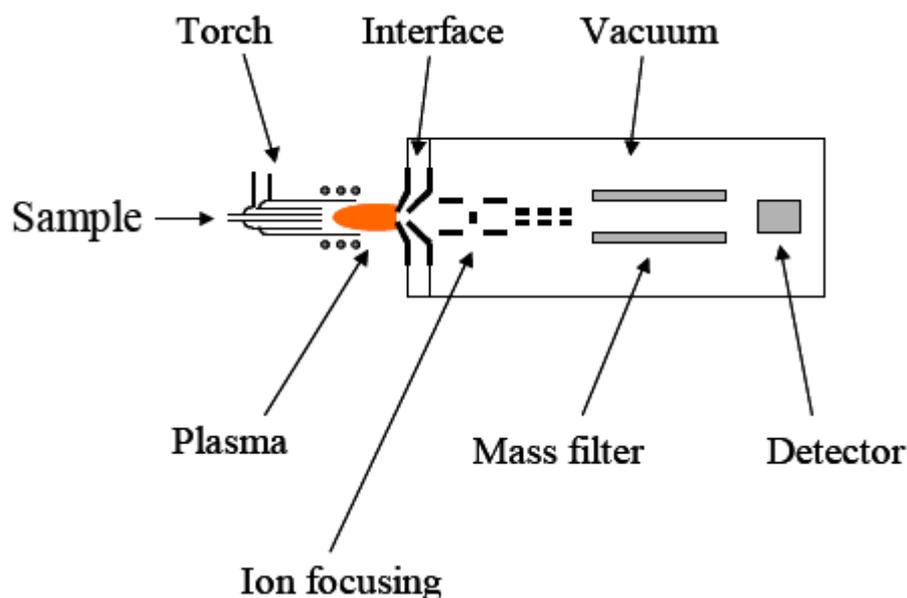


Figure 3: Inductively Coupled Plasma – Mass spectrometry (ICP-MS)

Sample solutions are nebulized into the plasma torch. The plasma torch is constituted by three concentric tubes (outer tube, middle tube and sample injector). The first is used to maintain the plasma (outer tube), the second controls the position of the plasma within the torch and the third transports the sample into the plasma. Argon gas flows in the gaps between the tubes while application of high radiofrequency RF results to the creation of plasma. As the sample aerosol pass through the plasma, different temperature phases exist, which vaporize, atomize and finally ionize that. The resulting ions are then passed through the interface region consisted by two cones known as sampler and skimmer. The main characteristic of this area is to transport the ions efficiently from the plasma into the vacuum system due to the difference in pressure between these two areas. Once the ions are emerged from interface region they are directed to the vacuum system compromised by a turbomolecular and a mechanical rough pump. Ions in this part are separated by gas molecules to allow in this way their transport to the detector. In order to avoid a diverging of the ions during their transport to mass spectrometer, the lens system is applied behind the interface. At this part a metallic cylinder with the same charge as ions, achieves to form a focused ion beam. The mass spectrometer

then separates the ions according to their mass-to-charge ratio (m/z) and filter out all the non-analyte ions remained. The ions which reach at the detector provide an electronic signal.^{3,9}

4.3 Interference

The most common interferences that occur when analyzing metals with ICP-MS are classified in two broad categories: spectral or isobaric and non spectral or matrix-induced. Spectral interference appears when two isotopes of different elements have the same or identical m/z . The mass spectrometer therefore presents difficulties to detect their signals. Spectral interferences are divided into 3 types: isobaric, molecular (polyatomic) and double charged ion interferences. In the first case isobaric occurs when two different isotopes have the same mass. These interferences are highly depending on the structure of the sample. Correction can be done by measuring the intensity of another analyte isotope of the interfering element and subtracting the appropriate correction factor from the intensity of the interfered isotope. In the second case, polyatomic is formed when matrix ions collide and react with argon or other elements occur in the plasma for example O, N, and Cl. These interferences are usually originate from acids substances used in sample preparation. This type of interference is corrected by analyzing interference solutions or using non infrared analyte isotopes. Finally double charged ion interferences occur when detecting sample ions presenting the double mass of the analyte and thus the same mass charge. This is often corrected by optimising instrument operating conditions.

Non spectral interferences refer to analysis of samples with high total dissolved solids such as analysis of seawater with high content of salts. The most common effects are suppression and enhancement of analyte signal. This type of interference can be overcome by applying dilution methods on the sample or using a sample introduction system in order to remove dissolved salts.^{3,9}

5. Laser Ablation

The introduction and conjunction of the Laser ablation system in the mid 80's, as a sampling accessory for ICP-MS has been allowed direct analysis of solid samples without any sample pretreatment. LA-ICP-MS has the advantage of simplicity and rapid analysis while allows trace element determination in the range of ppt. It presents less interference compared to ICP-MS since there is no use of solvents to interact with argon while contamination during analysis is minimized. Moreover analysis of solid samples allows the analysis of micro quantities but also the analysis of concrete points on a sample.¹³

5.1 Instrumentation of Laser Ablation System

A typical Laser Ablation system is composed of a laser source, optical devices, a sample cell, a transfer tube to carry the ablated sample into the ICP-MS and a camera. A schematic diagram of the device is shown in Figure 4 while a description of the principle is followed.

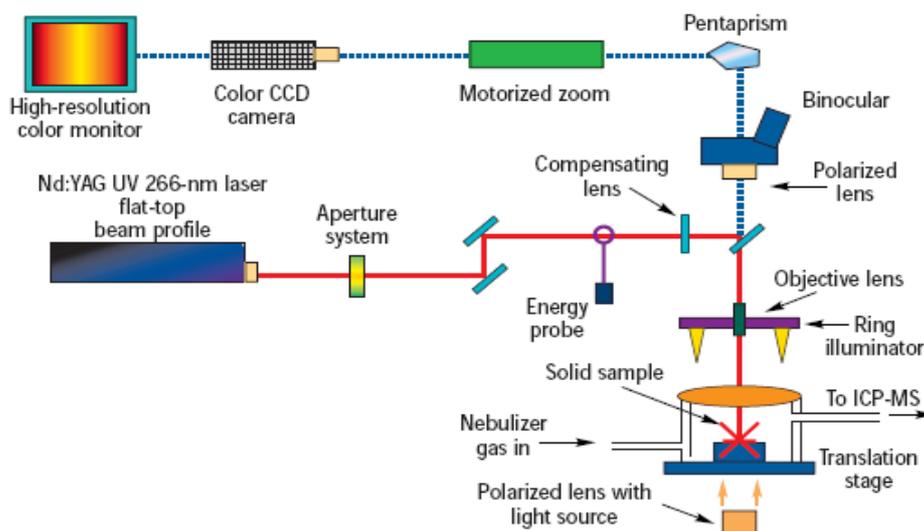


Figure 4: Laser Ablation system¹⁹

Samples are placed on a mechanically adjustable sample cell while the sample surface can be viewed via a CCD camera. An ultraviolet (226 nm, frequency quadrupled) pulsing laser beam is released by a Nd: YAG laser ablation system. A number of optical devices give the possibility of alignment and regulation of laser beam to the examined sample. The laser beam is directed via reflection and then

interacts with the solid material. When laser radiation is absorbed in the surface area of the sample, the electrons in the solid become excited. The excited electrons transfer their energies to the structure and the sample melts and vaporizes. Ions released during this process form a plasma plume above the sample surface. The expanding high-pressure plasma causes further vaporization of the solid and emission of particulates, forming an aerosol. The resulting gas contains the interested analytes. At the end, the ablation cell is flushed with argon gas to transport the ablated sample via plastic tubing to the ICP torch.^{13,14}

5.2 Limitations of LA-ICP-MS

5.2.1. Calibration

A main limitation by using Laser ablation system constitutes the calibration method used to ensure precision of the measurements. The clues that detector provides is limited in the depiction of element signals. If element concentrations are to be assessed, calibration is needed. A common practice which is typically used for the comparison of results, is the use of certified reference materials (CRM). Calibration in this case is made by plotting Intensity against element concentration of standards with known composition. However, a limited number of reference materials have been produced for the use of Laser Ablation. Most of them refer to materials such as glass and minerals concerning geological studies. Thus analysis of solids with unknown composition and without reference material is a difficult issue to produce reliable data that are important to verify the precision of the measurement. A common practice which is used, to overcome these difficulties is internal standardization. In this case an element with similar ablation characteristics to the interested analytes is selected and added to the samples before analysis. The software adjusts the analyte concentrations by comparing the intensity values of the internal standard intensities. An other option that is often followed is the preparation of reference material in the laboratory. In this process matrix samples are spiked with known concentrations of the target analytes to verify recoveries. This is achieved to distinguish sample matrix interferences and check laboratory performance.^{9,3}

6. Studied Metals

This part discusses the main sources of Lead (Pb), Nickel (Ni), Copper (Cu), Zinc (Zn) and Cadmium (Cd) as well as main characteristics concerning their main use and the effects of toxic levels in organisms. These metals were selected due to their widespread use through anthropogenic activities and their performance in previous studies on the concrete passive samplers used in this thesis.

Lead (Pb)

Lead is a highly toxic element. It can accumulate in human bone marrow where it becomes main bone component and influences the nervous system. In the nature it is contained in various minerals such as galena (PbS), massicot (PbO), cerussite (PbCO₃), anglesite (PbSO₄)¹. The main sources for lead pollution originate from combustion of petrol additives since it is main component, paints, plumbing material, ammunition for shooting birds, manufacture of games and electric conductors as protective coating, ceramics and glass industry, insecticides and pesticides. Lead in aquatic systems has high affinity to be absorbed on particles and it usually appears in sediments. In surface water it is usually found in low concentrations as dissolved element of Pb⁺² and Pb⁺⁴.^{1,5}

Nickel (Ni)

Nickel is an essential metal and occur naturally in low levels. It appears low toxicity to humans and animals. However studies have shown high toxicity at elevated concentrations causing damage to the lungs and kidneys. It mainly originates from dry cell batteries and metallurgical industries. Traffic is also reported as a main source of nickel by leaking from car brakes, tyres and asphalt. In surface waters it is usually found in the form of Ni²⁺.^{1,15}

Copper (Cu)

Copper is an essential metal for normally health growth but it has tendency to become very toxic to organisms in concentrations below 1 ppm. The main sources of copper pollution are smelting and mining, brass manufacture, electroplating and excessive use of agrochemicals. Copper is also widely used in water pipes. Corrosion of piping material contributes to high concentration in drinking water. Further Cu sources derive from highway and roof runoff in the aquatic systems. In the first case, wear of brake pads contain quantities of Cu and secondly rain erodes copper used in the construction of roofs. Metallic taste and diarrhea are the most reported consequences in humans.^{5,15}

Zinc (Zn)

Zn is an essential metal and has relatively low toxicity to animals and humans. Mining and smelting are the most common activities associated with Zinc pollution. It is widely used in galvanized steel and released in the aquatic systems by weathering and corrosion. Studies have shown increased allergies and minor health problems associated with Zn exposure. In surface waters a small amount remains dissolved. The level of dissolved zinc in water increase as the acidity of water increases.¹⁵

Cadmium (Cd)

Cadmium is a highly toxic metal. Main sources has been constituted the use in batteries (Ni-Cd), paints and chemicals, insecticides, lithography, typography, glass industry. Cadmium is also highly used in phosphate fertilizers. Cd can accumulate in kidneys of animals and cause kidney dysfunction. The most toxic form of this element is Cd^{+2} .¹⁵

7. Experimental Analysis

7.1 Calibration of Chemcatcher

Calibration of passive sampler Chemcatcher was achieved by two ways. Filtering and pilot installation constitute the 2 basic activities. Assessing and comparing the calibrations for a number of analytes provide a better understanding of their uptake rate through the diffusion limiting membrane to the chelating disk and allow characterization of passive sampler's performance. These methods were validated for five elements (Ni, Cd, Cu, Pb, and Zn). In addition, carbon (C) was selected as internal standard due to the constant relative concentration that presents in the chelating membrane. Different solutions of the 5 elements were spiked on chelating filters. These samples were then dried and analyzed by LA-ICP-MS. Based on the LA-ICP-MS results obtained; we converted the sample intensities to average values and checked the linearity by plotting intensity against mass of accumulated metals per disk for filtering calibration, and loading ($\mu\text{g}/\text{disk}$) against time (hours) for tank calibration. Moreover, results obtained from previous studies by conventional method (extraction and ICP-MS analysis) were used to compare metal uptakes.

7.2 Performance of Chemcatcher through Filtering apparatus

This method involves preparation of standard solutions contaminated with metals and their application to the two membranes used in samplers, by using the filtration apparatus. Solutions of 0.2, 0.5, 1, 2, 5 and 10 ppb were prepared. Desirable pH and ionic strength conditions maintained by using a KH_2PO_4 -NaOH buffer. The filtrate was collected and analysed by ICP-MS to determine the retention efficiency of the chelating membrane. Analysis of the chelating disks by LA-ICP-MS enabled the determination of the sensitivity relative to the amount of metals on the discs. In addition, solutions of 1 ppb with different amounts of buffer (no buffer, 1/10, 1/2) were applied to both membranes. The objective of this work was to obtain information on water chemistry in the solution used for calibration. Figure 5 shows in details the application of both membranes to the filtering apparatus.

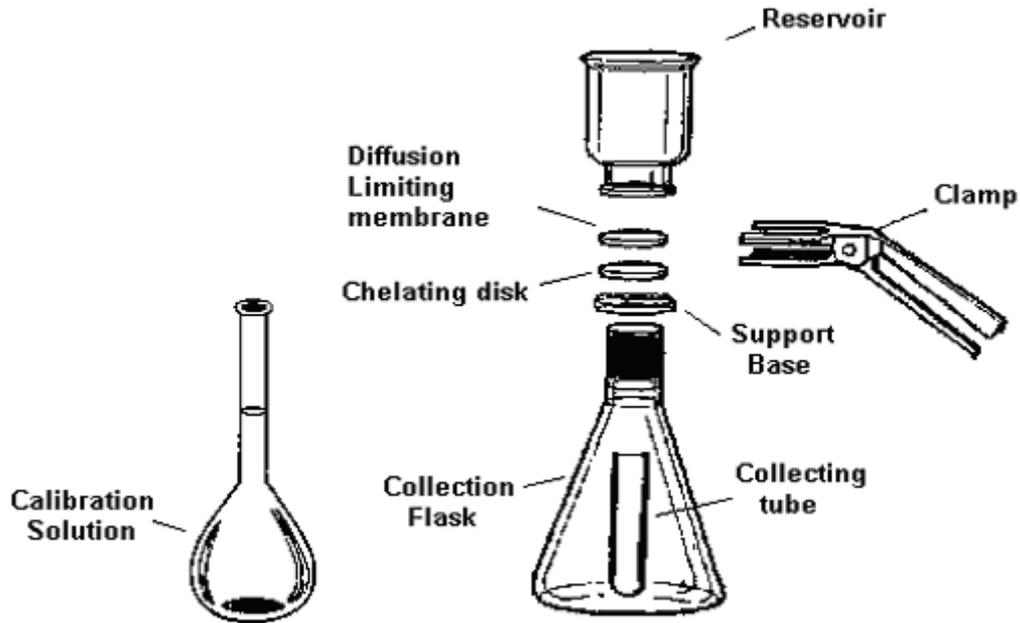


Figure 5: Detailed illustration of chelating and cellulose acetate membrane application on the filtering apparatus

7.3 Performance of Chemcatcher in controlled tank

This process includes application of passive samplers in controlled tank, containing known concentration of analytes and simulating ambient conditions. Aim of this work was to calculate the sampling rates (R_s) of each element by plotting the metal uptake against exposure time (hours). Results from this procedure enable the quantitative estimation of element concentration on the chelating disc and evaluate the effect of ambient conditions such as temperature and turbulence on the diffusion process.

Well defined sampling rates R_s are also necessary to enable calculation to obtain the time average concentration. R_s is defined as the ratio of the slope of the uptake curve divided by solution concentration. (Equation 2).

$$R_s = 1/C_w * dM/dt \text{ (Equation 2)}$$

where

R_s : sampling rate of analyte (L/h)

dM/dt : ratio of the slope of the uptake curve [Loading ($\mu\text{g}/\text{disk}$) against Time (hours)]

C_w : solution concentration ($\mu\text{g}/\text{L}$)

The slope of the uptake curve derive by calculating the loading of each element using sensitivity (a) and constant b obtained from calibration curves ($y = ax + b$) in the filtering apparatus. The following equation provides the loading in the chelating disk detected for exposure in the tank:

$$\text{Loading} = [\text{Intensity (Average values)} - b] / a \quad (\text{Equation 3})$$

The system used in this part, was constructed in the laboratory. It consists of a round 25 liters tank rinsed with 100ppb solution. The tank is placed in 250 liter vessel as shown in figure 5. The vessel, containing water, is used to regulate solution temperature at desirable ambient conditions. The temperature was adjusted at 11°C with the help of a refrigeration apparatus placed in the vessel. The passive samplers were placed on a turntable plastic stirrer by rotating at a controlled rate of 40 rpm. 100ppb solution of 25 lt volume adjusted with 34,085gr potassium dihydrogen phosphate (KH_2PO_4) and 5,082gr natrium hydroxide (NaOH), was injected into the rinse tank using a exterior mechanic pump at a flow rate of 2 ml/lt. Solution was flowing out of one side of the rinse tank and allowed the solution in the tank to have a controlled concentration of analytes. Seven samples were applied in the tank by which the three were collected at the end and the other four were taken approximately every 24 hours after the second day. After deployment, samples were placed and dried in desiccators at ambient conditions, and kept in the laboratory until the analysis day. Particular attention was given to avoid any contact of samples with air and metal surfaces that could cause alteration in their chemical character.

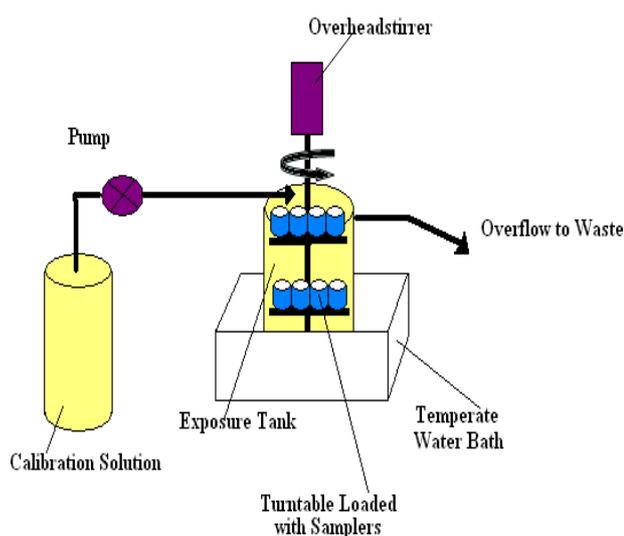


Figure 6: Calibration system constructed at Chalmers University. Calibration solution flows through the tank in which the samplers are exposed on a turntable that is rotated at controlled speed. Temperature is adjusted using a water bath.

7.4 Reagents and material

- Milli-q system Millipore Bedford MA USA 18.2 Mo cm, TOC <5mg/lt
- High purity 65% HNO₃
- ICP-use concentrated multiple metals solution with the concentration of 1000mg/l for each following metals: Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Ti, Zn.
- 3M Empore™ Chelating disc 47 mm diameter
- Sartorius cellulose acetate membrane 0.45 μm
- 0.1M Ammonium Acetate (pKa=4.76) Buffer NH₄Ac, pH=5.3, Ionic strength=0.081M
- 3 M Nitric Acid HNO₃
- NaOH - KH₂PO₄ Buffer
- Rh (Internal standard for ICP-MS analysis)

7.5 Preparation of Calibration Solutions

Aqueous standard solution of 1ppm was prepared by diluting 1 ml concentrated multiple metals solution with the concentration of 1000 ppm, in 1000 ml ultrapure water. Phosphate buffer at a final pH=7 and ionic strength=0.01 M PO₄ was prepared by dissolving 0.2032 gr NaOH and 1,363 gr KH₂PO₄ in the 1000ml solution. Aim of the high ionic strength was to prevail changes in water chemistry due to low concentrations of metals. Additional standard solutions were obtained by diluting this solution with ultrapure water in 100 ml volume to give concentrations ranging from 0.2ppb to 100ppb. All samples were prepared in clean polyethylene containers while actions took place in a fume hood in order to avoid contamination.

Standard Solutions	Concentration (ppb)	Volume of ultrapure water
A	0.2ppb	100ml
B	0.5ppb	100ml
C	0.8ppb	100ml
D	1ppb	100ml
E	2ppb	100ml
F	5ppb	100ml
G	10ppb	100ml

Table 1: Preparation and identification of Calibration Solutions

7.6 Preparation of Passive samplers

Before deployment, all passive samplers devices used in analysis were soaked in 10% nitric acid for 24 hours and finally rinsed with ultra pure water (Milli-Q system, Millipore). The membranes were conditioned according to manufacturer's directive. Instructions impose the precondition of the chelating disc by using glass filtration apparatus under vacuum conditions. Initially the membrane washed with 20 ml ultra pure water. Then the disc soaked with 20 mL of 3.0M nitric acid followed by two 50 mL water washes. The disc was let to dry between each wash. Last step was the wash with 50 mL of 0.1M ammonium acetate buffered at pH 5.3. The ammonium form constitutes the most active form of the chelating disk.¹⁶ Diffusion Limiting Membrane was diluted with 1% HNO₃ and dried in air for 1 minute before located on the sampler.

7.7 Analysis by LA-ICP-MS

Analysis of chelating discs was carried out using a CETAC LSX 200 Laser Ablation system connected via a 1 m PTFE transfer tube to a Perkin Elmer Elan 6000 ICP-MS apparatus. The LSX-200 is equipped with a quadrupled Nd:YAG laser with an output wavelength of 266 nm while argon is used as a carrier gas to transfer the ablated aerosol into the ICP torch. The ICP-MS is a quadrupole mass system with cross flow nebulisation and a Fazel-Scott spray chamber. Samples were placed on the mechanically adjustable sample cell that LSX-200 contain while the sample surface could be viewed remotely via a monitor with a 80-800x zoom, allowing ablation choices over the sample surface. Tables 2 and 3 show the operating conditions during analysis for Laser Ablation system and ICP-MS respectively.



Figure 7: ICP-MS System used at Chalmers University

ICP-MS conditions	Data acquisition	Peak hopping
	Dwell time	100 ms
	Plasma power	1000 W
	Plasma gas flow rate	161 min ⁻¹
	Carrier gas flow rate	1 min ⁻¹
	Auxiliary gas flow rate	0.91 min ⁻¹
	Reading/replicate	25
	Sweeps/replicate	10

Table 2. Instrumental settings for ICP-MS

Laser ablation conditions	Energy level	1,0-1,5 mJ
	Scan speed	100 $\mu\text{m s}^{-1}$
	Carrier gas	Argon
	Replicates	1
	Wavelength	UV 266 nm
	Dwell time	10 ms
	Spot size	300 μm
	Repetition rate	20 Hz

Table 3. Instrumental settings for Laser Ablation



Figure 8: Laser Ablation System used at Chalmers University

8. Results and discussion

8.1 Laser operating conditions

The results of the measurements presented in this chapter, depend on the optimization of parameters and analytic characteristics of the Laser Ablation system. This investigation constitutes an essential step before the application of LA-ICP-MS. More specifically, it was studied the influence of spot size, repetition rate, laser speed and energy on the chelating discs. These characteristics were recorded and studied for first time on the concrete matrix. This step was made to determine the most optimal experimental conditions that should be applied. Laser operating conditions were optimized by ablating a chelating disk applied in the tank for 5 days. Main criterion of the experiment was to ablate the membrane significantly in order to carry all the analytes retained to the disc, into ICP-MS. Attention was also given not to ablate the underlying sample cell substrate. Ablation was performed in the form of scan lines and spots across the membrane surface at different scanning speed, energy and repetition rate. The laser beam spots and lines were tested at energies at 5, 10, 15, 20; pulse repetition rates at 5MHz, 10MHz, 15MHz, 20MHz and speeds at 20 $\mu\text{m/s}$, 50 $\mu\text{m/s}$ and 100 $\mu\text{m/s}$. It has been realized that scan lines are more suitable to the ablation of the discs. Easier to process and analysis of a larger area of the disc than spots offer, judged our next step. Energy at 15, laser beam size 7, repetition rate at 20 Hz and the laser speed of 100 $\mu\text{m/sec}$ were preferred as a better solution. Figures 9, 10, 11 show the responded intensity against spot size, energy and laser speed respectively. As it can be distinguished the selected parameters present the highest performance of the instrument when laser ablates the chelating membranes.

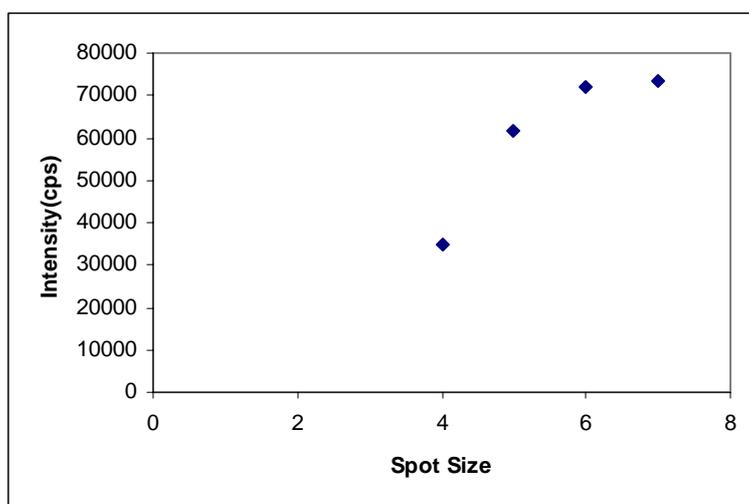


Figure 9: Intensity (cps) against Spot size (μm) at energy 20 MHz and laser speed 100 $\mu\text{m/s}$

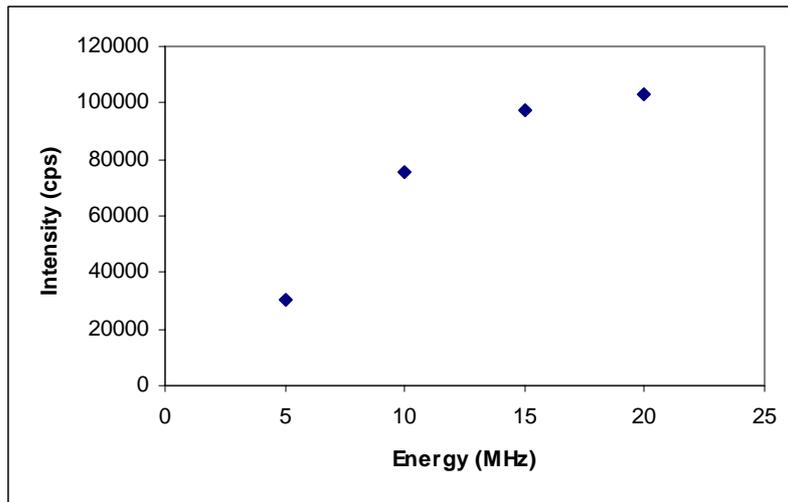


Figure 10: Intensity (cps) against Energy (MHz) at Spot size 7 μm and laser speed 100 $\mu\text{m/s}$

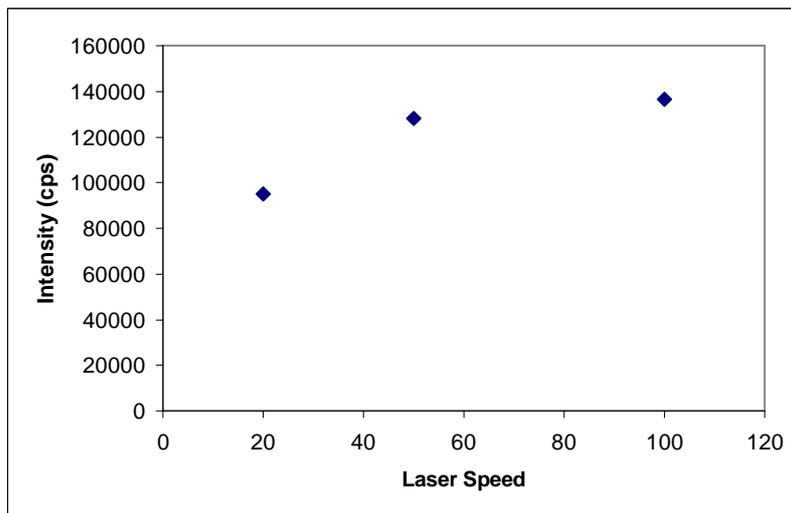


Figure 11: Intensity (cps) against Laser Speed ($\mu\text{m/s}$) at energy 20 MHz and Spot size 7 μm

8.2 Distribution of analytes in filter membranes

Figure 12 shows a typical ICP-MS spectrum. Axis ψ represents the ICP-MS response/intensity and the axis x the time of analysis. This diagram obtained by analyzing a chelating disk contaminated with 100 ppb of the interested analytes (Ni 58, Cu 63, Zn 64, Cd 114, Pb 208). The peak appears when the laser starts ablating the sample. Each peak section of the plateau represents a part of the sample. Values before and after the stabilization of the signal are excluded in the analysis. Intensity is converted to values by averaging each of the peaks.

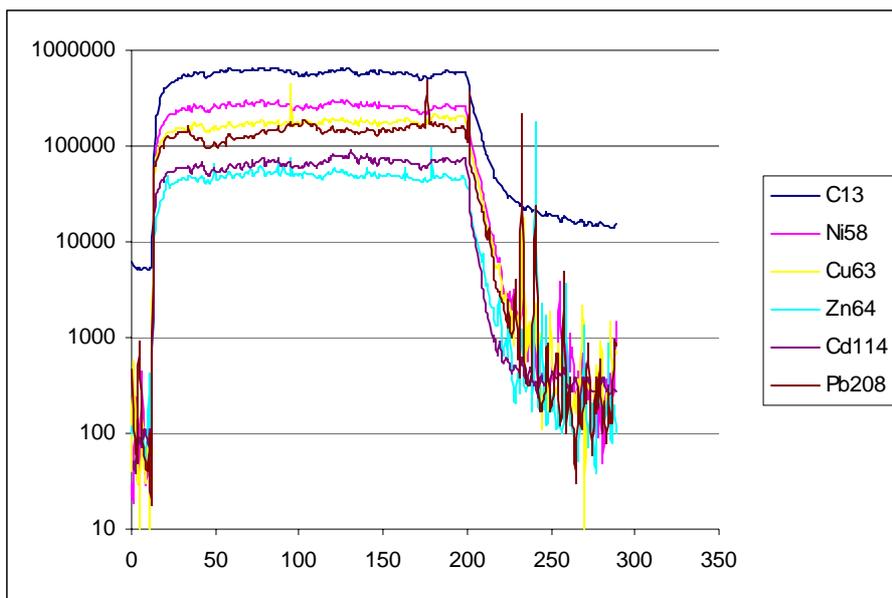


Figure 12: A typical ICP-MS spectrum

In order to ensure the homogenous distribution of the metals of interest in the membrane, the standard deviation and the relative standard deviation were calculated. R.S.D. values for Ni, Cu, Zn and Cd114 are within 6% to 11%, indicating good precision. Lead presents a higher value but in low levels.

	Average	Standard Deviation (S.D.)	Relative Standard Deviation (R.S.D.)
C	583538.4	35678.32	6.1%
Ni58	261173.5	18307.66	7%
Cu63	176740	24765.13	14%
Zn64	49441.62	5849.65	11.8%
Cd114	66843,71	7387.059	11%
Pb208	145700.5	32382.62	22.2%

Table 4: The average, Standard deviation and relative standard deviation of the measured sample 5 (c) for showing the metal distribution in chelating disks

8.3 Effect of Buffer on metal uptake

The following diagram presents the effect of buffer in the calibration solutions. It was found that buffer reacts with the metals in the water and thus affects the metal uptake by chelating disks. This behavior can be attributed in the competitive effect of ion complexation with phosphorous PO_4^- and OH^- . Most of the elements present similar trends at different variations except Pb that present a high value at the low concentration of 1/10. Higher intensity values and thus higher uptake of metals to chelating disk is reported at the high concentration of buffer. However, interest is presented at the smaller concentrations (1/10) and at the null use of buffer. The values as distinguished in the figure are higher than those when half quantity of buffer is added. The optimal results were taken with the addition of 0.2032 g NaOH 1,363 g KH_2PO_4 in the 1000 ml solution.

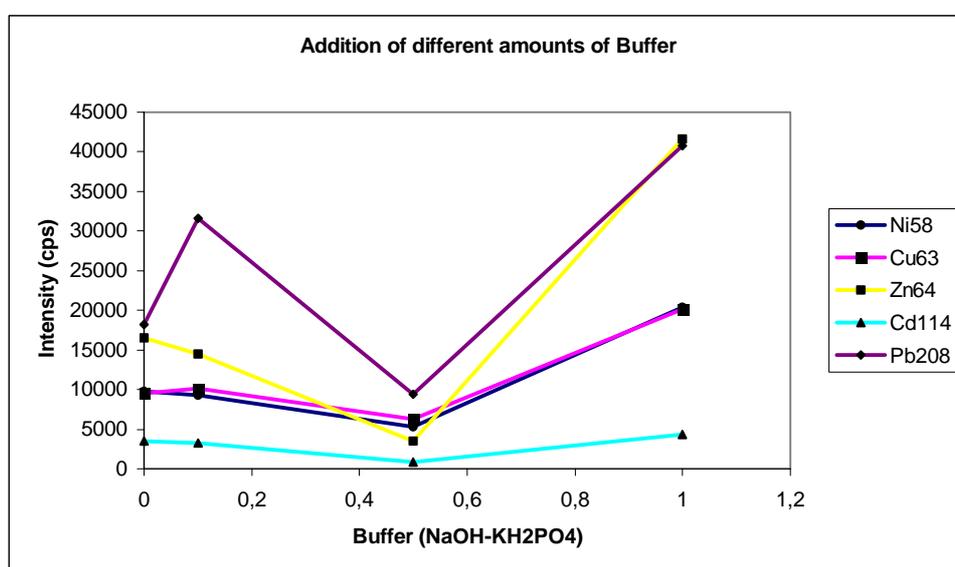


Figure 13: Addition of different amounts of buffer (0, 1/10, 1/2, 1) NaOH-KH₂PO₄ in the standard solutions

8.4 Calibration of Chemcatcher

8.4.1 Performance of Chemcatcher through Filtering apparatus

Plotting the theoretical accumulated amount of analytes on the disk ($\mu\text{g}/\text{disk}$) against the LA ICP-MS response/intensity (cps), calibration curves for each measured element are displayed on the following figures. All correlations were found significant at the 0.9 confidence level except Pb and Zn at 0.8.

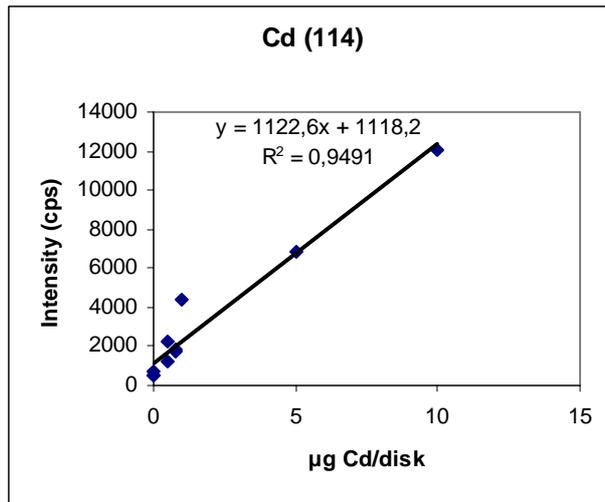


Figure 14: The Calibration Curve for the element Cd114. Performance of Chemcatcher through Filtering apparatus

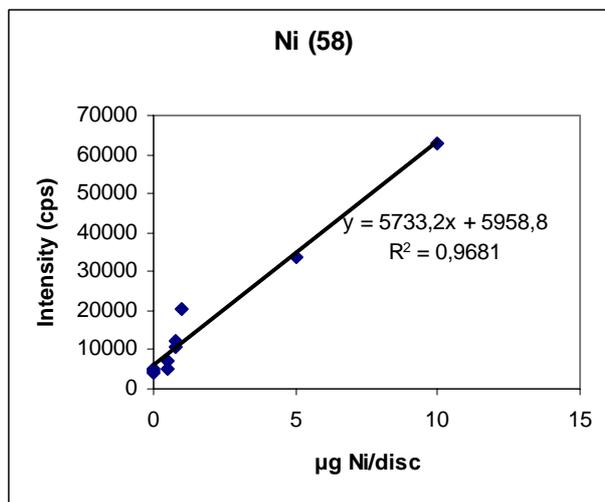


Figure 15: The Calibration Curve for the element Ni58. Performance of Chemcatcher through Filtering apparatus

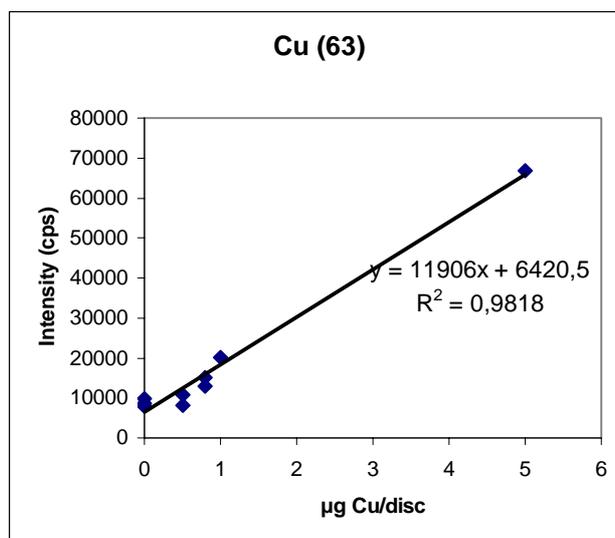


Figure 16: The Calibration Curves for the element Cu63. Performance of Chemcatcher through Filtering apparatus

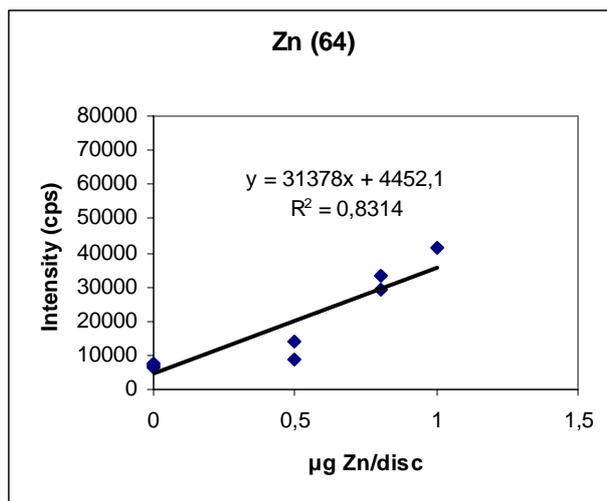


Figure 17: The Calibration Curves for the element Zn64. Performance of Chemcatcher through Filtering apparatus

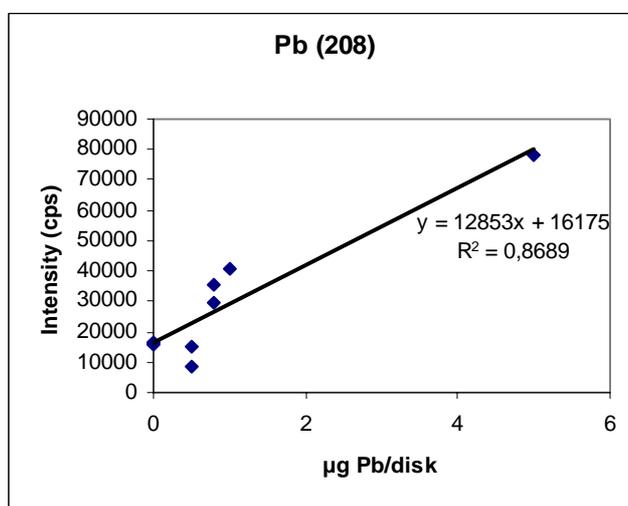


Figure 18: The Calibration Curve for the element Pb208. Performance of Chemcatcher through Filtering apparatus

Elements	A	R ²
Ni58	5753.2	0.9681
Cu63	11906	0.9818
Zn64	31378	0.8314
Cd114	1122.6	0.9491
Pb208	12853	0.8689

Table 5: Sensitivity and R² values for elements Ni58, Cu63, Zn64, Cd114, and Pb208 detected in the filtering apparatus

	C13	Ni58	Cu63	Zn64	Cd114	Pb208
Blank	480393	4952	9780	7476	705	16216
Blank	486032	4179	8567	6644	501	15529
Blank	499427	4438	7866	7181	468	16447
Blank (average)	613869	25664	35382	69512	2399	63501
0,5 ppb	591472	7355	10768	14062	2293	14991
0,5 ppb	576401	5273	8181	8929	1222	8741
0,8 ppb	645728	12021	13028	29409	1697	29425
0,8 ppb	609605	10916	15059	33199	1853	35694
1 ppb	609118	20424	20155	41676	4371	40787
1 ppb	630167	25470	19275	-	3265	33384
1 ppb	617296	13302	13319	-	4843	11015
5 ppb	651142	33670	66775	-	6849	78283
10 ppb	673348	62998	-	-	12103	-

Table 6: ICP-MS response/intensity (average values) of all samples applied in filtering apparatus

8.4.2 Performance of Chemcatcher in controlled tank

Plotting the the accumulated mass (µg/disk) on chelating disk against time period (hours), calibration curve for each measured element are displayed on the following figures. Concentrations of Lead Pb have shown great deviation of the desirable results. This can be caused by Pb complexation of ions in the buffer solution. Previous studies have shown similar trends regarding the detection results of lead. Ni and Cd correlation were found significant at the 0.9 confidence level; however Cu and Zn appear less precise, at 0.8.

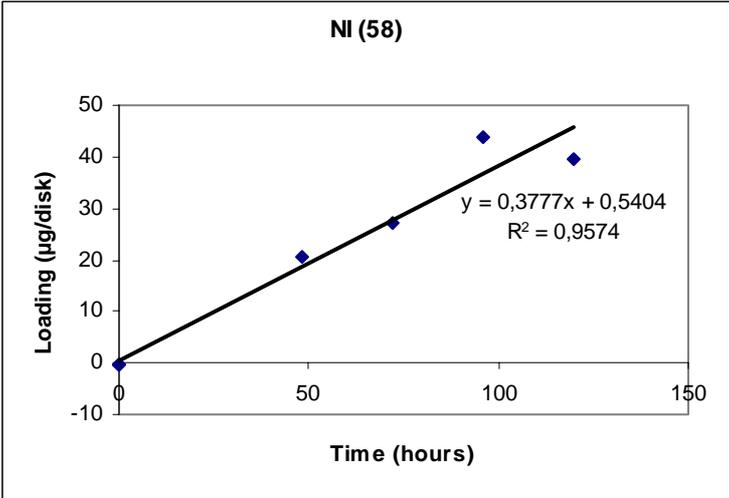


Figure 19: The Calibration Curve for the element Ni(58). Performance of Chemcatcher in controlled tank.

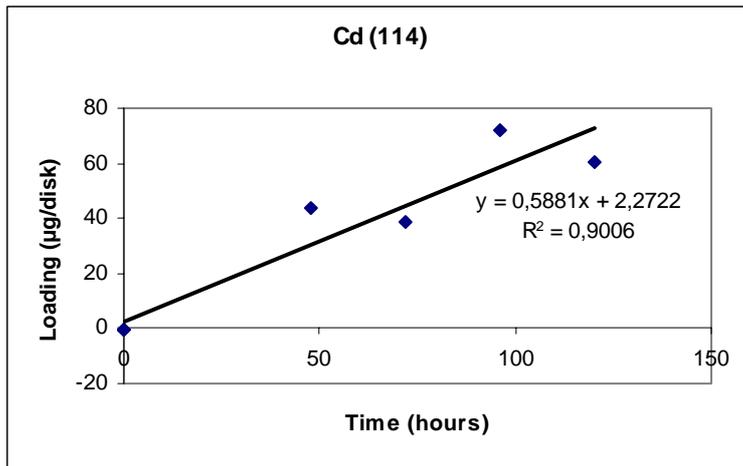


Figure 20: The Calibration Curve for the element Cd(114). Performance of Chemcatcher in controlled tank.

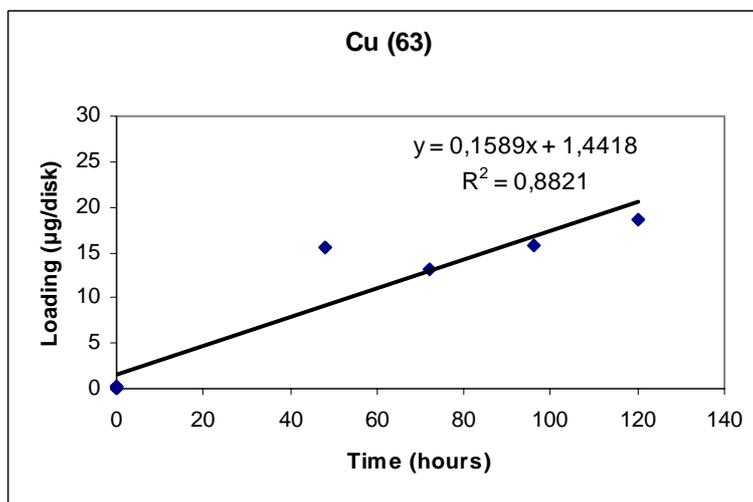


Figure 21: The Calibration Curve for the element Cu(63). Performance of Chemcatcher in controlled tank.

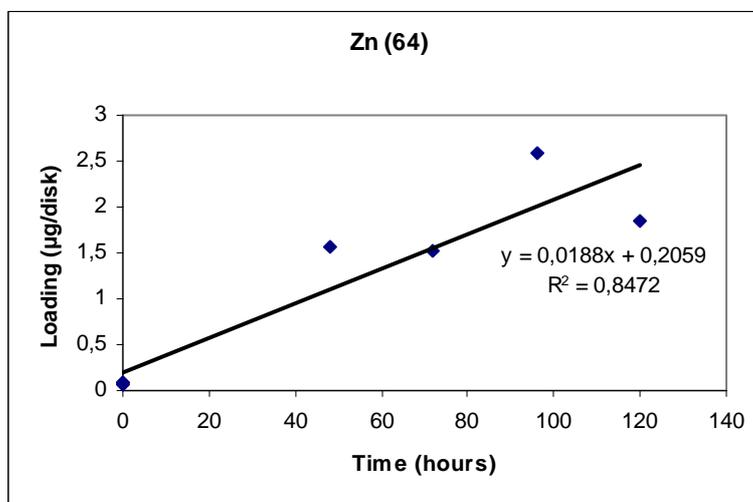


Figure 22: The Calibration Curve for the element Zn(64). Performance of Chemcatcher in controlled tank.

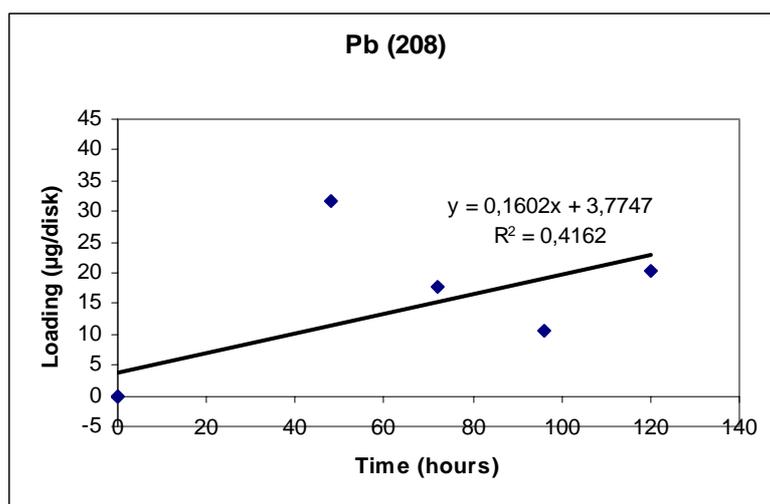


Figure 23: The Calibration Curve for the element Pb(208). Performance of Chemcatcher in controlled tank.

Elements	A	Rs	R ²
Ni58	0.363	3.7	0.9574
Cu63	0.1406	1.5	0.8821
Zn64	0.0175	0.1	0.8472
Cd114	0.5403	5.8	0.9006
Pb208	0.1602	1.6	0.4162

Table 7: Sensitivity and R² values for elements Ni58, Cu63, Zn64, Cd114, and Pb208 detected in the tank

Sample	Ni58Intensity	Loading	Cu63Intensity	Loading	Zn64	Loading	Cd114	Loading	Pb208	Loading
Blank	4980,74	0,01	9837,08	0,02	7520,11	0,00	708,83	0,01	16311,46	0,03
Blank	4154,56	0,00	8517,37	0,01	6605,91	0,00	498,53	0,01	15438,62	0,04
Blank	4293,80	0,00	7610,58	0,01	6947,77	0,00	452,88	0,01	15913,27	0,03
Blank (Average)	152745,10	1,98	349359,50	1,53	104449,60	0,11	57969,18	0,63	1433857,00	3,08
Sample 1 (2 day)	124380,10	1,60	190587,10	0,82	53317,54	0,05	50052,71	0,54	423286,20	0,91
Sample 2 (3 day)	161793,20	2,10	163576,30	0,70	52529,34	0,05	44910,88	0,49	244548,30	0,52
Sample 3 (4day)	257770,50	3,38	193193,80	0,83	85505,67	0,09	82264,94	0,91	151829,50	0,32
Sample 3 (a) (4day)	244795,90	3,21	341744,20	1,50	80827,79	0,09	72037,46	0,79	541141,00	1,16
Sample 3 (b) (4day)	239333,90	3,14	195664,10	0,85	65074,14	0,07	77789,44	0,86	170278,80	0,36
Sample 3 (c) (4day)	216487,70	2,83	145307,00	0,62	41158,93	0,04	55985,29	0,61	120422,20	0,25
Sample 4 (5day)	233539,20	3,06	227571,80	0,99	62353,62	0,06	68604,06	0,75	277280,70	0,59

Table 8: ICP-MS response/intensity (average values) of all samples applied in controlled tank

8.5 Amount of analytes passing through the chelating membranes

All the filtered standard solutions were analyzed by ICP-MS after diluting with 1% volume of nitric acid (HNO₃) and adding 10ppb of Rhodium as internal standard. This work was done to estimate the amount of analytes passing through the samplers and assess the reservation of metals in the disk. The following table illustrates the concentrations for each element detected in the filtered solution. The highest concentrations appear with the highest applied concentrations in the standard solutions. Lead shows a high level of concentration when 1 ppb is applied in the membrane. Concentrations are generally presented in low levels. High levels of Zn indicate serious contamination during analysis.

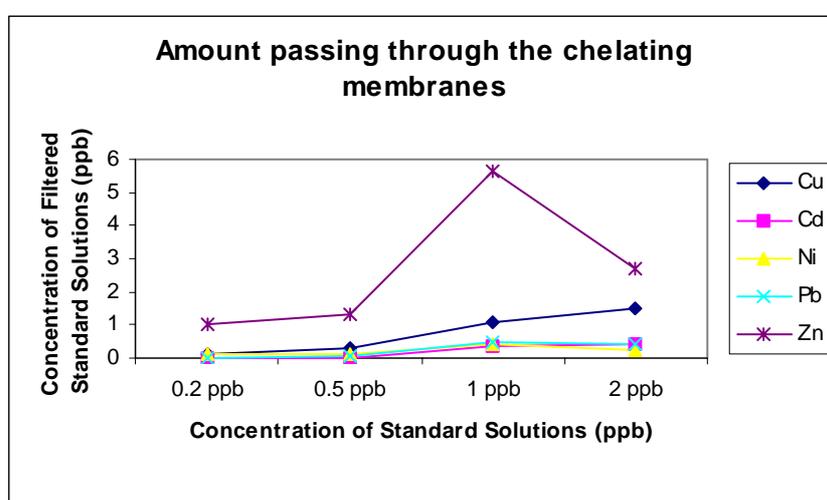


Figure 24: Amount of analytes (µg/Lt) passing through the chelating membranes, analysis with ICP-MS.

Applied Concentration (ppb)	Concentration in percent of analytes in the filtered standard solutions after deployment to samplers				
	Cd	Ni	Pb	Zn	Cu
0,2 ppb	0.07%	5%	0.7%	51.36%	6.8%
0,5 ppb	0.3%	2.13%	1.1%	25.86%	5.9%
1 ppb	3.6%	4.4%	5.02%	56.2%	10.9%

Table 9: Amount of analytes (µg/Lt) passing through the chelating membranes – Analysis by ICP-MS

8.6 Comparison with ICP-MS data

Results from previous measurements in controlled tank studies by Runeberg and analysis of chelating disks with conventional method ICP-MS are presented in the following table. Main aim constitutes the comparison of Rs for the elements Cd114, Ni58, Zn64, Pb208 and Cu63. Values provided by the measurements with ICP-MS, are reported in various temperatures 4°C, 11°C and 18 °C while turbulence rate is recorded at the constant rate of 70 rpm. The main differences that govern the two studies are the contrast at the stirring rate and exposure time, 40rpm – 70 rpm and 5 days – 14 days, respectively. Rs values by ICP-MS as distinguished in the table are presented high when temperature is 18°C. Temperature generally affects kinetic processes and thus higher uptake is expected with increase of temperature. Values obtained by LA-ICP-MS follow similar trends. The values of 3.7 and 1.5 for Ni and Cu respectively, are comparable similar in magnitude to these reported by Runeberg. However, lead and cadmium were noted at higher values, indicating higher uptake. Such a fact implies that dilution methods with acids may affect the solubility of these metals by the chelating membrane. However it still remains unknown subject and thus further experiments should focus on that. Zn shows a low sampling rate, this indication may arise from various sources of error during experimental analysis and it still remains unknown subject.

Element	ICP-MS value (Rs) (70 rpm, 4 °C)	ICP-MS value (Rs) (70 rpm, 11 °C)	ICP-MS value (Rs) (70 rpm, 18 °C)	LA-ICP-MS value (Rs) (40rpm, 11°C)
Ni58	2.4	4.7	5.7	3.7
Cu63	2.2	4.3	4.9	1.5
Zn64	2.6	5.2	5.3	0.1
Cd114	2.7	5.1	5.1	5.8
Pb208	0.46	0.52	0.66	1.6

Table10: Sampling Rate of analyte (Rs) for Cd114, Ni58, Zn64, Pb208 and Cu63 based on studies in controlled tank studies and analysis of samples by the two analytical techniques, ICP-MS and LA-ICP-MS

The difference that occurs between these two methods may be due to various analytical conditions such as time of exposure to the tank, the number of samples and the different rotation speed and temperature. Previous studies have demonstrated that biofouling and turbulence are also two main parameters affecting metal uptake. In the first case biofouling cause difficulties in the diffusional properties of cellulose acetate membrane (Sartorius). Biological growth on the surface of the membrane prevents the sorption of metals. However this depends mainly on water quality that passive samplers are exposed. Turbulence has been shown to provide higher uptake of analytes when rotation speed is high. Research by Bjorklund has demonstrated higher lead uptake when higher rotation speed is applied⁵. More research should be focus on the above parameters in order to gain more information about the way they act on passive samplers.

Conclusion

A calibration approach was performed in an effort to investigate passive samplers performance and evaluate concentration levels with the use of LA-ICP-MS. Performance was conducted with the exposure of samplers in controlled tank and filtering apparatus in order to obtain a thorough estimate of metal uptake by chelating and metal diffusion through cellulose acetate membranes and the main factors controlling them.

The performed analysis, although subject to a certain level of uncertainty due to the highly possibility of contamination during experimental analysis, led to some interesting results. Higher uptake of metal concentrations was recorded at the addition of high buffer concentration, revealing the impact of the buffer. In addition, high concentrations were measured in the filtrated standard solutions, indicating the weakness of both membranes to retain the metals significantly. Moreover initial experiments with application of higher concentration in the range of 100 ppb to 1ppm have revealed the reached capacity of membranes. This fact implies the disability of the passive sampler to be applied in highly contaminated aquatic systems. In addition short period of exposure in the tank has demonstrated less accuracy in the detection of lead. Current research at Chalmers University focus on the behaviour of lead in the concrete matrix.

With the exception of Zn, the R_s sampling rates were shown high values and thus higher uptake than those values provided by the conventional extraction method of ICP-MS. The observed exceedances of R_s values for Cd and Pb provide an indication that direct analysis of samplers with laser ablation system appear clear advantages.

However further investigations will need to reveal an overall assessment for these elements. Recommendations that arise at this final part of the thesis refer to a number of considerations. Longer period of exposure and a large number of passive samplers should be applied in the tank, in order to ensure more precision in the plotting of calibration curves and thus a better R_s values, revealing in this way the usefulness of LA-ICP-MS method. Further experiments will also need to determine how different environmental factors like temperature, turbulence and biofouling affect the diffusion rate of metals across the sampler.

Acknowledgement

I would like to thank my supervisor Sebastien Rauch for his guidance and fruitful discussions through this project. I would also like to thank Katarina Runeberg for her scientific advice and encouragement. Jesper Knutsson is also acknowledged for helping to perform the experiment in the laboratory.

Reference

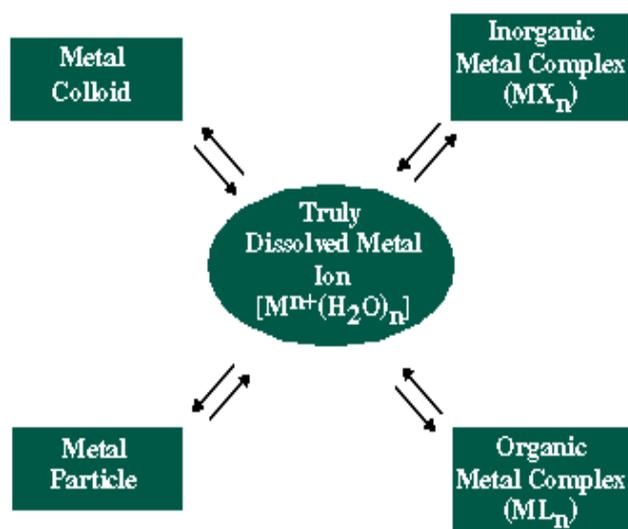
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Appendix

A



B

<u>Year</u>	<u>Passive sampling technique</u>	<u>Application</u>
1974	In situ dialysis	Theoretical description of in situ dialysis
1977	Equilibrium dialysis	Identification of colloidal metal species
1987	Dialysis with receiving resins	Bioavailable metal determination
1991	Diffusion equilibrium in thin film devices (DET)	Trace element speciation in natural waters and sediments
	Supported liquid membrane devices (SLM)	Cd, Co, Cu, Ni, Pb and Zn in natural waters
1994	Supported liquid membrane devices (SLM)	Cu speciation studies
1995	Diffusion gradient in thin film (DGT)	Determination of Cd, Cu, Fe and Mn in pore water
1997	Heavy metal chelation on a textile-based solid	Spiking samples with performance references compounds (PRC) in natural waters
2000	Diffusion-limitating sampling with solid receiving phase (today called Chemcatcher)	Quantification of organic and inorganic pollutants
	Passive integrative mercury sampler (PIMS)	Neutral mercury species

2002	Stabilised liquid membrane device (SLMD)	Controlled release of complexing agent thought LDPE bag, for metal sampling in natural waters
	Nafion-coating on diffusion membrane (Chemcatcher)	Prevention of biofouling
2003	Nylon bags and dialysis tubes with metal sordent	Determination of bioavailable Cd species in marine waters
2004	Permeation liquid membrane (PLM)	Cu and Pb speciation in natural waters