

Silje Marie Skogvold

# Development and properties of nontoxic solid electrodes for environmental surveillance

Application in automatic on site determination  
of metals in natural water and industrial solutions

Thesis for the degree of Philosophiae Doctor

Trondheim, February 2009

Norwegian University of Science and Technology  
Faculty of Natural Sciences and Technology  
Department of Chemistry

 **NTNU**  
Norwegian University of  
Science and Technology

**NTNU**

Norwegian University of Science and Technology

Thesis for the degree of Philosophiae Doctor

Faculty of Natural Sciences and Technology  
Department of Chemistry

© Silje Marie Skogvold

ISBN 978-82-471-1389-9 (printed ver.)  
ISBN 978-82-471-1390-5 (electronic ver.)  
ISSN 1503-8181

Doctoral theses at NTNU, 2009:11

Printed by NTNU-trykk

## Acknowledgements

The work presented in this doctoral thesis has been carried out at the Department of Chemistry at the Norwegian University of Science and Technology (NTNU) between 2003 and 2008. Financial support from the Norwegian Research Council is gratefully acknowledged.

First of all I would like to thank my supervisor Professor Øyvind Mikkelsen. Thank you for believing in me, for being positive and full of ideas, for the enormous amount of knowledge you possess, and for always having time for a chat even in the most hectic periods. Thanks also for all the interesting projects I have had the pleasure to be a part of, and for all the interesting and fun trips we have had together. I would also like to thank Professor Emeritus Knut H. Schröder for being my supervisor the first years of my ph.d period.

I have had some great years at the Department of Chemistry at NTNU, and I would like to thank all former and present members of the environmental and analytical chemistry group and other fellow students and employees at the Department of Chemistry. There are many people who deserve to be mentioned; Solveig, Øyvind, Yngvil, Beatriz, Ingvild, Elisabeth, Tonje, Kristine, Marion and Camilla are some of them. Thank you for many pleasant group meetings, lunches, coffee breaks and dinners. I would like to express my gratitude to Kristin who has been a very good friend since our first years at NTNU. Thanks for many (and long...) chats about all and nothing, for listening to all my worries and for giving me advices whenever I needed some. I would also like to thank Kristina for being a great “office mate”, for interesting discussions and for all help and good advices. Thanks to Syverin Lierhagen for ICP-MS measurements and Stein Almo for help with electronic equipment. I also thank Astrid Lund Ramstad for cooperation on the EXAFS project.

Making and designing my electrodes had not been possible without the extraordinary help from Ketil and the other guys in the workshop. Thank you for always being so helpful with designing different electrodes, cells, connections and whatever we might need. You also deserve credit for stepping up and fixing things in a rush whenever we needed it.

I have had the pleasure to visit two international research groups, the University of Lille and the University of Bath. I would like to thank Dr. Gabriel Billon, Ludovic Lesven and the rest of the group in Lille for welcoming me and for cooperation on several projects. A thank also goes to Dr. Toby Jenkins at the Department of Chemistry and his group at the University of Bath. The Faculty of science and technology, NTNU and the International section, NTNU deserve gratitude for funding these stays abroad. ESRF and NFR are also thanked for funding EXAFS studies in Grenoble.

I have also had the privilege to attend several international conferences which have given me valuable experience and motivation. Financial support from the analytical chemistry group at the Norwegian Chemical Society and The Faculty of science and

technology is greatly acknowledged. Thanks also to all co-authors on posters, lectures and papers. Your contribution is highly appreciated.

Finally, I would like to thank my family and friends for always supporting me. Thanks to Anne for being a good friend and for sharing my passion for RBK. I am forever grateful to Tomas for being my better half, for actually taking the time to read my thesis and for always putting things in perspective. Thank you for your ability to see solutions when I see only problems, for your valuable computer skills, and for always having faith in me. My beautiful daughter Thea deserves gratitude for bringing so much joy into my life, for waking me every morning with a smile and for always giving me something to look forward to. Thank you for giving me new perspectives and priorities in life and for making me want to be a better person.

Trondheim, October 2008

*Silje Marie Skogvold*

## List of papers included in the thesis

### **Paper I**

Silje M. Skogvold, Øyvind Mikkelsen and Knut H. Schröder. Electrochemical Properties and Application of Mixed Silver-Bismuth Electrodes. *Electroanalysis*, 17, 2005, 21, 1938-1944

### **Paper II**

Silje M. Skogvold and Øyvind Mikkelsen. Electrochemical properties and range of application of mixed gold bismuth electrodes. *Electroanalysis*, 20, 2008, 16, 1738-1747

### **Paper III**

Silje M. Skogvold, Øyvind Mikkelsen, Gabriel Billon, Cedric Garnier, Ludovic Lesven and Jean-Francois Barthe. Electrochemical properties of silver-copper alloy microelectrodes for use in voltammetric field apparatus. *Analytical and Bioanalytical Chemistry*, 2006, 384, 1567-1577

### **Paper IV**

Øyvind Mikkelsen, Silje M. Skogvold, Knut H. Schröder. Continuous Heavy Metal Monitoring System for Application in River and Seawater. *Electroanalysis*, 17, 2005, 5-6, 431-439

### **Paper V**

Øyvind Mikkelsen, Silje M. Skogvold, Kristina Strasunskiene, Knut H. Schröder, Camilla C. Johnsen, Marion Rydningen, Patrick Jonsson and Anders Jonsson. Automatic Voltammetric System for Continuous Trace Metal Monitoring in Various Environmental Samples. *Electroanalysis*, 19, 2007, 19-20, 2085-2092

### **Paper VI**

Øyvind Mikkelsen, Silje M. Skogvold, Knut H. Schröder, Magne Ivar Gjerde and Thor A. Aarhaug. Evaluations of solid electrodes for use in voltammetric monitoring of heavy metals in samples from metallurgical nickel industry. *Analytical and Bioanalytical Chemistry*, 2003, 377, 322-326

### **Paper VII**

Ludovic Lesven, Silje M. Skogvold, Øyvind Mikkelsen and Gabriel Billon. Determination of manganese in natural media by anodic stripping voltammetry using a rotating dental amalgam electrode. *Accepted by Electroanalysis*, September 2008.

### **Paper VIII**

Øyvind Mikkelsen, Silje M. Skogvold, Tonje B. Østebrød, Kristina Strasunskiene, Knut H. Schröder, Lillemor Claesson and Alasdair Skelton. Continuous monitoring of heavy metals in ground water as a tool for the detection and verification of earthquake precursors. *In preparation*.



## Summary

There is an increasing demand by citizens and environmental organisations for cleaner rivers and lakes, ground water and coastal beaches that has been evident for considerable time. Protection of water sources is now a prioritized area in many countries due to the European Water policy and the new EU Strategy for marine and maritime research. An important aspect of the water policies is on site environmental monitoring to ascertain the status of our water resources.

The interest in environmental surveillance has led to extensive research on methods and sensors suitable for automatic analyses of environmental toxicants like heavy metals. Several analytical methods are available for determination of metals in environmental and industrial solutions. Most frequently used are atomic absorption spectrometry (AAS) and inductively coupled plasma mass spectrometry (ICP-MS) which are laboratory systems reporting the total concentrations of metals. In contrast to automatic monitoring, frequently manual sampling for laboratory analysis is in many cases inconvenient, expensive and gives an undesired time lag from the appearance of an accidental or illegal pollutant to the detection of it. There are only a few methods available for automatic on site monitoring, and among these are dynamic electroanalytical techniques. Voltammetry has for instance shown to be suitable for continuous automatic monitoring, combining speed, sensitivity and low costs as well as providing the possibility of performing speciation studies. The choice of electrode material is very important in voltammetry, and several attempts have been made to find solid electrodes with properties desired for field analyses. The greatest challenge has been to find nontoxic electrode materials with high overvoltage towards the hydrogen evolution reaction (HER) and sufficient long-time stability, which has also been the aim of this thesis.

Nontoxic solid electrodes consisting of silver mixed or alloyed with a metal possessing high overpotential towards HER were introduced in 2000. In addition to good sensitivity for several metals, a significant increase in the overpotential towards HER was obtained for a solid silver amalgam electrode and a mixed silver-bismuth electrode. These promising results have made the basis for the work done in this thesis, which in brief outline has been development and investigation of some new electrode materials in addition to further studies on the use of the solid silver amalgam electrode in various water solutions.

The electrochemical properties of mixed silver bismuth electrodes have been investigated with focus on hydrogen overvoltage, sensitivity for selected metals, and use in automatic monitoring equipment. Increased overpotential towards the hydrogen evolution reaction was found as a result of increasing amount of bismuth added to the silver. The increased cathodic potential window was demonstrated in acid solution where zinc was successfully detected on the mixed electrodes, but failed on pure silver electrodes. Zinc, cadmium and lead were detected in the low  $\mu\text{g/l}$  range, and measurements in polluted river water showed sufficient long-time stability for use in automatic field equipment.

Another interesting electrode material for use in the positive and low negative potential area is mixtures of gold and bismuth. Electrodes based on gold have proved to be especially useful for the determination of metals in the positive potential area, like mercury and copper. By adding small amounts of bismuth, an electrode with similar sensitivities as bare gold, but with higher hydrogen overvoltage and better long-time stability, was obtained. Increased overpotential towards the hydrogen evolution reaction (HER) was found as a function of increased bismuth content in the gold-bismuth mixture. The analytical use and stability over time for these electrodes were demonstrated by detection of copper and mercury in  $\text{NH}_4\text{Cl}$ , purified scrubbing water and polluted river water.

Microelectrodes are interesting as electrodes in environmental monitoring due to many advantageous properties. Semi-microelectrodes of silver-copper alloys (silver 830 and silver 925) were therefore evaluated for use in voltammetric analyses. Increased overpotential towards the hydrogen evolution reaction (HER) was found as a function of increased amount of copper in the alloy. Low concentrations of zinc, cadmium and lead were measured in ultrapure water with good linearity. The alloy electrodes were also found to be sensitive to nitrate, and nickel was determined by complexation with dimethylglyoxime. The use of an AgCu electrode was tested in river water by installation in an automatic voltammetric system for determination of zinc and lead in the polluted river *Deûle* in France.

Continuous monitoring of metals in industrial solutions is often performed using automatic equipment with a dropping liquid mercury electrode. Due to restrictions regarding the use of mercury, a replacement of mercury with other nontoxic electrode materials is required. Solid electrode materials were therefore tested for detection of metals in process water and wastewater from metallurgical nickel industry. A solid silver amalgam electrode was successfully used for determination of zinc as intermetallic Ni-Zn compound. A silver-bismuth mixed electrode was used for simultaneous detection of nickel and cobalt, while analyses of lead in the  $\mu\text{g/l}$  range in nickel-plating solution were performed with a bare silver electrode. These electrodes were tested in a new commercial automatic on-line system, and the results were found to be in agreement with an older mercury drop system. The results indicate that voltammetric detection of heavy metals in process water from metallurgical nickel industry with use of solid electrodes may successfully replace mercury-based systems.

The use of solid silver amalgam electrodes have been evaluated in connection with an automatic trace metal monitoring station. The system is fully automated and has been mounted in four different geological sites for continuous monitoring of electroreducible concentrations of iron, zinc and copper. The four sites represent different water solutions like polluted river water, coastal seawater, drainage water and waste water. Manual sampling with determination by ICP-MS was performed frequently for comparison and quality assurance. The system was maintained twice a month in river water, and once or twice a week when used in waste water. The presented voltammetric system fulfils the requirements for automatic and remote monitoring of heavy metals in waters. The use of solid silver amalgam as electrode material avoids the use of liquid mercury or mercury salts in voltammetric analyses, and thus offers a nontoxic electrode



system which can be used in field equipment. The difference in the sample matrixes and locations demonstrates the wide application range for this system. The solid silver amalgam electrode has shown good sensitivity for several metals and sufficiently long-time measuring stability without the need for frequent manual maintenance.

An interesting use of the automatic trace metal station was also demonstrated by determination of metals in ground water on Iceland. In 2002 a theory suggesting metals as earthquake precursors in basaltic rocks was introduced. When monitoring metals in ground water, the automatic trace metal station reported significant changes in pH and electrolabile amounts of zinc, iron and copper 7-8 days before an earthquake. These changes in concentration lasted until the occurrence of the earthquake. The results confirm the importance of automatic real time monitoring and show that the automatic trace metal station in combination with a solid silver amalgam electrode is suitable for long-time surveillance without the need for frequent manual maintenance.

The use of a solid silver amalgam electrode for determination of manganese in natural water has also been demonstrated. Manganese is normally present in very low concentrations in oxygenated freshwater, but the concentrations may increase drastically when sediment pore waters are mixed with the overlaying water due to high concentrations in pore water. Detection of manganese by voltammetry has been difficult due to its very negative redoxpotential on mercury electrodes, but this work shows how it can be successfully detected with the solid silver amalgam electrode. A well-defined peak for the oxidation of Mn(0) to Mn(II) was observed around -1.45 V in NH<sub>4</sub>Cl solution. The method was demonstrated for on-line detection of manganese in a contaminated river, and increased manganese concentration was found as a function of boat traffic on the river.

The work presented in this thesis shows that the introduction of solid silver amalgams and mixed electrodes has created new possibilities for continuous trace metal monitoring. The combination of nontoxic materials, increased cathodic potential window, better long-time stability and good sensitivity for several metals makes these electrodes suitable for use in automatic field equipment.



## Table of contents

<b>ACKNOWLEDGEMENTS</b> .....	<b>1</b>
<b>LIST OF PAPERS INCLUDED IN THE THESIS</b> .....	<b>3</b>
<b>SUMMARY</b> .....	<b>5</b>
<b>1 INTRODUCTION</b> .....	<b>11</b>
1.1 VOLTAMMETRY .....	13
1.2 ELECTRODE MATERIALS.....	14
1.2.1 <i>The hydrogen evolution reaction</i> .....	14
1.2.2 <i>Mercury based electrodes</i> .....	15
1.2.3 <i>Alternative electrode materials</i> .....	17
1.2.4 <i>Other factors influencing the electrode properties</i> .....	22
1.3 PRACTICAL USE IN ENVIRONMENTAL AND INDUSTRIAL SOLUTIONS .....	23
1.4 SURFACE STUDIES .....	25
<b>2 SUMMARY OF THE PAPERS INCLUDED IN THE THESIS</b> .....	<b>27</b>
2.1 PAPER I, II AND III .....	27
2.2 PAPER IV .....	28
2.3 PAPER V AND VI.....	29
2.4 PAPER VII.....	30
2.5 PAPER VIII.....	30
<b>3 CONCLUSION</b> .....	<b>32</b>
<b>4 FUTURE ASPECTS</b> .....	<b>33</b>
<b>5 REFERENCES</b> .....	<b>35</b>
<b>PAPER I - VIII</b> .....	<b>45</b>



## 1 Introduction

There is an increasing demand by citizens and environmental organisations for cleaner rivers and lakes, ground water and coastal beaches that has been evident for considerable time. This fact was confirmed by a representative opinion poll carried out by the EU where nearly half of the respondents reported to be worried about water pollution when asked about their main environmental issues. Protection of water sources like rivers and ground water is now a prioritized area in many countries due to the European Water policy (European Commission 2007). A new EU Strategy for marine and maritime research has recently also been adopted supporting the importance of securing an environmental and sustainable use of seas and oceans (European Commission 2008). An important aspect of the water policies is on site<sup>1</sup> environmental monitoring to ascertain the status of our water resources, and it is necessary to establish technology for surveillance of marine areas, rivers, ground water and inland surface waters. To avoid increasing pollution of water resources it is also important to establish monitoring equipment for real time surveillance of for instance water outlets from industry and waste water plants, and run-off from old mining areas and dumpsites. In water quality control, continuous surveillance is necessary to maintain the level of toxic compounds within legally demanded limits. Automatic monitoring of trace metals is also preferable for most practical situations, for example in industrial process control and warning systems where rapid measurements are essential if a corrective action has to be made quickly (Wang et al. 1999). Companies in the industrial sector may also gain economically from rapid automatic monitoring of their process solutions. Real time results make it possible to secure the product quality, and control the amount of chemicals needed in connection to waste water treatment.

In addition to organic toxicants, heavy metals may cause severe damage to organisms in the aquatic environment and in the nearby area. Heavy metal determination has traditionally been carried out in the laboratory, in connection with time-consuming sampling, transportation, preparation and storage steps. In addition to the time saved, on site determination also reduce errors due to contamination, losses, and equilibrium changes associated with the sample collection, and can greatly reduce the cost of metal analysis (Wang et al. 1999).

When monitoring metals for environmental reasons it is important to take into account that the toxicity of a specific metal or compound is strongly connected to its binding conditions, and thus its bioavailability. Measuring the total metal concentration does not give sufficient information to valuate the consequences for the environment, and it is therefore necessary to measure the specific species present. Studies on the toxicity of heavy metals to fish and other aquatic organisms have shown that the toxicity is mainly related to the activity of the free metal ions and not the total metal concentration (Turner

---

<sup>1</sup> Automatic monitoring may be in situ, on-site, on-line or at-line, but what the different terms imply may differ. In this thesis the terms in situ is used for measurements directly in the test solution and on-line is used for measurements where a sample is automatically collected and analysed on the site. On site determination include both in situ and on-line.

1984). This is of course a general statement which has many exceptions. The kinetic also plays an essential role determining the toxicity of a specie. Species in the labile phase undergoing fast reactions is easily take up by organisms and may lead to an immediate hazardous effect. Other species either difficultly soluble or bound to organic complexes may not constitute an immediate hazard, but present a potential toxicity that can be released by changes in the physical or chemical environment. The labile concentrations are therefore the most important to monitor for environmental reasons, but the optimal solution would be determination of both the labile and the total concentration.

The most used techniques for metal determination are spectroscopic techniques like atomic absorption spectroscopy (AAS) and inductively coupled plasma mass spectroscopy (ICP-MS) (Douglas et al. 1985; Janusa et al. 2002). These techniques have the advantage of being very sensitive and can be used to determine a wide variety of elements. The major drawbacks are however very complicated equipment, high costs and the fact that they only determine the total concentration. Speciation analysis can be done by coupling them with extraction and separation procedures, but this complicates the analysis and increases the risk of contamination, modifications of the sample and the costs (Buffle et al. 2005). Electrochemical methods are widely used in metal determination, and are also among the few methods that meet the many criteria demanded in automatic on site determination. A combination of high sensitivity, minimum sample manipulation, long-time stability, low maintenance, multicomponent analysis, low cost, low energy consumption and preferably the possibility of miniaturization are some of the criteria mentioned (Buffle et al. 2000). Of the electroanalytical methods, ion-selective electrodes (ISE) would be most convenient for automatic surveillance as these give a continuous display of the concentrations. However, ISEs are not sufficiently sensitive, although recent work has succeeded in lowering the detection limits for several metals (Bakker et al. 2005). It is still likely that organic complexation of metals will make it difficult to detect trace metal concentrations in natural waters with ion-selective electrodes. Voltammetry on the other hand has shown to be suitable for on site metal detection. It is a fast and easy analytical technique to carry out, the instrument is inexpensive and the operating costs are low. The portable instrumentation and low power demands of voltammetric analysis satisfy many of the requirements for on-line and in situ measurements. The voltammetric method is used to determine a variety of both organic and inorganic species, but this thesis will focus on the determination of metals.

Voltammetry has the advantage of reporting the electrolabile content, which includes free aqua ions, inorganic complexes and readily dissociable organic complexes and any ions released from complexes during analysis. This makes it possible to determine the chemical speciation of metals directly in the sample. The toxic fraction of a metal and the electrolabile fraction have often been named equal, but studies comparing these two have reported various results (Florence et al. 1992; Young et al. 1979). Florence et al. found that the direct electrolabile species strongly underestimate the toxic fraction, but by using media exchange the results were similar. By combining voltammetric determination with other methods like ICP-MS or sampling probes like DGT (diffusion gradient in thin films) in combination with ICP-MS it is possible to get important

information about the distribution of a compounds species, and thus both the acute and potential toxicity. The use of different techniques is also valuable as quality assurance.

## 1.1 Voltammetry

Voltammetry is an electroanalytical technique where quantitative or qualitative information of a specie of interest is achieved by measuring current as a function of potential. There are different modulation techniques used in water analysis but the most important are anodic stripping voltammetry (ASV) and adsorptive stripping voltammetry (AdSV). Other stripping techniques are cathodic stripping voltammetry (CSV) and potentiometric stripping analysis (PSA). Voltammetric techniques also include linear sweep voltammetry (LSV), differential pulse voltammetry (DPV), and square wave voltammetry (SWV) which are fast but not very sensitive techniques. Cyclic voltammetry (CV) is used to study electrode processes and finding optimum analytical conditions since it is not sensitive enough for determination of trace metals in natural waters (Buffle et al. 2000).

The invention of stripping analysis led voltammetry to be among the most popular techniques for the determination of trace metals (Florence 1984). The remarkable sensitivity of the stripping techniques is attributed to a preconcentration step where the target metals are accumulated on or in the working electrode. The preconcentration can be done either by adsorption or by reduction and deposition on (or in) the electrode material (Buffle et al. 2000). The quantification is then done by a stripping step where the metals accumulated are oxidised and the resulting current is recorded as function of applied potential.

The properties and concentration of the analyte influences the choice of the voltammetric method and the electrode material. Anodic stripping voltammetry is the most common stripping technique used to determine concentrations of trace metals. Cathodic stripping voltammetry is said to be the mirror image of anodic stripping voltammetry. The only difference between those is the common use of the methods, as the properties of the accumulated substance determine the direction of the electrode polarization. Anodic polarization is applied to amalgams, metal deposits and some adsorbed organic compounds that are oxidized within the working window of the electrode. Cathodic polarization is suitable for oxides, mercuric and mercurous salts, adsorbed metal ion complexes and reducible organic molecules (Scholz 2002). Adsorptive stripping voltammetry is normally used to determine organic compounds, but is also used in analyses of inorganic cations by complexation with surface-active complexing agents (Dewald 1996). The modulation used in the stripping step may also vary with different analytes, and the most common ones are differential pulse which has the most rigorously discriminating capacitive current and square wave which is the fastest stripping technique (Scholz 2002).

Voltammetry analyses determine, as mentioned in the introduction, the electrolabile concentration, and this part is in many cases similar to the most toxic amount. Speciation studies have been one of the most important applications of stripping analysis in water analyses (Florence 1986). Anodic stripping voltammetry may for

instance be used to detect the toxic species arsenic(III) specifically (Salaun et al. 2007) and pseudopolarography can be used to determine the stability of metal complexes by a systematic variation of the deposition potential (Croot et al. 1999). Different fractions including the total metal concentration may also be detected through some simple pretreatment of the sample.

Although voltammetry already in the seventies was used by Zirino and co-workers in automated instruments for determination of metals in seawater (Zirino et al. 1978), little attention has been given to development of in situ monitoring equipment until the last decade. One of the major drawbacks with in situ voltammetric monitoring has been the lack of suitable reliable sensors for long-time monitoring (Buffle et al. 2000). A result of the increasing focus on automatic on site monitoring is the proposals of a variety of more or less successful equipment and sensors. An overview of both traditional and new alternative electrode materials will be given in chapter 1.2, and a short introduction to different proposed on site and on-line equipment will be given in chapter 1.3.

## 1.2 Electrode materials

The working electrode material is of crucial importance in voltammetric analyses. The choice of electrode material determines not only which species that may be measured, but also the degree of interferences, additional chemicals needed and maintenance. Important working electrode properties include a wide potential window, high signal-to-noise ratio, high electrical conductivity and surface reproducibility. Furthermore, electrode materials should be easy to produce, be chemically stable, have a high sensitivity towards several metals and give a reproducible response (Wang 2006). The growing demand for continuous on-line monitoring of trace metals has also led to additional requirements such as uncomplicated scan procedures, long-time stability, minor maintenance and low toxicity (Skogvold et al. 2006).

### 1.2.1 *The hydrogen evolution reaction*

One of the greatest challenges dealing with electrode materials has been the overvoltage towards the hydrogen evolution reaction (HER). The hydrogen evolution reaction limits the usable cathodic potential area of an electrode, and limits the range of application. The complicated process leading to the measurable hydrogen overpotential at metal electrode surfaces has challenged electrochemists for more than a century, and famous scientists like Tafel, Heyrovsky and Volmer are inseparably connected with the important field of electrode kinetic (Bockris et al. 1993).

Mechanistic studies of the hydrogen evolution reaction have suggested two pathways for the reaction. The first step, where protons discharge onto the surface sites (Volmer reaction), is similar for both pathways. In the second step adsorbed H atoms may diffuse towards each other across the electrode surface and undergo a chemical reaction to form  $H_2(g)$  (Tafel reaction), or a second proton may discharge on the top of the adsorbed H forming  $H_2(g)$  (Heyrovsky reaction) (Conway 1999).



The kinetics of the hydrogen evolution reaction have been characterized by widely differing values of the exchange current density,  $i_0$ , and by the extent of H coverage at e.g. Hg, Ni or Pt cathodes (Butler 1936; Conway et al. 1956; Conway et al. 1992). Empirical relations between metal properties and the exchange current densities have been investigated by Ruetschi and Delahay (Ruetschi et al. 1955). Major further advances were made by Parsons (Parsons 1958), Conway and Bockris (Conway et al. 1957) during the fifties and sixties. This work showed that "volcano-type" curves are formed when  $\log i_0$  values for a series of metals are plotted against the standard Gibbs energy of chemisorption of H. This relation was a particular important contribution, and through this work and parallel work by Gerischer (Gerischer 1958), the catalytic activity of different single metals for the Volmer-Tafel and the Volmer-Heyrovsky mechanisms were correlated to the strength of chemisorbed hydrogen.

The results obtained in these earlier studies made the foundation for a lot of work done in the same area later on. Understanding the hydrogen evolution reaction is an important aspect in understanding the properties of electrode materials, and thus gaining information on how to develop new electrode materials with higher hydrogen overvoltage.

In the early days of electrochemistry most work was done on solid electrodes like platinum and gold, but when polarography was introduced in 1922 by Heyrovsky, the liquid mercury electrode soon became the dominating electrode material due to its unique properties (Heyrovský et al. 1965). Of special importance was its high hydrogen overvoltage. During the last decade several new solid and film electrodes have been developed in order to replace liquid mercury. This has provided a wide selection of electrode materials which will be presented in the next chapter. Some of the different forms, sizes and geometries used will also be mentioned.

### 1.2.2 Mercury based electrodes

Liquid mercury has for many decades been the dominating electrode material in voltammetric analysis. This is mainly due to its high overvoltage towards the hydrogen evolution reaction that extends the cathodic working window significantly and makes it possible to measure compounds in the very negative potential area. Liquid mercury also possesses a smooth surface which is reproducible and can easily be renewed by forming a new mercury drop (Wang 2006). The formation of liquid metal amalgams during the reduction process also prevents the formation of intermetallic compounds and contributes to well defined voltammetric curves. Well known drawbacks with the mercury drop electrode are the easy oxidation of mercury occurring from about 0 V which makes it unusable for determination of metals in the anodic potential area, problems related to use in automatic systems and the toxicity of mercury (Berlin et al. 2007).

Some of the most frequently used mercury electrodes are the dropping mercury electrode (DME) used in polarography and the hanging mercury drop electrode (HMDE). Both methods require large amounts of liquid mercury, and due to the toxicity of mercury, alternative electrodes were developed aimed at reducing the amount of

mercury used. Some of these are the dilute amalgam electrodes, amalgam film electrodes and mercury meniscus electrodes. In 1947 Airey mentioned a mercury film electrode (MFE). He observed that the negative potential range for a platinum electrode and a silver electrode was extended by plating a mercury film onto the surfaces of the wires (Airey 1947). Mercury film electrodes, consisting of a very thin mercury layer or many small mercury droplets on a conducting surface, are now widely used in stripping analysis. In addition to platinum and silver, also other metals have been used as substrate for mercury film electrodes, including iridium (Devitre et al. 1991), gold, nickel (Yoshida 1981) and carbon in different forms (Monterroso et al. 2004; Svancara et al. 1994). MFE's are often used in situ measurements, and extensive research in this area have been performed by Luther III and co-workers, using solid gold microelectrodes plated with mercury (Brendel et al. 1995; Luther et al. 1998), and by Buffle and his group using a micro array system with an iridium matrix plated with mercury (Tercier et al. 1998; Tercier et al. 1995). There are different ways of making a mercury film electrode, and one is electroplating of the film from a solution containing mercury salts. Other methods consist of repeatedly dipping metal electrodes directly in liquid mercury (Novotny et al. 2000; Yosypchuk et al. 2002a), or mixing mercury salts with other electrode materials to generate a mercury film (Khoo et al. 2002). A general problem with deposition of mercury onto metal substrates is the partly formation of amalgams that decreases the stability over time, and a lot of research has been done to prevent this problem (Bas et al. 2002). All these electrodes greatly reduce the amount of mercury used, but the toxicity of the electrodes is not eliminated.

Mikkelsen and Schröder introduced in 2000 a solid silver amalgam electrode based on dental amalgam (Mikkelsen et al. 2000a; Mikkelsen et al. 2000b) similar to the one used in dental fillings. In this electrode silver powder and liquid mercury is mixed in a 1:1 ratio, making a homogenous stable alloy,  $\text{Ag}_2\text{Hg}_3$ , with silver in excess, which is nontoxic for analytical purposes. The electrode material is made with a well established technique from dental practice and advanced equipment for preparation of amalgams which makes the amalgamation between silver and mercury particularly strong and stable (Mikkelsen et al. 2003a). The solid silver amalgam electrode acts as a silver electrode, with good sensitivity to several metals, and with increased hydrogen overvoltage. The idea behind the introduction of the dental amalgam electrode was to overcome the problem with the stability observed on mercury film electrodes, by making a real solid alloy of mercury and a second metal. The second metal could be any metal, however silver is especially favourable since silver it self has a relatively high overpotential towards HER, and oxidizes close to mercury giving a maximum working window also in the positive direction. The solid silver amalgam electrode has successfully been implemented in field apparatus for on-line monitoring of metals in natural water and waste water (Mikkelsen et al. 2005; Mikkelsen et al. 2003b; Mikkelsen et al. 2006; Mikkelsen et al. 2007).

The earlier mentioned film electrodes made by amalgamating soft metal powder by dipping it in liquid mercury, were later proposed as solid metal amalgam electrodes (MeSAE). Such electrodes have been made with different metal powder (Ag, Cu, Au, Ir) and are often modified either with mercury to form mercury films or meniscus or with organic reagents, enzymes, polymers or oxides (Yosypchuk et al. 2002b).

There are now restrictions regarding disposal of mercury waste and the general handling of mercury in the laboratory as well as in field equipment. The concerns about mercury toxicity combined with an increased focus on automatic field monitoring have led to an extensive search for new mercury free electrode materials suitable for replacing mercury in voltammetric analysis.

### *1.2.3 Alternative electrode materials*

Several new electrode materials for use in analytical voltammetry have recently been reported, including alternative liquid metal electrodes like the hanging galinstan drop electrode, carbon electrodes, bare solid metal electrodes and film electrodes. The hanging galinstan drop electrode (Surmann et al. 2005) represents an interesting alternative to the mercury electrode for laboratory use, but the galinstan material consisting of an eutectic alloy of gallium, indium, and tin, easily clogs, wet and adhere to glass capillary and other materials, and is therefore very difficult to include in field apparatus.

Solid electrodes have been used for several decades and serves as interesting alternatives for liquid mercury, especially for use in automatic field apparatus. Unfortunately, most solid metallic and carbon-based electrodes have low overvoltage towards the hydrogen evolution reaction (HER) which significantly limits the cathodic potential window. However, solid electrodes have successfully been used to determine metals in the anodic potential area where mercury can not be used since solid electrodes in general have a wide anodic potential window. A challenge related to use of solid electrodes is to understand the conditions on the surface and how they affect the electrode processes. In contrast to the mercury drop electrode it is difficult to produce a new clean and reproducible surface on solid electrodes (Adams 1969). The solution-electrode interface is a very important part of the sensing system and long-term stability of the physical and chemical structure of this interface is important to achieve in routine environmental monitoring. Electrode surface fouling by adsorption or oxidation are thus major problems in voltammetric analysis (Buffle et al. 2000). One solution to this problem is chemical cleaning by applying a large negative potential to the working electrode.

An important aspect in the search for new environmental electrodes has been to find ways to extend the potential windows of the already known electrode materials in addition to proposals of new materials. This chapter will give an overview of different carbon and metal electrodes that are used in voltammetric analyses with focus on electrodes suitable for on-line automatic analysis in the field.

### **Carbon based electrode materials**

Carbon has been a widely used electrode materials since Michael Faraday used charcoal electrodes, and has also been extensively studied for use as working electrode both with and without modification (McCreery 1991). Carbon electrodes in general have a broad

potential window and low background current. They are chemical inert, have a rich surface chemistry and are suitable for various sensing and detection applications. However, electron transfer rates observed at carbon electrodes are often slower than those found at metal electrodes (Wang 2006). Several pretreatment methods have been proposed to increase the electron transfer rate at carbon electrodes, and the analytical performance of the electrode is strongly affected by the chosen pretreatment procedure as well as the type of carbon used. Carbon based electrodes are in general inexpensive and are available in a variety of forms. They can be divided in heterogeneous or homogenous materials, and the most popular forms are glassy carbon, carbon paste, carbon fibre, graphite, screen-printed carbon strips, carbon films or other composites. Glassy carbon electrodes (GCE) are the most popular carbon material in metal analysis, but due to the low sensitivity obtained with unmodified GCE the surface is often modified with metals, organic substance, polymers or other modifiers (Stozhko et al. 2008a). A review of several different modifiers is given by Stozhko et. al. GC is widely used as substrate for mercury film electrodes, but also serves as substrate for other materials like gold (Svancara et al. 1997), platinum (Wang et al. 2006a), antimony (Hocevar et al. 2007b) and bismuth (Wang et al. 2000). Some of the problems with use of GCE are degradation of the modified surface, distortion of peak shape and the emergence of additional peaks, as observed with the mercury film electrode (Petrovic et al. 1997). A great variety of cleaning and preparation procedures are also used to make the GCE surface reproducible (Stozhko et al. 2008a). Carbon paste is another carbon material well used for metal determination. Carbon paste electrodes have a well-developed surface with a high adsorptivity for various substances, and are therefore most used as modified electrodes. The modifiers are various organic substances that are either immobilized on the surface or directly mixed with the paste, or metals and metal oxides. The high adsorptivity can also be used for adsorptive accumulation of substances to be measured (Stozhko et al. 2008a).

The progress in modern engineering has led to development of new carbon based materials with assigned properties including different graphites, nanotubes, carbon fibre electrodes, microelectrodes and boron doped diamonds. Especially boron doped diamond (BDD) has many favourable properties, including a very broad potential window, and has opened up new opportunities for work under extreme conditions (Compton et al. 2003; Wang 2006). A boron doped diamond electrode has been used for determination of several metals and compared with a mercury film GCE with good results, though the sensitivity was a bit lower (McGaw et al. 2006). One problem with boron doped diamond electrodes is that they are very difficult to make for ordinary research laboratories.

In laboratory analyses modified carbon based electrodes have shown to be useful for determination of a variety of different substances, especially in the anodic potential area. However, in automatic on-site monitoring there are other requirements that need to be fulfilled. Modifications of carbon surfaces require additional reagents, and complex scan procedures have to be used in order to get an active and stable surface. Other challenges related to carbon electrodes are how to make the modified surface of the electrode reproducible and thus the response stable, how to avoid adsorption of organic substances and formation of passive films especially in real samples (Stozhko et al.

2008b). The GC electrode also need mechanical conditioning and regeneration of the surfaces and CPE's have a complicated preparation process and a short self-life (Brainina et al. 2000). Carbon electrodes in general (except for BDD) also have a low hydrogen overvoltage and are therefore considered an addition to mercury electrodes rather than a substitute.

### **Metal based electrode materials**

In addition to carbon electrodes, electrodes based on metals have been widely used to determine metals with redox activity in the anodic potential area. As mentioned earlier, solid electrodes were already used in the beginning of the 19<sup>th</sup> century before the invention of polarography. A lot of research was also done later to increase the understanding of electrochemical processes on solid surfaces in comparison to reactions on the liquid mercury surface. Solid electrodes have now experienced a new era with the restrictions related to use of mercury, and with the need for automatic on site monitoring.

A wide variety of noble metals have been used as electrode materials, due to their relatively inert surface and wide anodic potential area. Platinum (Hernandez et al. 1996) and gold (Bonfil 2000) are most used in voltammetric analysis, but other materials tested or used are silver (Bonfil 2002b), iridium (Cox et al. 1989), palladium (Wang et al. 2006b), bismuth (Wang 2005; Wang et al. 2000), copper (Wang et al. 2006b), nickel (Yuan et al. 2001), lead (Shao et al. 2008), aluminium (Tu et al. 2008) and antimony (Hocevar et al. 2007b). These metals have either been used as bare metal electrodes, film electrodes or as substrates for film electrodes. Platinum, gold and silver have been used as bare electrodes in determination of both organic compounds and metals. Silver and gold electrodes have shown to be useful for determination of lead and cadmium by subtractive ASV, and gold electrodes are also very sensitive to copper and mercury (Bonfil 2000; 2002a; b). An alloy of gold and silver has also been tested, but not many advantages over the pure metal electrodes were found (Bonfil et al. 2003). Platinum electrodes are mostly used for determination of organic compounds, and alloys of platinum and gold have also been investigated (Moller et al. 2004). One drawback with solid electrodes consisting of bare metal is the long-time stability, which is insufficient for continuous on-line monitoring due to a relatively fast passivation of the surface (Grubac et al. 2004; Lee et al. 2001). Passivation may occur by adsorption of hydrogen, formation of oxide films or by adsorption of surface active compounds. A challenge has therefore been surface renewal, which for in situ implementation is only possible by electrochemical or chemical cleaning (Buffle et al. 2000).

Several film electrodes have been suggested as a solution to surface renewal. By applying a new film before every measurement the passivation problem is partly overcome, but the reproducibility of the film is insufficient for automatic measurements in field equipment. Ag, Au and Pt along with iridium have all been used as substrates for mercury film electrodes. Other film electrodes are bismuth film electrodes (Hutton et al. 2001; Kefala et al. 2003; Vytras et al. 2002) and gold film electrodes (Svancara et al. 1997) on different substrates. Film electrodes of antimony have also been suggested as an alternative to mercury due to its high hydrogen overvoltage (Hocevar et al. 2007b),

but since antimony itself is toxic it is not really a better alternative. There is also a widespread use of film electrodes as modified electrodes by application of various polymers and nafion films, but the implementation of these for in situ determination is complex, and the reproducibility and long-time stability is not good enough.

Another drawback with most solid electrodes are the before mentioned low overvoltage towards the hydrogen evolution reaction, that makes them unsuitable for use in the cathodic potential area. There are solid metals that possess high hydrogen overvoltage, but unfortunately most of these metals (lead, mercury, thallium, cadmium, antimony and bismuth) are considered highly toxic. Bismuth is in this relation unique due to its high overvoltage for HER and its very low toxicity. This combination has made bismuth very promising as an electrode material in both film and bulk electrodes (Hutton et al. 2001; Hutton et al. 2004; Pauliukaite et al. 2004; Wang 2005; Wang et al. 2000).

#### *Bismuth based electrodes*

Considerable attention has been given to bismuth based electrodes since preliminary studies indicated that they can be favourably compared with mercury in stripping analysis (Hocevar et al. 2002; Wang et al. 2001b). Electrodes based on bismuth have been used for determination of several trace metals in anodic stripping voltammetry (ASV) and adsorptive stripping voltammetry (AdSV) in a variety of environmental samples, biological samples, food products and industrial samples (Kokkinos et al. 2008). The unique behaviour of bismuth electrodes is related to the formation of low-temperature alloys. Bismuth forms binary- or multicomponent alloys with several heavy metals like cadmium, lead, thallium and antimony that makes the nucleation process during the deposition easier (Wang 2005).

The bismuth film electrode was introduced in 2000 (Wang et al. 2000), and is still the most widely used bismuth-based electrode. The bismuth films consist of individual metal crystallites with surface morphology depending on the plating conditions. Electroplating of the film on glassy carbon, carbon paste or other carbon substrates is the most used formation method (Kokkinos et al. 2008). Microelectrodes coated with bismuth have also been made using carbon fibres/disks or gold and platinum wires/disks (Baldo et al. 2003; Baldrianova et al. 2006; Hocevar et al. 2002; Wang et al. 2000). Variable plating conditions have been reported, and the composition of the plating solution and the pH is important factors that affect the quality of the bismuth film (Kokkinos et al. 2008). For automatic in situ determination, and thus in situ formation of the film, it will not be possible to get a reproducible film and it is also necessary to add several reagents.

A polycrystalline bulk ring-disk bismuth electrode was in 2002 proposed as an alternative to mercury (Pauliukaite et al. 2004). Due to diffusion of metals in the bulk wider peaks are produced, but the advantage is a new surface by polishing and that no electroplating is necessary. Other ways to produce bismuth bulk electrodes is mixing Bi powder with paste (Buckova et al. 2005; Hocevar et al. 2005). Bismuth electrodes have also been used modified with polymers to avoid undesired adsorption of, and fouling by, surface active compounds (Wang et al. 2001a).

The cathodic limit of bismuth electrodes are similar to the cathodic limit of mercury electrodes under the same conditions, but the anodic limit is more negative resulting in a more narrow potential window (Svancara et al. 2003). Bismuth is however not as suitable as liquid mercury in acidic solutions. Interferences reported for bismuth electrodes are adsorption of surface active compounds, formation of intermetallic compounds and mechanical degradation of the bismuth film. Even so, bismuth is still found to have the potential to replace mercury due to its many attractive properties like being environmental friendly, being partly insensitive to dissolved oxygen, good sensitivity for several metals, the high hydrogen overvoltage and the fact that bismuth is solid at room temperature (Kokkinos et al. 2008). Reviews on bismuth electrodes are given by Wang (2005) and Kokkinos and Economou (2008).

#### *Mixed metal electrodes*

Another very interesting use of bismuth in electrode materials was introduced by Mikkelsen and Schröder when they demonstrated that the overpotential for HER of noble metals can be altered significantly by adding a second compound which possesses high overvoltage for the hydrogen evolution reaction (Mikkelsen et al. 2000b). By alloying or mixing small amounts of e.g. mercury, bismuth or copper with silver, the cathodic potential window was significantly extended compared to the bare silver electrode (Mikkelsen et al. 2000a; Skogvold et al. 2006; Skogvold et al. 2005). The mixed silver bismuth electrode was introduced as an attempt to increase the long-time stability as well as the hydrogen overvoltage for solid electrodes. Adding from 0 to 15% bismuth to the silver, the hydrogen formation reaction was shifted from -0.3 V to -1.0 V (Skogvold et al. 2005). As for the solid silver amalgam electrodes described in chapter 1.2.2, the mixed silver bismuth electrodes act as silver electrodes but with higher hydrogen overvoltage. In addition to the increased overpotential towards HER, the mixed electrodes are passivated slower than the bare metals, and they have an acceptable low toxicity to be allowed in field equipment. The solid silver amalgam electrodes and mixed silver bismuth electrodes can however not be used to determine metals in the positive potential region due to the oxidation of silver. In 2007 an electrode based on bismuth and gold was suggested for use in the positive potential area as well as in the low cathodic potential area (Skogvold et al. 2008). Electrodes based on gold have proved to be especially useful for the determination of metals in the positive potential area, like mercury and copper (Bonfil 2000; Bonfil et al. 2000). By adding small amounts of bismuth an electrode with similar sensitivities as bare gold but with higher hydrogen overvoltage and better long-time stability was obtained. Bismuth film and bulk electrodes cannot be used in the anodic area due to oxidation of bismuth. The small amounts of bismuth added in the mixed electrodes do not limit the anodic potential area as it gives a bismuth peak that is stable and can easily be removed by subtractive ASV. Limitations of the electrode properties due to formation of oxides on bismuth have not been observed either. Even if bismuth present on the surface is passivated by oxide formation, the total effect on the hydrogen overvoltage is still present. This may be due to physical effects as described later.

Alloy electrodes are also suitable as microelectrodes as shown with the silver-copper alloy electrodes (Skogvold et al. 2006). The advantage of such semi-microelectrodes is that determination of several metals can be performed without the addition of a supporting electrolyte. Silver and copper have similar properties concerning the hydrogen overvoltage (Conway 1999), and it was therefore surprising to find that adding small amounts of copper to the silver increased the hydrogen overvoltage.

The reasons for the positive effects observed with mixed and alloy electrodes have not been fully explored yet. Changes in the surface chemistry can be explained from changes in the electronic structure of the surface, resulting in modifications in the adsorption energy and thus altering the barrier for reactions. This effect may be local to an alloying atom, or it may be of longer range. Further, the introduction of different species into a metal creates chemically different sites on the surface. This provides a range of different sites for e.g. adsorption, and will also change the distribution of transition states available for reaction or dissociation. The increasing hydrogen overvoltage could therefore be explained from a decrease in the total coverage of adsorbed hydrogen on the electrode surface, or from changes in the activation energies for the hydrogen evolution reaction. The results obtained with silver-copper alloys confirm that when an alloy is formed, its physical and chemical properties including the overvoltage towards hydrogen evolution may be significantly different from the pure metals, as shown elsewhere (Hayden et al. 1999). In the case of Ag-Bi alloys the increased hydrogen overvoltage may also be considered as a result of the spontaneous enrichment of the surface metal layer by the surface active component (Bi) of the alloy (Eustathopoulos et al. 1999). It is known that the compositions of a metal and an alloy in the bulk and at the surface substantially differ, as shown for pure gold and an Au-Ag alloy (Dakkouri et al. 1999; Safonov et al. 2006). In order to completely understand the electrochemistry of the alloy and mixed electrodes further surface studies have to be performed.

The combination of improved long-time stability, higher hydrogen overvoltage, good sensitivity for important trace metals and the need for only minor maintenance achieved with mixed and alloy electrodes makes them ideal for use in on-line automatic monitoring equipment.

Within the field of environmental monitoring, unattended in situ measurement in a significant extent has up till now been limited to a few parameters including pH, some anions like nitrate and phosphate, conductivity and temperature. Voltammetry combined with the use of solid alloy electrodes, renders interesting possibilities for continuous measurements of important inorganic environmental toxicants. The possibility of measuring organic species has not been explored yet, but it is likely that the alloy and mixed electrodes would be suitable for this purpose as well.

#### *1.2.4 Other factors influencing the electrode properties*

In addition to the composition of the electrode material, size and geometry also affect the properties of the electrodes including life-time, stability, sensitivity and degree of maintenance needed. The size of an electrode is normally divided in macro (large) or



micro (small). The commonly used geometry for macroelectrodes is the disk electrode, but other geometries like planar electrodes, tubular electrodes and wall jet electrodes have also been used (Buffle et al. 2000). The geometry of macroelectrodes does not affect the current response, but for ultramicroelectrodes the geometry determines the diffusion and thus the current response. The new technological progresses and the need for in situ determination have resulted in several microelectrodes including individual microdisk electrodes (de Vitre et al. 1991), arrays (Belmont et al. 1996), and microwires (Billon et al. 2004; Salaun et al. 2006). The advantages connected to use of microelectrodes for in situ determination are measurements without the addition of supporting electrolyte, high sensitivity and resolution, and the need for controlled convection of the solution is not critical. The size and geometry may also minimize power consumption and manufacturing costs, and maximize the life-time of the metal sensors. Drawbacks with microelectrodes are the tough requirements related to the equipment used, and fabrication may be a complex process. The same substrates used for macroelectrodes (Pt, Au, Ag, Ir, C) are used for microelectrodes, but making micro size electrodes of alloys and mixed metals is very difficult. Adding bismuth to gold for instance, makes a mixture that is too fragile to produce microelectrodes. Single microelectrodes and microelectrode arrays are also used coated with mercury, but show the same limitations as similar macroelectrodes. The exception is mercury-coated Ir electrodes which have been successfully used for determinations in natural waters (Tercier et al. 1995). The current in a voltammetric cell system is influenced by the hydrodynamic conditions which in its turn are affected by the electrode geometry, size and the type of convection used. The types of electrodes may thus also be divided into stationary, rotating or vibrating depending on the type of convection used in the preconcentration step.

### **1.3 Practical use in environmental and industrial solutions**

Working in real samples like seawater, river water and process solutions require more from the equipment itself than laboratory experiments, but recent technological advances have successfully overcome many of the previous obstacles for field operations (Wang et al. 1999). There are many factors to take into account, not only related to the complex matrixes, but related to the use of automated equipment on site as well. Natural waters often contain surface active compounds that may hinder the stripping measurements by inhibiting both the preconcentration and the stripping phases in ASV and especially in AdSV analysis. Adsorption of surface active compounds may also interfere in AdSV analysis and this requires drastic clean-up procedures (Buffle et al. 2000). Adsorption on the electrode surface is mainly a problem in the positive and low negative potential area, and compounds adsorbed on the surface can be removed by applying a very negative potential. The matrix may also change in the monitoring period and the results should therefore be as independent of the matrix as possible. One particular problem is oxygen in oxic waters and sulphide in anoxic waters that may cause interferences in the analysis. The concentrations to be measured are often very low in natural water so sensitive sensors and equipment is necessary. However, in process solutions the matrix may be a bit more complex with high concentrations of some compounds and low concentrations of others. This offers great challenges for the sensors used. In automatic monitoring minimum sample transformation during analysis

is also required. This will minimize consumption of reagents and thus minimize the amounts of reagents to be discharged, in addition to lower the energy consumption. Complex scan procedures and analytical steps should also be avoided to minimize the time and energy used and to simplify the instrument including needed pumps and valves. The system should also be flexible and easy to calibrate, and easy to deploy and maintain in field conditions. There are also tough requirements connected to the sensors used, not only the working electrode but the reference and counter electrode as well.

For in situ measurements irregular flux must be taken into account, hence the advantage with microelectrodes. Microelectrodes are said to be independent of stirring conditions, but the sensitivity may be increased by convection of the solution. To implement controlled convection for in situ measurement is complicated, but can be done by using a vibrating electrode (Chapman et al. 2007). For on-line determination the sample is collected and the stirring is controlled either by a rotating electrode or by a magnetic stirrer. More sources for possible contamination are then introduced with valves and pumps, and it is important to make sure that these do not affect the sample.

The systems used for on site determination have been classified as field-portable voltammetric instruments and non-portable on-line analysers for in field continuous automatic measurements. The portable instruments are in general laboratory equipments constructed so that they can be transported and are able to work on batteries. In the on-line analyzers all steps are computer controlled, thus minimizing contamination and analysis time, and improving the reproducibility (Buffle et al. 2000). Most on-line systems have been used aboard ships and as long as the samples have not been handled or exposed to the atmosphere they are considered very close to in situ measurements.

Although liquid mercury is unsuitable for use in in situ measurements, several automated voltammetric systems using various mercury electrodes have been developed. Examples are an automated instrument for shipboard determination of metal speciation in seawater using a HMDE (Achterberg et al. 1994), and a flow cell for on-line monitoring of metals in natural waters by voltammetry with a mercury drop electrode (Colombo et al. 1997). Mercury film electrodes have been widely used in on-line systems, and an interesting approach for in situ studies is worked out by Buffle and his group, using a micro array system, with an iridium matrix plated with mercury (Belmont-Hebert et al. 1998; M. Tercier-Waeber 1999; Tercier et al. 1998). Daniele et al. have presented a remote electrochemical sensor based on a gold fibre microelectrode for determination of copper and mercury in natural water by PSA (Daniele et al. 2000), and Luther et al. have used gold microelectrodes plated with mercury for in situ determinations in sediment pore waters (Luther et al. 1998). Other systems suggested for decentralized metal testing include remotely deployed submersible stripping probes, hand-held metal analyzers coupled to micro fabricated strips and miniaturized total stripping flow systems (Wang et al. 1999). The development of solid alloy and mixed electrodes has also led to new unique possibilities for constructing on-line apparatus for monitoring of environmental toxicants in various water solutions (Mikkelsen et al. 2001; Mikkelsen et al. 2005; Mikkelsen et al. 2003b; Mikkelsen et al. 2007).

There are many proposals for systems and sensors for on-line and in situ measurements and not all of them have been mentioned in this thesis. The selection given still shows the extent of research groups working in this area, thus confirming the demand for such equipment. Electrochemical sensors are used in numerous research areas and in a variety of environments leading to expectations of further improvements and new developments. The new technologies and strategies developed the last decades have already revolutionized the way of performing on site electrochemical experiments, and offers great promise for rapid, easy, and inexpensive on site metal determinations in the future (Taillefert et al. 2000; Wang et al. 1999).

#### **1.4 Surface studies**

As mentioned earlier, the interface between the electrode surface and the solution is very important in voltammetric analysis. An important factor here is the electrode surface. It is of crucial importance to understand what happens on the surface of the different electrodes, thus understanding the structure of the surface and how it affects the electrochemical activity. There are a variety of different techniques for studies of the electrode surface and this chapter will give an overview of the most common ones.

To study the metal electrode surface is a very complex process. The electrochemical reactivity of a compound depends on the crystal plane of the electrodes, and for ideal reliability the electrode surface should be a well-defined crystal plane. Most surface studies have also been done on single-crystal surfaces (Wieckowski 1999), but electrodes used in voltammetric analysis are normally polycrystalline. A polycrystalline surface provides a statistical and more complex signal than single-crystal surfaces. The signal may also be affected by the electrode preparation (Buffle et al. 2000). Polycrystalline surfaces are very complicated systems, and for voltammetric analysis the most important and interesting aspect is the overall effect, not the local properties on the surfaces. Even so, studies of local effects and properties may give valuable information on the total surface properties.

One powerful technique for structural characterisation is extended X-ray adsorption fine structure (EXAFS) and surface EXAFS (SEXAFS) which can be used both in situ and ex situ (Wang 2006). EXAFS can also be used to study oxide formation (Arikawa et al. 1998) or deposition (Gomez et al. 1995) on electrode surfaces. Another well-known technique is scanning electron microscopy (SEM) which is used to get ex situ information on the morphology and chemical composition of a surface. SEM has for instance been used to study the distribution and composition of mixed silver-bismuth electrodes (Skogvold et al. 2005). This study revealed the distribution of bismuth in the mixture, and indicated that the content of silver and bismuth alloy was very low. Vibrational spectroscopies, like surface-enhanced Raman scattering (SERS) utilize the high sensitivity of molecular vibrations to monitor the surface composition before, during and after an electrochemical experiment. This is an in situ method primarily used for investigation of adsorbed species (Wang 2006).

Scanning probe microscopies (SPMs) are a group of microscopy techniques used to acquire high-resolution data of surfaces. They have similar subcomponents but differ in

their sensing probes. A probe tip is scanned over the surface and the interaction between the tip and the surface is monitored. The signals are displayed as gray scaled images reflecting the extent of the tip-surface interactions which are available in a short time. The use of scanning tunnelling microscope (STM), atomic force microscope (AFM) and scanning electrochemical microscope (SECM) have drastically improved the understanding of electrode reactions by imaging electrode surfaces directly (Wang 2006). With STM it is possible to get an image of the surface on the atomic scale and AFM provides a high resolution image of the topography of the surface. It is thus possible to see nanoscopic features on the surface while the electrode is under potential control. The most attractive technique for electrochemical studies is the SECM. Here the faradic currents at an ultramicroelectrode tip are measured while the tip is scanned over the electrode surface immersed in a solution containing electroactive species. The tip currents are a function of the distance between the tip and surface, as well as the conductivity and chemical nature of the surface. The image produced gives insight into the topography and the distribution of electrochemical and chemical activity (Wang 2006). SECM has for instance been used to examine the conductivity and reactivity of bismuth films on GCEs (Hocevar et al. 2007a) and for studies of the adsorption and desorption of hydrogen on platinum electrodes (Yang et al. 1996).

Electrochemical impedance spectroscopy (EIS) is another method for characterization of the electrical properties of materials and interfaces of conducting electrodes (Macdonald 1987). EIS has been used to study fundamental processes like adsorption, film formation, rate of charge transfer, ion exchange and diffusion that occur at the electrode-electrolyte interface (Pejic et al. 2006). Impedance is especially suitable for gaining information about electrode kinetics, corrosion and features of chemically modified electrodes. The kinetics of the hydrogen evolution reaction have been studied by impedance on various substrates including rhodium (Wrona et al. 1992) and platinum (Conway et al. 1998). Impedance measurements on binary alloys are a complicated process, but EIS have for instance been used to study oxide formation and hydrogen evolution on Au-Ag alloys (Safonov et al. 2006). Localized electrochemical impedance spectroscopy (LEIS) is a relatively new method providing the opportunity to study electrode processes on microscopic level, which would be very useful for studies of alloys and mixed electrodes.

The use of methods for surface characterization has increased due to the extensive research on new electrode materials not only in voltammetry but also in other electrochemical techniques. The fabrication of sensors with unique response characteristics has created a need to understand the relationship between surface structure and reactivity. This can only be achieved by information about the electrical processes that occur at the surface of the sensors, and thus understanding the chemical and physical properties of the sensor materials.

## 2 Summary of the papers included in the thesis

### 2.1 Paper I, II and III

The increased interest for continuous monitoring of heavy metals has led to extensive research on methods and sensors suitable for automatic on-line analyses. Voltammetry has shown to be a suitable method, combining speed, sensitivity and low costs as well as having the possibility of performing speciation studies. In voltammetry the choice of electrode material is very important, and several more or less successful attempts have been made to find solid electrodes with properties desired for field equipment. The greatest challenge has been to find nontoxic electrode materials with high overvoltage towards the hydrogen evolution reaction (HER) and sufficient long-time stability. Bare solid electrodes with two or more components consisting of silver mixed or alloyed with a metal possessing high overpotential towards HER were introduced in 2000. A significant increase in the overpotential towards HER was obtained in addition to increased long-time stability.

In paper I the electrochemical properties of silver electrodes with 2, 4, 6, 10 and 15% bismuth added were investigated. Increased overpotential towards the hydrogen evolution reaction was found as a result of increasing amount of bismuth added. This was also demonstrated in acid solution where zinc was successfully detected on mixed electrodes, but failed on pure silver electrodes. Formation and decomposition of oxide products formed on the different electrode surfaces were studied by cyclic voltammetry, and in addition to known species found on silver, also peaks attributed to bismuth were achieved and examined. Zinc, cadmium, and lead were measured in the low  $\mu\text{g/l}$  range on the mixed electrodes, and good linearity was found for 2 to 10  $\mu\text{g/l}$ . Lead was measured down to 0.1  $\mu\text{g/l}$ . Better long-time stability was also found for the mixed electrodes compared to bare silver electrodes in polluted river water.

In paper II the electrochemical properties of mixed gold-bismuth electrodes were evaluated. Increased overpotential towards the hydrogen evolution reaction (HER) was also here found as a function of increased bismuth content in the gold-bismuth mixture. Compared to a bare gold electrode, the overvoltage was increased by 80 mV for gold with 2% bismuth added (AuBi2), 170 mV for 6% bismuth added (AuBi6), and 580 mV for 25% bismuth added (AuBi25). Cyclic voltammetry in a NaOH solution was also carried out to study the formation of different oxide products on the surface. The practical use of such electrodes was demonstrated by differential pulse anodic stripping voltammetry (DPASV) for the detection of copper and mercury, and good linearity was found even for concentrations down to 0.25  $\mu\text{g/l}$ . In addition to stability tests in  $\text{NH}_4\text{Cl}$ , the analytical use and stability over time were evaluated in purified scrubbing water and polluted river water. The AuBi electrodes had a considerable increase in the long-time stability compared with a pure gold electrode.

In paper III microelectrodes of silver-copper alloys (silver 830 and silver 925) were evaluated for use in voltammetric analyses. Increased overpotential towards the hydrogen evolution reaction (HER) was found as a function of increased copper amount

in the alloy. It was found that these alloy electrodes behave somewhat between pure silver and pure copper electrodes. Differential pulse anodic stripping voltammetry (DPASV) was used to measure zinc, cadmium and lead in ultrapure water ( $18\text{ M}\ \text{cm}^{-1}$ ), and good linearity was found for all metals in the range of 0.5 to 5  $\mu\text{g/l}$  with 600 to 1200 s plating time. It was also found that cadmium and lead peaks were better separated on the alloy electrodes compared to on pure silver electrodes. Measurements of nickel were carried out on alloy electrodes by use of adsorptive differential pulse cathodic stripping voltammetry (Ad-DPCSV), and good linearity ( $r^2=1.000$ ) was found in the range of 0.5 to 5  $\mu\text{g/l}$  with an adsorption time of 30 s. The alloy electrodes were also found to be sensitive to nitrate, and a good linearity ( $r^2=0.997$ ) was found in the range of 1 - 100 mg/l using differential pulse voltammetry (DPV) scanning from -450 mV to -1500 mV. Further, the use of an alloy electrode containing 17% Cu was tested in real samples, by installing it in a voltammetric system for monitoring of zinc and lead in a polluted river, *Deûle*, near the town of Douai in northern France. Results were found to be in agreement with parallel measurements carried out by ICP-MS.

Papers I, II and III all show that mixed and alloy electrodes are suitable for use in automatic field equipment due to the combination of nontoxic materials, increased cathodic potential window, better long-time stability and good sensitivity for several metals.

## 2.2 Paper IV

A voltammetric system using a dropping mercury electrode is often used for continuous monitoring of metals in process water or waste water in industry. Such systems use significant amounts of mercury in only a few weeks, and then the large amounts of mercury waste have to be taken care of. This is normally done either by destruction or distillation for re-use. Destruction is very expensive and distillation is a very noxious process requiring strict safety procedures. The use of solid electrodes will effectively eliminate this problem along with other problems like clogging of the mercury capillary, concern about impurities in the mercury, and adsorptions effects specific for mercury. There are now strict regulations for use of mercury, leading to an out phasing of mercury as electrode material.

Paper IV evaluates alternative solid electrode materials for detection of metals in process water and wastewater from metallurgical nickel industry. A solid silver amalgam electrode, a silver electrode and silver-bismuth mixed electrodes were tested for determination of zinc, lead, cobalt and nickel. Zinc was detected by differential pulse anodic stripping voltammetry (DPASV) on a solid silver amalgam electrode as intermetallic Ni-Zn compound, and a linear response was found in the range 0.2–1.2 mg/l. Simultaneous detection of nickel and cobalt in the low  $\mu\text{g/L}$  range was successfully performed by use of adsorptive cathodic stripping voltammetry (AdCSV) of dimethylglyoxime complexes on a silver-bismuth mixed electrode, and good correlation was found with corresponding AAS results. Analyses of lead in the  $\mu\text{g/L}$  range in nickel-plating solution were performed with good sensitivity and stability by DPASV, using a working electrode of silver. A new commercial automatic at-line

system was tested, and the results were found to be in agreement with an older mercury drop system. These results indicate that voltammetric detection of heavy metals in process water from metallurgical nickel industry with use of solid electrodes may successfully replace mercury-based systems. Lead, zinc, cobalt, and nickel may be detected directly in the solutions with only minor sample pretreatment or dilutions. The solid electrodes showed stability over a period of one to several days without any maintenance needed, making them feasible for automatic on-line systems.

### **2.3 Paper V and VI**

Several analytical methods are available for determination of metals in the environment and industrial solutions. In contrast to automatic monitoring, frequent manual sampling for laboratory analysis is in many cases inconvenient, expensive and gives an undesired time lag from the appearance of an accidental or illegal pollutant to the detection of it. Voltammetry is one of the few methods available for automatic on-line monitoring, but the limitation has so far been the lack of suitable electrode materials. The introduction of solid silver amalgams and mixed electrodes have created new possibilities for continuous trace metal monitoring in the field using voltammetric equipment.

Paper V and VI both present an automatic voltammetric system for continuous monitoring of trace metals with a solid silver amalgam working electrode. The system is fully automated and has been mounted in four different geological sites for continuous monitoring of electrolabile concentrations of metals. Concentrations of zinc, copper and iron were monitored automatically every 30 minutes for six months in a polluted river impacted by a copper mine and in coastal seawater. The concentrations varied from 0.2 mg/l in seawater to 3 mg/l in polluted river water. Zinc and iron concentrations have also been monitored in drainage water and waste water every 30 or 60 minutes for periods up to 4 months. The observed concentrations varied from sub-mg/l to approximately 30 mg/l for zinc, and from approximately 1 mg/l to 150 mg/l for iron.

Manual sampling with determination by ICP-MS was performed frequently for comparison and quality assurance, and the results show good agreement. The system was maintained twice a month for river water, and once or twice a week when used in waste water. Both papers show that the presented voltammetric system fulfils the requirements for use in continuous remote monitoring of heavy metals in water solutions. The use of solid silver amalgam as electrode material avoids the use of liquid mercury or mercury salts in voltammetric analyses, and thus offers a nontoxic electrode system which can be used in field equipment. The huge difference in the sample matrixes and locations demonstrates the wide application range for this system. The solid silver amalgam electrode has shown good sensitivity for several metals and sufficiently long-time measuring stability without the need for frequent manual maintenance.

## 2.4 Paper VII

In aquatic systems, dissolved metals, even present at trace levels are generally accumulated all along the tropical chain and may result in global contamination of the biota. For instance, manganese, an essential micronutrient for all organisms, can be very toxic at high concentrations and contribute for example to the development of Parkinson's symptoms. Generally detected at very low concentration levels in the oxygenated freshwater, manganese concentrations can increase temporarily but drastically when sediment pore waters are mixed with the overlaying water during intensive fluvial traffic. Various techniques, including the most used atomic emission and absorption spectrometry, are used for determination of manganese. However, these techniques necessitate sampling, pre-treatment (including filtration and acidification) and analyses in the laboratory.

Paper VII introduces on-line detection of Mn(II) using differential pulse anodic stripping voltammetry (DPASV) on a solid silver amalgam electrode. A well-defined peak for the oxidation of Mn(0) to Mn(II) was observed around -1.45 V in NH<sub>4</sub>Cl solution. Concentrations down to 1 µg/l were measured in NH<sub>4</sub>Cl with a 900 s deposition time at -1.70 V, and good linearity was observed for standard additions in different concentration ranges (1 – 3 µg/l, 10 - 60 µg/l, and 50 - 250 µg/l). Significant interferences were found when lead and nickel were present in the solutions, while zinc, cadmium, copper and mercury not interfered within reasonable concentration ranges. The method was demonstrated for on-line detection of manganese in a contaminated river where the Mn(II) concentration varied between 3 µg/l and 15 µg/l. The relation between the Mn(II) concentration in the river water and the vessel traffic was observed to examine the correlation. Increased manganese concentration was found as a function of traffic on the river, mainly due to the high concentrations in the anoxic pore waters in the sediments. These results also show that the solid silver amalgam is suitable for determination of manganese in natural waters.

## 2.5 Paper VIII

Development of an automatic trace metal system using voltammetry with a solid silver amalgam electrode has provided an opportunity to monitor earthquake precursor in basaltic rocks. Earthquake is a phenomenon which affects people all over the world. In areas with high earthquake activity new earthquakes can occur at any time - often with severe material damage and even loss of human lives. In 2002 increased concentrations of some heavy metals was detected in ground water before the occurrence of an earthquake. These anomalies were not detected until after the earthquake had occurred, because of manual sampling and determinations in the laboratory using ICP-AES. Use of anomalies like this in for instance warning systems would be very interesting, but an essential and crucial factor is then rapid and automatic real time determination. Paper VII shows how this can be achieved using an automatic monitoring station based on voltammetry with a solid silver amalgam electrode.

In November 2006, an earthquake of  $M_w$  4.5 on Richters scale occurred in Húsavík (Iceland). Analysis of ground water showed no electrolabile metals 30 days before the



earthquake, but changes in the measured voltammogram was observed a few days before the earthquake. Significant changes in pH and electrolabile amounts of zinc, iron and copper were first detected 7-8 days before the earthquake, and measurable amounts were present until the occurrence of the earthquake. The results presented in paper VIII clearly show changes in the ground water prior to an earthquake, which is possible to monitor with the solid silver amalgam electrode.

### 3 Conclusion

The aim of this thesis has been to investigate properties of new electrode materials suitable for automatic on site determination. The papers constituting this thesis present applications of several mixed and alloy electrodes in different environmental and industrial solutions.

Mixed silver-bismuth and gold-bismuth electrodes were investigated with focus on hydrogen overvoltage, determination of metals and stability over time. Compared to the pure silver and gold electrodes, increased hydrogen overvoltage was found as a result of increasing amount of bismuth added. The mixed AgBi electrodes were used for determination of low concentrations of zinc, cadmium and lead, and the AuBi electrodes were used for determination of mercury and copper. The mixed electrodes were tested by application in an automatic trace metal station for on-line determination of metals in polluted river water and purified scrubbing water. Better long-time stability was found for the mixed electrodes compared to bare silver and gold electrodes in polluted river water. An AgBi electrode was also used for simultaneous detection of nickel and cobalt in process water from metallurgical nickel industry.

Microelectrodes of silver-copper alloys (silver 830 and silver 925) were also evaluated for use in voltammetric analyses. Increased overpotential towards the hydrogen overvoltage reaction (HER) was found as a function of increased copper amount in the alloy. The alloys were found to be suitable for determinations of zinc, cadmium, lead, nickel and nitrate. The use of an alloy electrode containing 17% Cu was also tested in real samples, by installing it in a voltammetric system for determination of zinc and lead in a polluted river in France.

Solid silver amalgam electrodes have been validated for use in automatic online equipment in various solutions. Zinc was detected as intermetallic Ni-Zn compound in process water from metallurgical nickel industry. Zinc has also, along with copper and iron, been monitored in periods up till six months in polluted river water, coastal sea water, drainage water and waste water. The solid amalgam electrode has also been used to monitor changes in electrolabile concentrations of metals in ground water in connection to earthquake activity, and determination of manganese concentrations in correlation with traffic on a polluted river in France.

The results presented in this thesis show that mixed and alloy electrodes are suitable for use in automatic field equipment due to the combination of nontoxic materials, increased cathodic potential window, better long-time stability and good sensitivity for several metals. The solid alloy and mixed metal electrodes are also easy and cheap to construct, and the difference in the sample matrixes and locations presented demonstrates the wide application range for these electrodes.

## 4 Future aspects

There is still a long way to go before an optimal on-line and in situ system is obtained, but many of the recently suggested systems offers great promise for rapid, easy, and inexpensive on site metal determinations. The first objective in optimization would be improvement of the already available systems and sensors. One important factor is the long-time stability of the working electrodes. There are different ways to prolong the long-time stability. One method is development of suitable cleaning procedures for instance by combining chemical cleaning with electrochemical cleaning. Many films and membranes have also been used to protect the electrode surface, and development of new, more stable films that can be used for a long time without degradation would be very convenient.

Microelectrodes, and especially ultramicroelectrodes, are very interesting for field applications. Alloys and mixed metals can be difficult to use as microelectrodes due to the porosity of the materials, and finding such materials suitable as microelectrodes would be very useful.

More extensive surface studies are also important to increase the knowledge of the alloy and mixed electrodes. The methods mentioned in chapter 1.4 would all provide valuable information on the electrode surfaces, from structure characteristics to information about local properties. There are several interesting aspects related to the mixed electrodes; what are the surface structures and are they very different from bulk structures? How is the kinetic for the adsorption of hydrogen, and thus the hydrogen evolution on such electrodes? How does the addition of a second metal affect the oxidation and thus the passivation of the electrodes? These are just some of the many interesting challenges that would provide important information for further development of electrode materials.

Preliminary Surface X-ray Absorption Fine Structure (SEXAFS) studies have already been carried out on different mixtures of AgBi, AuBi and AgCu. The ionic structures were analysed with focus on oxidation of the surfaces, and data were recorded for all metals in the samples. To get information on the rate of oxidation all samples were analysed both polished and oxidised. For the AgBi mixture, samples containing 0.8, 6 and 20% bismuth were analysed. The first preliminary results confirmed that more Bi-Bi (3.2 Å) distances are introduced with increased amount of bismuth in the mixture. The Bi-Bi distances related to the formation of Bi<sub>2</sub>O<sub>3</sub> are not present in the polished samples. In the oxidised samples, no distances related to Bi<sub>2</sub>O<sub>3</sub> were present for the AgBi mixture with 0.8% Bi, but Bi-Bi at 3.9 Å was observed which may indicate formation of BiO on the surface. In the other mixtures the Bi-Bi distance related to Bi<sub>2</sub>O<sub>3</sub> was present indicating formation of Bi<sub>2</sub>O<sub>3</sub> on the surfaces. More information will be obtained when the full structural study is completed. This project will be continued with EXAFS studies of the ionic structure of the bulk mixture on some of the same samples. It is also possible to perform in situ SEXAFS studies, where the electrodes may be under potential control and the analyses are performed in an electrochemical

cell. This would give unique possibilities for studying reactions on the surface, like oxidation, hydrogen evolution and deposition of metals.

Another interesting approach for understanding the hydrogen evolution on such mixed electrodes is the possibilities of studying local properties with a scanning electrochemical microscope (SECM). By applying a potential, where the hydrogen evolution reaction is just starting, to the mixed metal substrate, it might be possible to measure local pH changes with the probe. This may indicate on which sites the evolution of hydrogen starts, and if it is suppressed on for instance areas with high bismuth content. Some preliminary studies have been carried out on the gold-bismuth electrodes, but further studies need to be performed because of the many factors influencing the analyses.

In addition to cyclic voltammetry, electrochemical impedance spectroscopy (EIS) is a suitable method for studies of electrode properties and reaction kinetics. EIS is an easy method to carry out, but fitting the data might be a complex process, especially for complex systems like polycrystalline mixed and alloy electrodes. Preliminary studies have however been performed on the hydrogen evolution reaction and also on the passivation of the electrode surfaces.

There are many challenges related to the equipment used in on site determination, and it is important to bear in mind the counter electrode and the reference electrode as well. A known problem with the Ag/AgCl/KCl reference electrode is the leaching of chloride, especially in waters with low conductivity. This may influence the measurements and also implies that the reference needs some manual maintenance. There are normally a lot of organic compounds in natural waters, and an optimization of an automatic system would imply that the materials used in e.g. the cell, the valves and also the electrodes should resist adsorption of organic material. Many of the systems used in automatic monitoring are based on laboratory equipment, adjusted for use in the field. It is therefore important to develop equipment made solely for on site determination, and thus focusing on the important aspects like low power demands, simple scan procedures, environmental friendliness and long-time stability without manual maintenance. It is of course also important to have systems for rapid evaluation and transfer of the results so that they can be benefited from in short time.

Last but not least, the focus on speciation of metals should not be forgotten. More information is achieved by determining certain species of metals, and especially by combining voltammetric analyses with other techniques like ICP-MS or sampling techniques like DGT, a more complete picture of the water quality is obtained. Development of procedures for automatic determination of different species in a voltammetric cell suitable for on site analyses would also be very interesting.

## 5 References

- Achterberg E. P., van den Berg C. M. G. 1994. Automated voltammetric system for shipboard determination of metal speciation in sea water. *Analytica Chimica Acta* 284, 463-471.
- Adams R. N. 1969. *Electrochemistry at solid electrodes*. New York: Dekker.
- Airey L. 1947. The application of the cathode ray oscillograph to polarography - general lay-out and uses of the cathode ray polarograph. *Analyst* 72, 304-307.
- Arikawa T., Takasu Y., Murakami Y., Asakura K., Iwasawa Y. 1998. Characterization of the structure of  $\text{RuO}_2/\text{Ti}$  electrodes by exafs. *Journal of Physical Chemistry B* 102, 3736-3741.
- Bakker E., Pretsch E. 2005. Potentiometric sensors for trace-level analysis. *Trac-Trends in Analytical Chemistry* 24, 199-207.
- Baldo M. A., Daniele S., Bragato C. 2003. Bismuth film microelectrodes for heavy metals monitoring by anodic stripping voltammetry. *Journal de Physique IV* 107, 103-106.
- Baldrianova L., Svancara I., Economou A., Sotiropoulos S. 2006. Anodic stripping voltammetry at in situ bismuth-plated carbon and gold microdisc electrodes in variable electrolyte content unstirred solutions. *Analytica Chimica Acta* 580, 24-31.
- Bas B., Kowalski Z. 2002. Preparation of silver surface for mercury film electrode of prolonged analytical application. *Electroanalysis* 14, 1067-1071.
- Belmont-Hebert C., Tercier M. L., Buffle J., Fiaccabrino G. C., de Rooij N. F., Koudelka-Hep M. 1998. Gel-integrated microelectrode arrays for direct voltammetric measurements of heavy metals in natural waters and other complex media. *Analytical Chemistry* 70, 2949-2956.
- Belmont C., Tercier M.-L., Buffle J., Fiaccabrino G. C., Koudelka-Hep M. 1996. Mercury-plated iridium-based microelectrode arrays for trace metals detection by voltammetry: Optimum conditions and reliability. *Analytica Chimica Acta* 329, 203-214.
- Berlin M., Zalups R. K., Fowler B. A. 2007. Mercury. In *Handbook on the toxicology of metals*, ed. G. F. Nordberg, B. A. Fowler, M. Nordberg, L. T. Friberg, Amsterdam: Elsevier.
- Billon G., van den Berg C. M. G. 2004. Gold and silver micro-wire electrodes for trace analysis of metals. *Electroanalysis* 16, 1583-1591.
- Bockris J. O. M., Khan S. U. M. 1993. *Surface electrochemistry: A molecular level approach*. New York: Plenum.
- Bonfil Y. 2000. Determination of mercury and copper in waste water by anodic-stripping voltammetry at the gold electrode. *Reviews in analytical chemistry* 19, 201-216.

- Bonfil Y. 2002a. Characteristics of subtractive anodic stripping voltammetry of pb and cd at silver and gold electrodes. *Analytica Chimica Acta* 464, 99-114.
- Bonfil Y. 2002b. Determination of nanomolar concentrations of lead and cadmium by anodic-stripping voltammetry at the silver electrode. *Analytica Chimica Acta* 457, 285-296.
- Bonfil Y., Brand M., Kirowa-Eisner E. 2000. Trace determination of mercury by anodic stripping voltammetry at the rotating gold electrode. *Analytica Chimica Acta* 424, 65-76.
- Bonfil Y., Brand M., Kirowa-Eisner E. 2003. Characteristics of subtractive anodic stripping voltammetry of lead, cadmium and thallium at silver-gold alloy electrodes. *Electroanalysis* 15, 1369-1376.
- Brainina K. Z., Malakhova N. A., Stojko N. Y. 2000. Stripping voltammetry in environmental and food analysis. *Fresenius' Journal of Analytical Chemistry* 368, 307 - 325.
- Brendel P. J., Luther G. W. 1995. Development of a gold amalgam voltammetric microelectrode for the determination of dissolved fe, mn, o-2, and s(-ii) in porewaters of marine and fresh-water sediments. *Environmental Science & Technology* 29, 751-761.
- Buckova M., Grundler P., Flechsig G. U. 2005. Adsorptive stripping voltammetric detection of daunomycin at a bismuth bulk electrode. *Electroanalysis* 17, 440-444.
- Buffle J., Tercier-Waeber M. L. 2000. In situ voltammetry: Concepts and practice for trace analysis and speciation. In *In situ monitoring of aquatic systems: Chemical analysis and speciation*, ed. J. Buffle, G. Horvai, Chichester: Wiley.
- Buffle J., Tercier-Waeber M. L. 2005. Voltammetric environmental trace-metal analysis and speciation: From laboratory to in situ measurements. *Trends in Analytical Chemistry* 24, 172-191.
- Butler J. A. V. 1936. Hydrogen overvoltage and the reversible hydrogen electrode. *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences (1934-1990)* 157, 423 - 433.
- Chapman C. S., van den Berg C. M. G. 2007. Anodic stripping voltammetry using a vibrating electrode. *Electroanalysis* 19, 1347-1355.
- Colombo C., vandenBerg C. M. G., Daniel A. 1997. A flow cell for on-line monitoring of metals in natural waters by voltammetry with a mercury drop electrode. *Analytica Chimica Acta* 346, 101-111.
- Compton R. G., Foord J. S., Marken F. 2003. Electroanalysis at diamond-like and doped-diamond electrodes. *Electroanalysis* 15, 1349-1363.
- Conway B. E. 1999. Electrochemical processes involving h adsorbed at metal electrode surfaces. In *Interfacial electrochemistry: Theory, experiment, and applications*, ed. A. Wieckowski, New York: Marcel Dekker.

- Conway B. E., Barber J., Morin S. 1998. Comparative evaluation of surface structure specificity of kinetics of upd and opd of h at single-crystal pt electrodes. *Electrochimica Acta* 44, 1109-1125.
- Conway B. E., Bockris J. O. 1957. Electrolytic hydrogen evolution kinetics and its relation to the electronic and adsorptive properties of the metal. *Journal of Chemical Physics* 26, 532-541.
- Conway B. E., Bockris J. O., Linton H. 1956. Proton conductance and the existence of the h<sub>3</sub>o ion. *Journal of Chemical Physics* 24, 834-850.
- Conway B. E., Tilak B. V. 1992. Behavior and characterization of kinetically involved chemisorbed intermediates in electrocatalysis of gas evolution reactions. *Advances in Catalysis* 38, 1-147.
- Cox J. A., Das B. K. 1989. Voltammetric characterization and determination of thallium(III,I) at a glassy carbon electrode modified with a film containing iridium oxide. *Electroanalysis* 1, 57-61.
- Croot P. L., Moffett J. W., Luther III G. W. 1999. Polarographic determination of half-wave potentials for copper-organic complexes in seawater. *Marine Chemistry* 67, 219-232.
- Dakkouri A. S., Kolb D. M. 1999. Reconstruction of gold surfaces. In *Interfacial electrochemistry: Theory, experiment, and applications*, ed. A. Wieckowski, New York: Marcel Dekker.
- Daniele S., Bragato C., Baldo M. A., Wang J., Lu J. M. 2000. The use of a remote stripping sensor for the determination of copper and mercury in the lagoon of Venice. *Analyst* 125, 731-735.
- de Vitre R. R., Tercier M.-L., Tsacopoulos M., Buffle J. 1991. Preparation and properties of a mercury-plated iridium-based microelectrode. *Analytica Chimica Acta* 249, 419-425.
- Devitre R. R., Tercier M. L., Tsacopoulos M., Buffle J. 1991. Preparation and properties of a mercury-plated iridium-based microelectrode. *Analytica Chimica Acta* 249, 419-425.
- Dewald H. D. 1996. Stripping analysis. In *Modern techniques in electroanalysis*, ed. P. Vanýsek, New York: Wiley.
- Douglas D. J., Houk R. S. 1985. Inductively-coupled plasma mass-spectrometry (icp-ms). *Progress in Analytical Atomic Spectroscopy* 8, 1-18.
- European Commission. 2008. *An integrated maritime policy for the European Union*. [http://ec.europa.eu/maritimeaffairs/index\\_en.html](http://ec.europa.eu/maritimeaffairs/index_en.html). September 18 2008.
- European Commission. 2007. *Introduction to the new EU water framework directive* [http://ec.europa.eu/environment/water/water-framework/info/intro\\_en.htm](http://ec.europa.eu/environment/water/water-framework/info/intro_en.htm). September 18 2008.

- Eustathopoulos N., Nicholas M. G., Drevet B. 1999. *Wettability at high temperatures*. Amsterdam: Pergamon.
- Florence T. M. 1984. Recent advances in stripping analysis. *Journal of Electroanalytical Chemistry* 168, 207-218.
- Florence T. M. 1986. Electrochemical approaches to trace element speciation in waters. A review. *The Analyst* 111, 489 - 505.
- Florence T. M., Morrison G. M., Stauber J. L. 1992. Determination of trace-element speciation and the role of speciation in aquatic toxicity. *Science of the Total Environment* 125, 1-13.
- Gerischer H. 1958. Mechanismus der elektrolytischen wasserstoffabscheidung und adsorptionsenergie von atomarem wasserstoff. *Bulletin des Societes Chimiques Belges* 67, 506-527.
- Gomez R., Yee H. S., Bommarito G. M., Feliu J. M., Abruna H. D. 1995. Anion effects and the mechanism of Cu upd on Pt(111) - x-ray and electrochemical studies. *Surface Science* 335, 101-109.
- Grubac Z., Metikos-Hukovic M. 2004. EIS study of solid-state transformations in the passivation process of bismuth in sulfide solution. *Journal of Electroanalytical Chemistry* 565, 85-94.
- Hayden B. E., Hodgson A. 1999. Dissociation dynamics on ordered surface alloys. *Journal of Physics-Condensed Matter* 11, 8397-8415.
- Hernandez L., Zapardiel A., Bermejo E., PerezLopez J. A., PerezFernandez J. C. 1996. Electrochemical studies of ethamivan at glassy-carbon and platinum electrodes and its determination in urine by differential pulse voltammetry. *Analytica Chimica Acta* 336, 85-93.
- Heyrovský J., Kuta J. 1965. *Principles of polarography*. Prague: Publishing House of the Czechoslovak Academy of Sciences.
- Hocevar S. B., Daniele S., Bragato C., Ogorevc B. 2007a. Reactivity at the film/solution interface of ex situ prepared bismuth film electrodes: A scanning electrochemical microscopy (secm) and atomic force microscopy (afm) investigation. *Electrochimica Acta* 53, 555-560.
- Hocevar S. B., Ogorevc B., Wang J., Pihlar B. 2002. A study on operational parameters for advanced use of bismuth film electrode in anodic stripping voltammetry. *Electroanalysis* 14, 1707-1712.
- Hocevar S. B., Svancara I., Ogorevc B., Vytras K. 2007b. Antimony film electrode for electrochemical stripping analysis. *Analytical Chemistry* 79, 8639-8643.
- Hocevar S. B., Svancara I., Vytras K., Ogorevc B. 2005. Novel electrode for electrochemical stripping analysis based on carbon paste modified with bismuth powder. *Electrochimica Acta* 51, 706-710.



- Hutton E. A., Ogorevc B., Hocevar S. B., Weldon F., Smyth M. R., Wang J. 2001. An introduction to bismuth film electrode for use in cathodic electrochemical detection. *Electrochemistry Communications* 3, 707-711.
- Hutton E. A., van Elteren J. T., Ogorevc B., Smyth M. R. 2004. Validation of bismuth film electrode for determination of cobalt and cadmium in soil extracts using icp-ms. *Talanta* 63, 849-855.
- Janusa M. A., Beck J. N. 2002. Recent applications of flame atomic absorption spectrometry to environmental measurements. *Applied Spectroscopy Reviews* 37, 137-186.
- Kefala G., Economou A., Voulgaropoulos A., Sofoniou M. 2003. A study of bismuth-film electrodes for the detection of trace metals by anodic stripping voltammetry and their application to the determination of pb and zn in tapwater and human hair. *Talanta* 61, 603-610.
- Khoo Soo B., Guo Si X. 2002. Rapidly renewable and reproducible mercury film coated carbon paste electrode for anodic stripping voltammetry. *Electroanalysis* 14, 813-822.
- Kokkinos C., Economou A. 2008. Stripping analysis at bismuth-based electrodes. *Current Analytical Chemistry* 4, 183-190.
- Lee J. Y., Strasser P., Eiswirth M., Ertl G. 2001. On the origin of oscillations in the electrocatalytic oxidation of hcooh on a pt electrode modified by bi deposition. *Electrochimica Acta* 47, 501-508.
- Luther G. W., Brendel P. J., Lewis B. L., Sundby B., Lefrancois L., et al. 1998. Simultaneous measurement of o-2, mn, fe, i-, and s(-ii) in marine pore waters with a solid-state voltammetric microelectrode. *Limnology and Oceanography* 43, 325-333.
- M. Tercier-Waeber J. B., F. Confalonieri, G. Riccardi, A. Sina, F. Graziottin, G. C. Fiaccabrino and M. Koudelka-Hep. 1999. Submersible voltammetric probes for in situ real-time trace element measurements in surface water, groundwater and sediment-water interface. *Measurement science & technology* 10, 1202-1213.
- Macdonald J. R. 1987. *Impedance spectroscopy: Emphasizing solid materials and systems*. New York: Wiley.
- McCreery R. L. 1991. Carbon electrodes: Structural effects on electron transfer kinetics. In *Electroanalytical chemistry*, ed. A. J. Bard, New York: Marcel Dekker.
- McGaw E. A., Swain G. M. 2006. A comparison of boron-doped diamond thin-film and hg-coated glassy carbon electrodes for anodic stripping voltammetric determination of heavy metal ions in aqueous media. *Analytica Chimica Acta* 575, 180-189.
- Mikkelsen O., Schroder K. 2000a. Dental amalgam in voltammetry some preliminary results. *Analytical Letters* 33, 3253-3269.
- Mikkelsen O., Schroder K. H. 2000b. Alloy electrodes with high hydrogen overvoltage for analytical use in voltammetry. Some preliminary results. *Analyst* 125, 2163-2165.

- Mikkelsen O., Schroder K. H. 2003a. Amalgam electrodes for electroanalysis. *Electroanalysis* 15, 679-687.
- Mikkelsen O., Schroder K. H., Aarhaug T. A. 2001. Dental amalgam, an alternative electrode material for voltammetric analyses of pollutants. *Collection of Czechoslovak Chemical Communications* 66, 465-472.
- Mikkelsen O., Skogvold S. M., Schroder K. H. 2005. Continuous heavy metal monitoring system for application in river and seawater. *Electroanalysis* 17, 431-439.
- Mikkelsen O., Skogvold S. M., Schroder K. H., Gjerde M. I., Aarhaug T. A. 2003b. Evaluations of solid electrodes for use in voltammetric monitoring of heavy metals in samples from metallurgical nickel industry. *Analytical and Bioanalytical Chemistry* 377, 322-326.
- Mikkelsen O., van den Berg C. M. G., Schroder K. H. 2006. Determination of labile iron at low nmol l<sup>-1</sup> levels in estuarine and coastal waters by anodic stripping voltammetry. *Electroanalysis* 18, 35-43.
- Mikkelsen Ø., Strasunskiene K., Skogvold S., Schröder K. H., Johnsen C. C., et al. 2007. Automatic voltammetric system for continuous trace metal monitoring in various environmental samples. *Electroanalysis* 19, 2085-2092.
- Moller H., Pistorius P. C. 2004. The electrochemistry of gold-platinum alloys. *Journal of Electroanalytical Chemistry* 570, 243-255.
- Monterroso S. C. C., Carapuca H. M., Simao J. E. J., Duarte A. C. 2004. Optimisation of mercury film deposition on glassy carbon electrodes: Evaluation of the combined effects of pH, thiocyanate ion and deposition potential. *Analytica Chimica Acta* 503, 203-212.
- Novotny L., Yosypchuk B. 2000. Solid silver amalgam electrodes. *Chemické Listy* 94, 1118-1120.
- Parsons R. 1958. The rate of electrolytic hydrogen evolution and the heat of adsorption of hydrogen. *Transactions of the Faraday Society* 54, 1053-1063.
- Pauliukaite R., Hocevar S. B., Ogorevc B., Wang J. 2004. Characterization and applications of a bismuth bulk electrode. *Electroanalysis* 16, 719-723.
- Pejcic B., De Marco R. 2006. Impedance spectroscopy: Over 35 years of electrochemical sensor optimization. *Electrochimica Acta* 51, 6217-6229.
- Petrovic S. C., Dewald H. D. 1997. Square-wave anodic stripping voltammetry of Zn(II) as a method for probing instabilities at a glassy carbon mercury film microelectrode. *Analytica Chimica Acta* 357, 33-39.
- Ruetschi P., Delahay P. 1955. Hydrogen overvoltage and electrode material. A theoretical analysis. *The Journal of Chemical Physics* 23, 195-199.
- Safonov V. A., Choba M. A., Seropegin Y. D., Lubnin E. N. 2006. Salient features of the electrical double layer structure on mechanically renewed gold-silver electrodes in

aqueous solutions of a surface-inactive electrolyte. *Russian Journal of Electrochemistry* 42, 861-872.

Salaun P., Planer-Friedrich B., van den Berg C. M. G. 2007. Inorganic arsenic speciation in water and seawater by anodic stripping voltammetry with a gold microelectrode. *Analytica Chimica Acta* 585, 312-322.

Salaun P., van den Berg C. M. G. 2006. Voltammetric detection of mercury and copper in seawater using a gold microwire electrode. *Analytical Chemistry* 78, 5052-5060.

Scholz F. 2002. Stripping voltammetry. In *Electroanalytical methods: Guide to experiments and applications*, ed. F. Scholz, Berlin: Springer.

Shao H., Gan Y. P., Huang H., Zhang W. K. 2008. Electrochemical reduction behaviors of maleic acid and fumaric acid at lead electrode. *Acta Physico-Chimica Sinica* 24, 1264-1270.

Skogvold S. M., Mikkelsen O., Billon G., Garnier C., Lesven L., Barthe J. F. 2006. Electrochemical properties of silver-copper alloy microelectrodes for use in voltammetric field apparatus. *Analytical and Bioanalytical Chemistry* 384, 1567-1577.

Skogvold S. M., Mikkelsen Ø. 2008. Electrochemical properties and range of application of mixed gold bismuth electrodes. *Electroanalysis* 20, 1738-1747.

Skogvold S. M., Mikkelsen Ø., Schroder K. H. 2005. Electrochemical properties and application of mixed silver-bismuth electrodes. *Electroanalysis* 17, 1938-1944.

Stozhko N. Y., Malakhova N. A., Fyodorov M. V., Brainina K. Z. 2008a. Modified carbon-containing electrodes in stripping voltammetry of metals - part i. Glassy carbon and carbon paste electrodes. *Journal of Solid State Electrochemistry* 12, 1185-1204.

Stozhko N. Y., Malakhova N. A., Fyodorov M. V., Brainina K. Z. 2008b. Modified carbon-containing electrodes in stripping voltammetry of metals. Part ii. Composite and microelectrodes. *Journal of Solid State Electrochemistry* 12, 1219-1230.

Surmann P., Zeyat H. 2005. Voltammetric analysis using a self-renewable non-mercury electrode. *Analytical and Bioanalytical Chemistry* 383, 1009-1013.

Svancara I., Fairouz M., Ismail K., Metelka R., Vytras K. 2003. A contribution to the characterisation of mercury- and bismuth film carbon paste electrodes in stripping voltammetry. *Scientific Papers of the University of Pardubice, Series A* 9, 31-47.

Svancara I., Matousek M., Sikora E., Schachl K., Kalcher K., Vytras K. 1997. Carbon paste electrodes plated with a gold film for the voltammetric determination of mercury(ii). *Electroanalysis* 9, 827-833.

Svancara I., Pravda M., Hvizdalova M., Vytras K., Kalcher K. 1994. Voltammetric investigations on carbon-paste electrodes as supports for mercury films. *Electroanalysis* 6, 663-671.

Taillefert M., Luther G. W., Nuzzio D. B. 2000. The application of electrochemical tools for in situ measurements in aquatic systems. *Electroanalysis* 12, 401-412.

- Tercier M. L., Buffle J., Graziottin F. 1998. Novel voltammetric in-situ profiling system for continuous real-time monitoring of trace elements in natural waters. *Electroanalysis* 10, 355-363.
- Tercier M. L., Parthasarathy N., Buffle J. 1995. Reproducible, reliable and rugged hg-plated ir-based microelectrode for in-situ measurements in natural waters. *Electroanalysis* 7, 55-63.
- Tu X. H., Chu Y. Q., Ma C. A., Mo Y. P., Chen Z. Y. 2008. Electrochemical behavior of aluminium electrode in  $\text{LiNO}_3\text{-KNO}_3$  molten salt. *Acta Physico-Chimica Sinica* 24, 665-669.
- Turner D. R. 1984. Relationships between biological availability and chemical measurements. *Metal Ions in Biological Systems* 18, 137-164.
- Vytras K., Svancara I., Metelka R. 2002. A novelty in potentiometric stripping analysis: Total replacement of mercury by bismuth. *Electroanalysis* 14, 1359-1364.
- Wang J. 2005. Stripping analysis at bismuth electrodes: A review. *Electroanalysis* 17, 1341-1346.
- Wang J. 2006. *Analytical electrochemistry*. Hoboken, N.J.: Wiley-VCH.
- Wang J., Deo R. P., Thongngamdee S., Ogorevc B. 2001a. Effect of surface-active compounds on the stripping voltammetric response of bismuth film electrodes. *Electroanalysis* 13, 1153-1156.
- Wang J., Lu J., Hocevar S. B., Farias P. A. M., Ogorevc B. 2000. Bismuth-coated carbon electrodes for anodic stripping voltammetry. *Anal. Chem.* 72, 3218-3222.
- Wang J., Lu J. M., Kirgoz U. A., Hocevar S. B., Ogorevc B. 2001b. Insights into the anodic stripping voltammetric behavior of bismuth film electrodes. *Analytica Chimica Acta* 434, 29-34.
- Wang J., Tian B. M., Wang J. Y., Lu J. M., Olsen C., et al. 1999. Stripping analysis into the 21st century: Faster, smaller, cheaper, simpler and better. *Analytica Chimica Acta* 385, 429-435.
- Wang L. H., Wang C. C. 2006a. Electrochemical oxidation of aminophylline at film platinum electrodes, and its determination in cosmetic and pharmaceutical products. *Microchimica Acta* 153, 95-100.
- Wang Y., Qu J. H. 2006b. Electrocatalytic reduction of nitrate in water with a palladium-modified copper electrode. *Water Environment Research* 78, 724-729.
- Wieckowski A. 1999. *Interfacial electrochemistry: Theory, experiment, and applications*. New York: Marcel Dekker.
- Wrona P. K., Lasia A., Lessard M., Menard H. 1992. Kinetics of the hydrogen evolution reaction on a rhodium electrode. *Electrochimica Acta* 37, 1283-1294.

- Yang Y. F., Denuault G. 1996. Scanning electrochemical microscopy (secm): Study of the adsorption and desorption of hydrogen on platinum electrodes in  $\text{Na}_2\text{SO}_4$  solution (pH=7). *Journal of Electroanalytical Chemistry* 418, 99-107.
- Yoshida Z. 1981. Preparation of an ideal thin mercury film electrode and its electrochemical property. *Bulletin of the Chemical Society of Japan* 54, 562-567.
- Yosypchuk B., Novotny L. 2002a. Cathodic stripping voltammetry of cysteine using silver and copper solid amalgam electrodes. *Talanta* 56, 971-976.
- Yosypchuk B., Novotny L. 2002b. Nontoxic electrodes of solid amalgams. *Critical Reviews in Analytical Chemistry* 32, 141-151.
- Young J. S., Gurtisen J. M., Apts C. W., Crecelius E. A. 1979. The relationship between the copper complexing capacity of sea water and copper toxicity in shrimp zoeae. *Marine Environmental Research* 2, 265-273.
- Yuan A. B., Xu N. X. 2001. Electrochemical studies of the nickel electrode with cobalt modification. *Journal of Applied Electrochemistry* 31, 245-250.
- Zirino A., Lieberman S. H., Clavell C. 1978. Measurement of copper and zinc in San Diego Bay by automated anodic stripping voltammetry. *Environ. Sci. Technol.* 12, 73-79.



**Papers I-VIII are not included due to copyright**

