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Automatic monitoring systems for trace metals in natural and waste water

Nafion coated solid metal electrodes for sensitivity enhancement and stability improvement

Thesis for the degree of Philosophiae Doctor

Trondheim, September 2010

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ISBN 978-82-471-2295-2 (printed ver.)
ISBN 978-82-471-2296-9 (electronic ver.)
ISSN 1503-8181

Doctoral theses at NTNU, 2010:162

Printed by NTNU-trykk

SUMMARY

Voltammetry is one of a few analytical methods, suitable for on-line monitoring of trace metals and is sufficiently sensitive in the low µg/L range for this purpose. The advantages of in-situ use of voltammetry are low cost and no or minimal sample change, since the sample is taken automatically and analysis is performed immediately without a need to collect a sample manually risking contamination and metal loss. Automatic monitoring is essential to record the natural variations of metal concentration in natural or industrial water and registration of accident due to natural or anthropogenic reasons.

Remote monitoring of trace metals is of special importance due to their biological role. For that reason extensive research has been carried out internationally to develop suitable monitoring methods. The introduction of the innovative solid silver amalgam and other solid metal electrodes made the use of voltammetry suitable for remote monitoring without the use of toxic electrode materials.

An automatic trace metal system (ATMS) in combination with solid silver amalgam electrode has been applied for long time monitoring of zinc and iron in waste water. The system worked automatically with manual maintenance every five days. Sample taking, addition of electrolyte solution, stirring, chemical analysis, electrode cleaning and cell draining were carried out automatically, while electrode polishing, filter changing and calibration were carried out manually every five days. For comparison, verification and to provide a better insight into the complex waste water matrix manual samples have been taken regularly and analyzed with ICP-MS. From data obtained from those two analytical methods a speciation study was performed.

The automatic voltammetric system for continuous monitoring of trace metals has been applied in three different locations for monitoring of trace metals in different water samples. River water and drainage water has been used as complex natural water matrixes. A solid silver amalgam electrode has been used as a working electrode. The systems have been fully automated to measure the labile concentration of trace metals for a long time monitoring and store the collected data. Manual maintenance has been performed to calibrate the systems and to clean the working electrodes. Additionally, random samples have been collected manually and analyzed by ICP-MS for the total dissolved metal concentration for data verification and getting better insight into sample matrix.

Development of the ATMS has provided an opportunity to monitor earthquake precursor in ground water. A monitoring station has been installed in Husavik, Northern Iceland, for monitoring of trace metals in a ground water. The monitored concentration of metals clearly indicated changes in the ground water prior to the earthquake. The results revealed increased electrolabile concentrations of zinc, iron

and copper 7-8 days before the earthquake. The increased concentrations lasted until the occurrence of the earthquake and were possible to monitor by the ATMS.

The characterization and application of a Nafion coated solid silver amalgam electrode has been tested for the determination of trace metals by differential pulse anodic stripping voltammetry (DPASV). Effect of model surfactants, commonly presented in natural water sources has also been investigated. It has been found that Nafion coated electrode is useful in surfactant containing samples. The performance of the Nafion coated silver amalgam electrode has been investigated and compared to uncoated silver amalgam electrodes. The modification of the electrode yields higher sensitivity. Moreover, the long time use of Nafion film and practical application has been tested by the use of DPASV in polluted river water sample and has shown to work optimal for 2 weeks.

New electrodes made of silver germanium and silver antimony have been tested and found to be suitable for determination of metals by DPASV with very good linearity. This type of electrodes extends potential window to both positive and negative direction. Additionally, very good sensitivity for cadmium has been observed. The practical application has been tested for applying the electrodes in monitoring station to monitor zinc concentration in polluted river water. Moreover, Nafion coating has been applied and has been found to be advantageous considering electrode stability.

The aim of this work has been to test silver amalgam and other solid metal electrodes for application in natural and environmental water samples for use in long time on-line monitoring in field. The papers included in this thesis prove successful applications of these electrodes in different environmental matrixes. The results provide positive evidence about the ability of voltammetry in combination with solid metal electrodes (bare and modified with Nafion) as a working electrodes to be employed in automatic monitoring of trace metals in polluted water with minimal sample pretreatment and minimal maintenance of the system. The use of solid metal electrodes avoids the use of liquid mercury in voltammetric analyses, and offers an environmental friendly alternative suitable for use in field. Due to ease to use, non-toxic fabrication materials, wide cathodic potential window, long time stability, and good sensitivity these electrodes can be applied for continuous online monitoring in various environmental and industrial solutions. They are also easy to modify and this extends the application even further. Several experimental projects at different locations and in different water samples (river-, sea-, ground-, drainage- and waste water) have shown sufficiently long time stability without the need for physical presence for maintenance. These results strongly indicate that further developed and improved method may in future be used as a commercial warning system for environmental pollution accidents.

CONTENTS

List of papers included in the thesis

I. K. Strasunskiene, Ø. Mikkelsen, K. H. Schrøder, M. Rydningen, 2006. Continuous monitoring of trace metals in waste water effluents using voltammetric system. *Young researchers 2006, 279-286*. IWA publishing, London, UK.

Author contribution: I am the main author of the paper. I had performed all the field experiments in cooperation with a Master student at that time, M. Rydningen. I have done data analysis, evaluation and most of the writing with valuable comments and suggestions from the other co-authors.

II. Ø. Mikkelsen, K. Strasunskiene, S. M. Skogvold, K. H. Schrøder, C. C. Johnsen, M. Rydningen, P. Jonsson, A. Jonsson, 2007. Automatic voltammetric system for continuous trace metal monitoring in various environmental samples. *Electroanalysis,* 19, 2085-2092.

Author contribution: I had performed all the field experiments in one of the three locations described in this paper. I had contributed with data analysis, evaluation and writing of the paper.

III. Ø. Mikkelsen, S. M. Skogvold, T. B. Østerbrød, K. Strasunske, K. H. Schrøder, L. Claesson, A. Skelton. Continuous monitoring of heavy metals in groundwater as a tool for the detection and verification of earthquake precursors (*under preparation*).

Author contribution: I had contributed with laboratory and field experiments that had created a background to field experiments described in this paper. I had contributed with comments and refinement of the paper.

IV. Ø. Mikkelsen, K. Strasunskiene, S. M. Skogvold, K. H. Schroder, 2008. Solid alloy electrodes in stripping voltammetry. *Current Analytical Chemistry*, 4, 202-205.

Author contribution: This review paper is based on the experience from laboratory and field experiments performed earlier by all the authors. I had contributed revising different parts of the paper.

V. K. Strasunske, Ø. Mikkelsen, G. Billon, 2010. Nafion coated silver amalgam electrode for determination of trace metals by anodic stripping voltammetry. *Electroanalysis*, 22, 501-507.

Author contribution: I am the main author of this paper. I had performed all the laboratory and field experiments described in this paper, data analysis, evaluation and writing with valuable comments and suggestions from the other co-authors.

VI. K. Strasunske, Ø. Mikkelsen, E. Petroix, 2010. Silver germanium and silver antimony electrodes for determination of trace metals by anodic stripping voltammetry. Submitted to *Electroanalysis*.

Author contribution: I had performed all the field experiments, field data analysis and evaluation. I had performed part of laboratory data evaluation and written significant parts of the paper with valuable suggestions from Ø. Mikkelsen.

Abbreviations

AAS	Atomic absorbtion spectroscopy
ASV	Anodic stripping voltammetry
ATMS	Automatic trace metal system
BDD	Boron doped diamond (electrode)
BFE	Bismuth film electrode
CA	Cellulose acetate
CME	Chemically modified electrode
DME	Dropping mercury electrode
DPASV	Differential pulse anodic stripping voltammetry
EDTA	Ethylenediaminetetraacetic acid
GF AAS	Graphite furnace atomic absorbtion spectroscopy
HMDE	Hanging mercury drop electrode
ICP-AES	Inductively coupled atomic emission spectroscopy
ICP-MS	Inductively coupled plasma mass spectroscopy
MFE	Mercury film electrode
PI	Phase inversion (process)
SWASV	Square wave anodic stripping voltammetry
VIP	Voltammetric in-situ profiling (system)

Acknowledgements

The work presented in this thesis was carried out at the Norwegian University of Science and Technology (NTNU) between 2005 and 2010 under the supervision of professor Øyvind Mikkelsen. Financial support from the Department of Chemistry is gratefully acknowledged.

I am grateful to my supervisor professor Øyvind Mikkelsen for his positive attitude, his valuable ideas, for sharing his enormous amounts of knowledge and practical experience. Thanks for creating stress-free working environment, for his effort to find time to help, for providing me with a lot of ideas and giving me freedom to choose the working directions and face challenges myself. Thanks to professor emeritus Knut H. Schrøder for being my supervisor for the first years of my studies.

I thank my colleagues for warm social working environment. Special thanks to Silje Skogvold and Beatriz Louriño Cabana with whom I've been sharing office during different periods of this work. I thank them for being friendly, cheerful and helpful. Thanks to their natural ability to help me to see a bright side of life. Thanks to Silje for being the social centre of the group. Thanks to Beatriz for her help and support during my research stays in France.

I thank former Master students of the group of Analytical Chemistry to whom I have worked together with. Special thanks to Marion Rydningen with whom I've been working closely during my first years of PhD. Thanks for the productive cooperative work at the monitoring station, lots of discussions and big amount of work, for support and being positive. Thanks to Solveig Herman for her cooperation during our work supervising students at the laboratory experiments and her support and help taking courses. Thanks to Ingvild Tronstad and Elisabeth Neerland for their friendliness and good humor.

Thanks to Gabriel Billon for the productive cooperation during my research visits to France, also for his practical help and interesting scientific discussions. Thanks to Ludovic Lesven and Adeline Charriau for creating warm social working environment and their good humor during my research stay in Lille.

Thanks to technical staff of the faculty and department for their help. Special thanks to Kari Tanem, Gunnar Svare for providing me with all the necessary laboratory equipment and glasswares, their good humor and their advices. Thanks to them for always finding time to help whenever I was asking. Thanks to Stein Almo, Fredrik Strand, Jan Ole Sundli for the helping with problems regarding technical and electronical equipment, their ability to find and fix the problems and their suggestions for optimal equipment work. Thanks to Ketil Joner for manufacturing the electrodes, Roger Arvik for ordering reagents, Syverin Leirhagen for ICP–MS analyses and always having enough time to discuss the results. Thanks to Rahman for being a reliable office colleague and sharing office with me during my last year of

PhD. I thank him for creating a quiet environment that helped me to concentrate well during the period of the writing of the thesis.

Thanks to the administrative staff of the department for providing a necessary infrastructure and help to perform smoothly all indispensable administrative routines. Thanks for their effective help and for performing their daily duties with a smile.

Most of all I am very grateful to my family. Special thanks go to my beloved husband Darijus for being supportive and encouraging through all these years. Thanks for his encouragement to take the PhD and for his support to finish it, for his understanding and being positive, for enormous amounts of practical help, and for believing in me. Thanks for his encouragement to face the challenges and for his suggestions on how to solve the problems.

Thanks to my kids for helping me understand the important things in my life. I am grateful to my lovely son Simonas for giving my life new perspectives and for teaching me patience, to my sweet daughter Monika for her joy, smiles, and the opportunity to reflect on my work during the maternity leave. I thank them for making my every day special and my life meaningful.

Trondheim, October 2010
Kristina Strasunske

I. INTRODUCTION

Trace metals in natural water samples are measured routinely and controlled by municipalities. Concentration of trace metals in natural waters varies widely as a function of time, depending on the discharger source, season, types of urban activities, etc. To measure variations it is advantageous to carry out remote measurements automatically in the field instead of carrying out one or two weekly analyses in laboratories. This would allow to act as soon as possible in case of errors or illegal activities, and make possible to spread immediately such information for general, public e.g., via Internet.

The Water Framework Directive of the European Union includes a wide range of measures aimed at achieving good quality status in all waters (European Commission, 2007; European Commission, 2008). The number of methods, available for remote monitoring is relatively limited. This is due to the requirement of a long-term stability of the measuring system without a need for human presence. Furthermore, such systems must have a sufficient sensitivity for trace level detection. Another point is that equipment for environmental surveillance cannot introduce any risk for pollution. It is also desired that the equipment is not too expensive to carry out multiple daily measurements as well as enable numerous of installations. Therefore, voltammetry is one of a few analytical methods, suitable for on-line trace metal monitoring and sufficiently sensitive in the low μg/L range for this purpose.

The advantages of in-situ use of voltammetry are low cost and no or minimal sample pretreatment, since the sample is taken automatically and analysis is performed immediately without a need to collect a sample manually risking contamination and metal loss. Automatic monitoring is essential to record the natural variations of metal concentration in natural water samples and registration of accident due to natural or anthropogenic reasons. Automatic instrumentation renders a possibility of automatic surveilance and of early warning.

Electroanalytical methods have been widely used in scientific studies and monitoring of natural water as well as industrial samples. Voltammetry is one of the most widespread among these techniques. The method permits the determination of a great number of metals with a low detection limit (Brainina & Neyman, 1993). Remote monitoring of trace metals like zinc, iron, copper, cadmium, mercury is of special importance due to their biological role. For that reason extensive research has been carried out to develop suitable monitoring methods. The introduction of the innovative solid silver amalgam and other solid metal electrodes (Mikkelsen & Schrøder, 2000a; Mikkelsen & Schrøder, 2000b; Mikkelsen & Schrøder, 2004) made the use of voltammetry suitable for remote monitoring with sufficient sensitivity and without the use of a toxic liquid mercury. The automatic voltammetric system (ATMS) in combination with these electrodes, designed for early warning and continuous monitoring of water resources had successfully been applied for long time monitoring in river water (Lesven et al., 2009; Mikkelsen et al., 2005; Mikkelsen et al., 2007; Strasunske et al., 2010), sea water (Mikkelsen, et al., 2005), industrial water (Mikkelsen et al., 2003), drainage and waste water (Mikkelsen et al., 2007) and ground water (Mikkelsen et al., in prep.).

Voltammetry has the advantage of being useful for speciation studies. Knowledge of trace element speciation in waters is essential in order to understand aquatic toxicity and bioaccumulation, as well as the partitioning of elements between water, colloids and particulate phase. In natural waters only very small percentages of the dissolved metals are present as free metal ion – most of the metal is adsorbed to colloidal particles or combined in complexes. For aquatic toxicity studies, the aim of the measurement is to determine the fraction of total dissolved metal (the toxic fraction) that will react with and will be transported across a biological membrane such as a fish gill. Voltammetry is a very useful method to measure the fraction of the electroactive metal in a sample, i.e. the fraction of total dissolved metal that can be deposited onto the working electrode at the natural pH of the sample. The electroactive fraction is in many cases assumed to be approximately equal to the toxic fraction (Florence et al., 1992). Other analytical techniques, e.g. AAS, ICP-MS, GF-AAS, are not applicable to direct trace metal speciation studies because they measure the total metal concetration only. The measurement of the total concentration of metal in natural water to assess the toxicity can be misleading. Depending on the chemical forms of the metal, a water with high total metal concentration may in fact be less toxic than water with a lower concentration (Florence, 1977).

1.1. VOLTAMMETRY

Voltammetry is an electrochemical technique that is based on the measurement of the current response to an applied potential. The current is proportional to the metal concentration in the sample. This technique can measure any chemical species that is electroactive (Wang, 2000).

Voltammetry has been an important and widespread analytical technique. Since 1950 to 1980 it was the dominating analytical method for the determination of several important trace metals and important organic compounds. Although the range of organic and inorganic compounds that can be measured by voltammetry is very broad, the major type of application is analysis of metal ions (Buffle & Tercier Waeber, 2000; Buffle & Tercier Waeber, 2005). Some of the most important voltammetric techniques are briefly reviewed in the following subsections.

1.1.1. Pulse Voltammetry

Pulse voltammetrical techniques are aimed to lower the detection limits of voltammetric measurements. By substantially increasing faradaic and non faradaic current ratio, such techniques permit convenient quantification down to 10^{-8} M level. Because of their greatly improved performance, modern pulse techniques have largely supplanted classical polarography in the analytical laboratories. The various pulse techniques are based on a sampled current potential step experiment. A sequence of such potential steps is applied to the working electrode. After the potential is stepped, the charging current decays rapidly to a negligible value, while the faradaic current decays more slowly. Thus, by sampling current late in the pulse life, an effective discrimination against the charging current is achieved. The difference between the various pulse techniques is the excitation waveform and the current sampling regime (Wang, 2000).

Normal pulse voltammetry

Normal pulse voltammetry consists of a series of pulses of increasing amplitude. Between the pulses, the electrode is kept at a constant potential at which no reaction of the analyte occurs. The amplitude of the pulse increases linearly (Wang, 2000).

Differential pulse voltammetry

Differential pulse voltammetry is a very useful technique for measuring trace levels of organic and inorganic species. In this technique, fixed magnitude pulses – superimposed on a linear potential ramp – are applied to the working electrode. The current is sampled twice, just before the pulse application and again late in the pulse life, when the charging current has decayed. The first current is then instrumentally subtracted from the second and the difference is plotted versus the applied potential. The resulting differential pulse voltammogram consists of current peaks, the height of which is directly proportional to the concentration of the corresponding analytes. The differential pulse operation results in a very effective correction of the background current. Accordingly, measurements are allowed at concentration as low as 10^{-8} M (Wang, 2000).

1.1.2. Stripping analysis

Stripping analysis is a very sensitive electrochemical technique for measuring trace metals (Wang, 1985). Its remarkable sensitivity is attributed to the combination of an effective preconcentration step with advanced measurement procedures that generate a favorable signal-to-background ratio. Since the metals are preconcentrated into the electrode by factors of 100 to 1000, detection limits are lowered by 2-3 orders of magnitude compared to solution-phase voltammetric measurements (Wang, 2000).

Stripping analysis is a two step technique. The first step involves the electrolytic deposition of a small portion of the metal ions in solution onto the electrode surface to preconcentrate metals. This is followed by the stripping (the measurement) step of the deposit, which involves the dissolution (stripping) of the deposit (Wang, 2000).

Anodic stripping voltammetry

Anodic stripping voltammetry (ASV) is an extremely sensitive technique available for determination of trace metals in water samples and has the advantage of simultaneous determination of metals at concentrations as low as 10^{-10} M (Florence, 1984). It is the most widely used form of stripping analysis. In this case, the metals are preconcentrated by electrodeposition onto the electrode surface. The preconcentration is done by cathodic deposition at a controlled time and potential. The deposition potential is usually by 300 mV more negative than the least easily reduced metal ion to be determined. The metal ions reach the electrode surface by diffusion and convection, where they are reduced and concentrated. The convective transport is achieved by electrode rotation or solution stirring. The duration of the deposition step is selected according to the concentration level of the metal ion in question. Following the preselected time of the deposition, the forced convection is stopped and the potential is scanned anodically, either linearly or in a more sensitive potential-time (pulse) waveform that discriminates against the charging background current. During the anodic scan, the metals are reoxidised, stripped out from the electrode surface in an order that is a function of each metal standard potential. The voltammetric peak reflects the time dependant concentration gradient of the metal at the working electrode during the potential scan. Peak potential serves to identify the metals in the sample. The peak current depends upon various parameters of the deposition and stripping steps; as well as on the characteristics of the metal ion and the electrode geometry; and it is proportional to the concentration of the metal ions in the sample.

Potentiometric stripping analysis

Potentiometric stripping analysis is a technique where potentiostatic control is disconnected following preconcentration, and the concentrated metals are reoxidised by an oxidising agent presenting in the solution or an oxidising current. A stirred solution during the stripping step is used in order to facilitate the transport of an oxidant (Wang, 2000).

Adsorbtive stripping voltammetry

Adsorbtive stripping voltammetry significantly enhances the scope of stripping measurements towards numerous trace elements (van den Berg, 1991). This method involves formation, adsorbtive accumulation and reduction of a surface active complex of the metal. Most procedures involve the reduction of the metal in the adsorbed complex. The response of the surface confined species is directly proportional to its surface concentration (Wang, 2000).

Cathodic stripping voltammetry

Cathodic stripping voltammetry is the “mirror image” of ASV. It involves an anodic deposition of the analyte, followed by stripping in a negative going potential. The resulting reduction peak current provides the desired quantitative information (Wang, 2000).

1.1.3. Challenges in stripping analysis

The major types of interferences in stripping analysis are overlapping stripping peaks, caused by similarity in the oxidation potentials of the metals, the presence of organic surface active compounds that adsorb on the electrode surface and inhibit the metal deposition, and the formation of intermetallic compounds (Wang, 2000). The interference of overlapping stripping peaks can be minimised by introducing a separation step prior to the stripping measurement (Florence & Farrar, 1974) using a supporting electrolyte with a suitable complexing agent that shifts the stripping peak potentials according to the stability, composition and concentration of the complexing agent (Bonelli et al., 1980), using of surface active agents to mask or shift the stripping peaks (Glodowski & Kublik, 1980) and lowering the deposition potential until the metal with the more negative deposition potential is not deposited (Florence, 1974). Interference of intermetallic compounds can be minimized by reducing a deposition time (Batley & Florence, 1974), adding a “third” element that forms a more stable intermetallic compound with one of the components of the binary system (Copeland et al., 1974; Neiman et al., 1980) and by choosing a suitable supporting electrolyte (Cofre & Brink, 1992). In order to overcome the organic interferences, removal or destruction of organic matter by UV irradiation (Monticelli et al., 2009; Obata et al., 2006) or ozone oxidation (Clem & Hodgson, 1978) procedures may be considered prior to the stripping analysis of the organic-rich samples. For samples with low organic content, a standard addition method can be used (Brihaye & Duyckaerts, 1983). Finally, electrode modification by different films for this purpose is used (it is reviewed in the section under electrode modification).

1.2. ELECTRODES IN VOLTAMMETRY

The choice of working electrode in voltammetry is of outmost importance. The requirements for the electrodes are as follows: electrochemical inertness over a broad potential window, high overvoltage towards hydrogen and oxygen evolution, low residual current, low ohmic resistance, the possibility of a sufficiently simple surface regeneration. All these mentioned factors should provide high accuracy and sensitivity; good reproducibility and low detection limit (Brainina & Neyman, 1993). Stability over time is also a very desirable property considering electrode use for in-situ long time monitoring.

The response of the electrode depends on the electrode material, processes taking place on the electrode surface and electrode surface conditions (Brainina & Neyman, 1993). Some of the most common working electrodes are reviewed in the following sections.

1.2.1. *Mercury electrodes*

Since the invention of polarography by Heyrovsky (Koryta, 1960), mercury has been established as the electrode of choice. The dropping mercury electrode (DME) and the hanging mercury drop electrode (HMDE) have been used successfully in countless applications for determination of organic and inorganic compounds. The DME is now replaced by HMDE (Economou & Fielden, 2003). The HMDE is a popular working electrode for a stripping analysis and cyclic voltammetry (Wang, 2000). One of the most attractive properties of HMDE is the high overvoltage towards the hydrogen evolution reaction, extending the working window significantly in the negative direction that enables to measure compounds appearing in the more negative potential range even in relatively acid solutions. Another advantage using mercury is that diluted, liquid amalgams are formed with many metals during the reduction process, which is important in stripping techniques and contributes to better-defined voltammetric curves and partly prevents intermetallic compound formation. The third advantage is the possibility to restore a new and clean electrode surface unaffected from any previous scan, simply by knocking off the old drop and by forming a new one (Wang, 2000).

Some examples of the HMDE application include the determination of atrazine (dos Santos et al., 2004), determination of Sn (II) in Technetium cold kits (Decristoforo et al., 1998), determination of captopril (Passamonti et al., 1987), determination of traces of surfactants in distilled, potable, untreated water and supporting electrolyte (Bernadkiewicz et al., 1981), determination of lead in igneous rocks (Calderoni, 1981), determination of trace amounts of mercury and oxygen in aqueous solutions (Kemula & Sacha, 1979).

The drawbacks of the HMDE, that, unlike the solid electrodes, they are mechanically unstable (the drops are easily dislodged), and therefore not suitable for on-line field analysis (Economou & Fielden, 2003). Moreover, the HMDE is not suitable for modifications by chemical reagents or permselective coatings that improve the analytical properties (selectivity or sensitivity). Well known other drawbacks of the mercury drop electrode is the easy oxidation of mercury occurring from about 0 V, potential risks of poisoning, contamination and disposal, and the skepticism to use mercury in field systems due to claimed toxicity aspects. Mercury is a first rate hazard leading to severe poisoning and heavy diseases (Chang & Cockerham, 1994). The potential risk associated with mercury have led that some countries, like USA and Japan completely banned mercury (Gustafsson, 1995). Electrodes made of non-toxic materials tend gradually replace mercury electrodes in electroanalysis (Stozhko et al., 2008).

1.2.2. *Mercury film electrodes*

Mercury film electrodes (MFE) are an alternative to mercury electrodes and have been widely used for a stripping analysis and flow amperometry (Wang, 2000). They are prepared by coating a suitable substrate (usually glassy carbon or metal) with thin film (10 – 100 µm) of metallic mercury. The advantages are small size, larger surface-to-volume ratio, mechanically more stable than mercury drops, offer great scope of different cell configurations and possibility of modification of the surface. Additionally, the consumption of metallic mercury is minimized, comparing to HMDE.

Mercury film electrodes are widely used for various analyses. The application examples include the determination of sulfur compounds in gasoline (Serafim & Stradiotto, 2008), ultratrace determination of atrazine in soil and water (Maleki et al., 2007), simultaneous determination of lead, copper and cadmium (Sherigara et al., 2007) and measurements of trace beryllium (Wang et al., 2006).

The mercury film, formed on a glassy carbon surface is actually composed of many droplets. As a result of being not pure mercury surface, such film electrodes exhibit a lower hydrogen overvoltage and higher background currents. The other limitations are lower precision, limited potential range, difficulties to achieve a stable baseline and the difficulty in preparation, cleaning and reactivation of the mercury film (Economou & Fielden, 2003).

The disadvantages of mercury film electrodes on metal substrate are unstable thickness and composition of the mercury film as a result of mercury penetration into the bulk of the metal, resulting in an unstable electrode surface area and therefore poor reproducibility. Another problem is formation of different concentration amalgams as well as possible interaction of the analyte metals deposited on the electrode with substrate metal (Brainina & Neyman, 1993). Additionally, mercury salts, used for the film may also be toxic (Chang & Cockerham, 1994; Stumm & Morgan, 1996).

Mercury film ultramicroelectrodes, based on coverage of carbon fiber or carbon microdisk surfaces, have also received increasing attention. Some examples of such electrodes application include the determination of lead in natural waters by stripping voltammetry (Bumber et al., 2000) and determination of lead in human hair by anodic stripping voltammetry (Peng & Jin, 1992). Very good sensitivity for lead is reported using mercury monolayer carbon fiber electrode (Munteanu et al., 2009).

1.2.3. Carbon electrodes

Carbon materials are mercury free current conducting electrode materials, possessing some attractive features and are currently widely used in electroanalysis. Carbon electrodes are used for various sensing and detection applications due to their broad potential window, low background current and low cost (Wang, 2000). The carbon surface can adsorb various compounds by nonspecific physical sorbtion and the specific chemisorbtion. The complexation capacity of carbon materials is higher than that of metals. Carbon surface is electrochemicaly inert over a wide range of potential. These properties make the carbon electrodes very wide used (Stozhko et al., 2008).

Carbon materials can form strong covalent bonds with some surface modifiers and are suitable for electrode modification. Therefore, carbon is the most common substrate for mercury film electrodes (Brainina & Neyman, 1993; Wang, 1985). Carbon electrodes modified with mercury film are less affected by surfactants than are solid electrodes. These types of electrodes are widely used in electroanalytical applications (Adeloju & Pablo, 1994; Farghaly, 2004; Guo & Guadalupe, 1999; Ping Wu, 1994). The reason for this is that the carbon electrodes modified with mercury combine the advantages of carbon and mercury electrodes, including a wide interval of the working potential, the rare occurrence of intermetallic interaction at these electrodes, and adequate reproducibility of the electrode surface.

One of the disadvantages of carbon electrodes is that electron transfer rate is slower comparing to metal electrodes. The electron transfer reactivity is strongly affected by the origin and history of the carbon surface (Chen & McCreery, 1996; McCreery, 1991). The type of carbon as well as the pretreatment method has a profound effect on the electrodes analytical performance. The most popular carbon electrode materials are glassy carbon, carbon paste, carbon fiber, screen printed carbon strips, carbon films, various graphites or boron doped diamond (Wang, 2000). Some of the most common types are reviewed in the following sections.

Glassy carbon

Glassy carbon has been very popular because of its excellent mechanical and electrical properties, wide potential window, chemical inertness (solvent resistance), and relatively reproducible performance (Wang, 2000). It is isotropic, almost glass-tight, very hard, a good conductor, stable in very corrosive media and has low porosity. The adsorbtivity is low compared to other structured graphite materials and it results in low sensitivity of the unmodified electrodes (Hardcastle et al., 2000; Tomcik et al., 2003). The detection limit is reduced by increasing accumulation time, using additional accumulation operations, like ultrasonic extraction or modifying the surface (Stozhko et al., 2008).

The glassy carbon material is prepared by a carefully controlled heating program of a premodelled polymeric resin body in an inert atmosphere (Bokros, 1977). Surface pretreatment by polishing is usually employed to create active and reproducible electrodes to enhance their analytical performance. Additional activation steps such as electrochemical, chemical, heat or laser treatments are also used. The improved electron transfer reactivity has been attributed to removal of surface contaminants, exposure of fresh carbon edges and an increase in the density of surface oxygen groups (McCreery, 1991).

Some of the application of glassy carbon electrodes includes the determination of manganese (Di & Zhang, 2003), determination of free chlorine (Kodera et al., 2005), determination of bovine serum and transferin (Suznjevic et al., 2001), and determination of EDTA species in water (Zhao et al., 2003).

Carbon paste

Carbon paste electrodes are made from a homogenized paste consisting from a graphite powder mixed with various organic binders (pasting liquids). Compared to other carbon electrodes, they have a well developed surface with a high adsorbtivity of various compounds. This property is successfully used for the modification and adsorbtive accumulation of the substances to be measured (Stozhko et al., 2008). The modifier is simply mixed together with the graphite/binder paste. A disadvantage of carbon paste electrodes is the tendency of the organic binder to dissolve in solutions containing appropriate amount of organic solvent (Wang, 2000).

Carbon paste electrodes have the advantage of low cost and very low background current (Olson & Adams, 1960; Olson & Adams, 1963; Rice et al., 1983; Urbaniczky & Lundstrom, 1984). The paste composition strongly affects electrode reactivity with increase in pasting liquid content decreasing electron transfer rates, as well as the background current (Rice et al., 1983). In the absence of pasting liquid dry graphite electrodes yield very rapid electron transfer rate, approaching those of metallic surfaces. Despite their growing popularity, the exact behavior of graphite paste electrode is not fully understood (Wang, 2000).

Carbon paste electrodes are commonly used for the determination of metal ions. Some of the application examples include the determination of manganese (Rezaei et al., 2008), nanomolar concentrations of cadmium (Shamsa & Torabi, 2006), trace silver (Li et al., 2005) and trace lead (El Mhammedi et al., 2009b).

Carbon fiber

Carbon fiber electrodes are produced in connection with the preparation of high strength composites, by high temperature pyrolysis of polymer textiles or via catalytic chemical vapor deposition (Wang, 2000). Different carbon fiber microstructures are available, depending upon the manufacturing process. They can be classified into a three broad categories: low-, medium- and high-modulus types. The last type is most suitable for electrochemical studies because of its well ordered graphite-like structure and low porosity (Csoregi et al., 1993). Improved electron transfer performance can be achieved by various electrode pretreatment procedures, including electrochemical activation or heat treatment (Feng et al., 1987). Most analytical applications rely on fibers of 5-20 μm diameters that provide the desired radial diffusion. The main advantage of carbon fiber microelectrodes is their small size. Additionally, they have a large chemical resistance and are good current conductors (Stozhko et al., 2008). The examples of application of these electrodes include the determination of zeptomole quantities of lead (Munteanu et al., 2009), biological thiols (Munteanu et al., 2009), picomolar concentrations of copper (Munteanu et al., 2009) and metronidazole (Bartletta et al., 2005).

Boron doped diamond

The frequent use of carbon electrodes in electrochemical applications makes the production of diamond films on carbon substrates an alternative procedure for increasing the lifetime and electrode superficial area. In addition, the conductivity control of diamond films through the boron doping level control may guarantee a suitable electrode keeping its necessary chemical inertness (Ferreira et al., 2002).

Diamond displays many unique properties such as chemical inertness, extreme hardness and thermal conductivity, low friction coefficient, and high charge carrier mobilities. Natural diamond with extremely high inherent electrical resistivity cannot be used as an electrode material. However, boron-doped diamond (BDD) becomes conductive. A distinct feature of BDD in electrochemistry is a very high overpotential for both oxygen and hydrogen evolution (Pleskov et al., 1987) and wide potential window ranging from -0.75 to 2.35 V. Additionally, no oxide formation and reduction reactions between oxygen and hydrogen evolution occur on BDD surface. The BDD electrodes also possess very low capacitance and the largest potential window measured in aqueous electrolytes compared with conventional electrode materials including carbon-based and metallic electrodes. Low adsorption of contaminants leads to low fouling and this feature is very important for an extended use (Luong et al., 2009). Therefore, the BDD electrodes exhibit high stability, high sensitivity, and a low detection limit. Diamond electrodes can be modified by nanoparticles via ion implantation or electrodeposition. The advantageous properties of the electrodes are their inherent stability with very low background currents (Luong et al., 2009). Some of the disadvantages are high price and difficulty to make in ordinary laboratories. Some of the examples of the application of diamond electrodes include the determination of metals in aqueous samples (Dragoe et al., 2006; McGaw & Swain, 2006).

1.2.4. Microelectrodes

Miniaturization is a growing trend in the field of analytical chemistry (Wang, 2000). Microelectrodes have gained wide acceptance over the last 15 years due to their favorable analytical properties of enhanced mass transfer, low capacitive currents and minimal ohmic drop. The miniaturization of the working electrodes not only has obvious practical advantages, but also opens some fundamentally new possibilities (Bond, 1994; Wightman, 1981). The term "microelectrode" is reserved for the electrodes with at least one dimension not greater than 25 μm (Wang, 2000). Due to their small dimensions, microelectrodes can be used in conjunction with very small sample volumes, measurements of local concentration profiles, detection in microflow systems and narrow electrophoresis capillaries. The major difference between macro- and microelectrodes is that planar diffusion occurs on the former compared to radial diffusion on the latter (Wang, 2000). Interesting applications include time-resolved probing of dynamic processes in single cells (Kennedy et al., 1993), in vivo monitoring of neurochemical events and use of nanoscopic electrode tips for single molecule detection high resolution spatial characterization of surfaces

(Anderson & Ewing, 1999; Fan et al., 1996). Other attractive property of the microelectrodes is small total currents, making possible to work in highly resistive solutions that would develop large ohmic drop with conventional electrodes. Microelectrode experiments have been reported in low dielectric solvents (Olmos et al., 2000; Safford & Weaver, 1992), aqueous solutions at high temperatures (Daniele et al., 2000), low temperatures (Safford et al., 1992), gaseous phase (Krausa & Schorb, 1999) and in solutions of low ionic strength (Ciszkowska & Stojek, 1999). In addition, those electrodes can be used with little or no supporting electrolyte (Daniele et al., 1996; Jaworski et al., 1995).

The use of electrolyte free media can greatly extend the electrochemical potential window, thus allowing studies of species with very high oxidation potentials. The greatly reduced electrical double layer capacitance of microelectrodes results in electrochemical cells with small RC time constants. It allows high speed voltammetric experiments to be performed on a microsecond time scale and hence to probe kinetics of very fast electron transfer and coupling chemical reactions or the dynamics of processes (Andrieux et al., 1990). Enhanced rates of mass transport of electroactive species arise from the radial diffusion to the edges of microelectrodes. The rate of mass transport to and from the electrode and hence the current density increases with decrease in the electrode size. As a consequence, microelectrodes exhibit an excellent signal to a background ratio in comparison to conventional electrodes. In addition, steady state currents are rapidly attained and the contribution of convective transport is negligible. The wide range of applications of the microelectrodes includes the determination of heavy metals in honey (Sanna et al., 2000), cadmium, lead and copper in rain samples (Abdelsalam et al., 2002), lead in sediment and interstitial water (Pizeta et al., 2005), ultra trace amounts of timolol maleate (Norouzi et al., 2005).

The common materials for constructing microelectrodes are carbon fibers and wires of noble metals such as silver, platinum or gold. The size and geometry of the microelectrodes may also minimize production costs. However, an accurate constructing procedure, long polishing and activation procedures, and mechanical fragility limit the application to short periods. Silver-copper alloy microelectrode has been used for monitoring zinc and lead in river water (Skogvold et al., 2006).

1.2.5. Solid metal electrodes

Solid metal electrodes with extended anodic potential windows have attracted considerable analytical interest. Of the many different solid materials that can be used as working electrodes, the most often used are platinum and gold. Silver, copper, bismuth are also used. An important factor, using solid electrodes is the dependence of the response on the surface of the electrode. The use of such electrodes requires electrode pretreatment and polishing to obtain reproducible results. Mechanical polishing and potential cycling are commonly used (Wang, 2000). Unlike mercury electrodes, solid electrodes present a heterogeneous surface with respect to electrochemical activity (Engstrom, 1984). Such surface heterogeneity leads to deviations from the behavior expected for homogeneous surfaces. The most commonly used solid metal electrodes are reviewed in the next sections.

Gold and platinum electrodes

Platinum and gold are the most used metallic electrode materials (Adams, 1969; Wang, 2000). Such electrodes offer very favorable electron transfer kinetics and a large anodic potential range. In contrast, low hydrogen overvoltage at these electrodes limits the cathodic potential window (to the -0.2 to -0.5V, depending on the pH).

In contrast to the HMDE, solid gold and platinum electrodes do not have a renewable surface and reproducibility is the challenge. Some of the examples of applications of the gold electrodes include determination of inorganic species of arsenic (Yamada et al., 2008), arsenic in aqueous solutions, natural waters and biological material (Kopanica & Novotny, 1998), free chlorine (Kodera et al., 2005), arsenic speciation in potable water (Huang & Dasgupta, 1999), small quantities of arsenic in pure gold samples (Billing et al., 2002), trace telurium in real samples (Khoo & Ye, 2002), selenium in water samples (Bryce et al., 1995), lead and cadmium in natural waters (Bonfil et al., 2002), copper in acetic soil extracts (Beni et al., 2005), copper in drinking water and sea water (Bonfil et al., 1999) and mercury in refined beet sugar (Sancho et al., 2001).

Gold electrodes are also widely used as substrates for self assembled organosulfur monolayers or for stripping measurements of trace metals. Spontaneously adsorbed monolayers of n-alkanethiols ($(XCH_2)_nSH$ with $n > 10$) on gold surfaces, based on the strong interaction between gold and sulfur, are particularly well suited for controlling and manipulating the reactivity at the interface. Such monolayers are commonly formed by immersing the gold electrode overnight in ethanolic solutions containing milimolar concentrations of alkanethiol. The formation of self–assembled organosulfur monolayers has attracted considerable attention due to its many potential scientific and technological applications (Mandler & Turyan, 1996; Zhong & Porter, 1995). In addition to fundamental studies of the structure of such monolayers and long range electron transfer, such applications include chemical sensors and biosensors, information storage devices and lithography (Wang, 2000).

Platinum is widely used as an electrode material. Application of this type of electrodes is limited by positive potentials and therefore such electrodes are supplementary to mercury electrodes (Brainina & Neyman, 1993). Some of the examples of the application of platinum electrodes include the determination of cadmium (El Mhammedi et al., 2009a), silver ions (Zejli et al., 2007), free chlorine (Kodera et al., 2005), mercury (Pinilla et al., 1996). The main drawbacks of platinum electrodes are at cathodic potentials adsorbed hydrogen layers and possible chemical reaction of the electrode material (Adams, 1969).

Silver electrodes

Silver electrodes are used as a substrate for mercury film electrodes or as electroactive electrodes. Silver electrodes have been reported to possess a very good sensitivity particularly for lead. Some of the examples of application of the silver electrodes include determination of nanomolar concentrations of lead and cadmium in drinking and natural water (Bonfil et al., 2002), sub-nanomolar concentrations of lead in river water and drinking water (Kirowa-Eisner et al., 1999) and cadmium and lead in tap water (Mikkelsen & Schrøder, 2001).

Bismuth and bismuth film electrodes

Bismuth electrodes are an interesting and environmental friendly alternative to mercury electrodes. Such electrodes display well defined peaks, undistorted and highly reproducible response, favorable resolution of neighboring peaks, high hydrogen evolution and good signal-to-background characteristics comparable to common mercury electrodes. The attractive stripping behavior of bismuth electrodes reflects the ability of bismuth to form multicomponent alloys with metals. Therefore bismuth electrodes are widely used with applications ranging from the determination of single metals to continuous remote sensing (Wang, 2005). Bismuth film electrodes have a wide cathodic potential range and somewhat limited anodic region due to the oxidation of bismuth.

Bismuth film electrodes (BFEs), prepared by plating a thin bismuth film on a suitable substrate material (usually different forms of carbon), introduced in 2000 by J. Wang have found a wide range of environmental and clinical applications. A disadvantage of BFEs compared to MFEs is a negative anodic limit, since bismuth oxidizes more easily than mercury and formation of non conductive bismuth oxides. The useful potential range is strongly affected by the pH of the solution (Economou, 2005). Formation of non conductive bismuth oxide layers due to passivation of a surface can also be a problem.

BFEs widest application area is trace metal stripping analysis. Some of the examples of application include the determination of lead and cadmium in various environmental samples, including drinking water (Baldo & Daniele, 2004; Paulikaite et al., 2002; Wang et al., 2001), soils (Hutton et al., 2004), biological fluids (Paulikaite et al., 2002), hair and tap water (Demetriades et al., 2004; Kefala et al., 2003; Kefala et al., 2006) and food (Baldo et al., 2003; Baldo & Daniele, 2004); nickel and cobalt in soils (Hutton et al., 2004) and river water (Chatzitheodorou et al., 2004), chrome in tap water, soils and tobacco (Chatzitheodorou et al., 2004).

It has been shown that BFEs are less prone to the interferences of surface active compounds compared to MFEs and especially, covered with Nafion membrane. Research results, reporting better resistance towards surfactants and higher sensitivity, have been published (Kefala et al., 2004; Wang et al., 2001).

1.2.6. Solid metal alloy electrodes

It has been demonstrated during the last decade, that the overpotential towards hydrogen on noble metals can be altered significantly by adding a second compound which possesses a high overvoltage for the hydrogen formation reaction. Even additions of a few percent of the second metal possessing high hydrogen overvoltage were shown to result in a significant increase in the overvoltage towards hydrogen (Mikkelsen & Schrøder, 2000a, Mikkelsen & Schrøder, 2000b; Mikkelsen & Schrøder, 2004, Mikkelsen et al., 2008). Some of the most used metal alloy electrodes are reviewed in the following subsections of this section.

Silver bismuth electrodes

Silver bismuth electrodes behave as a combination of pure silver and pure bismuth electrodes. The overpotential towards hydrogen increases with increasing amount of bismuth added to the alloy. The increase in overpotential makes it possible to detect zinc in acidic solutions. They also exhibit higher sensitivity and better stability as compared to pure silver electrodes and can be used for long time monitoring in natural water samples (Skogvold et al., 2005).

Gold Bismuth electrodes

Mixed gold bismuth electrodes have electrochemical properties somewhat between pure bismuth and pure gold electrodes. The gold bisumth electrodes are very sensitive for copper and mercury. Gold bismuth electrodes exhibit higher sensitivity and better stability as compared to pure gold electrodes. The increase in overpotential towards hydrogen increases with amount of gold added to the alloy. Detection of copper and mercury can be carried out at bare gold electrode; however, long time stability is the crucial factor for use in field apparatus for a long time monitoring. These electrodes have been applied for a long time monitoring in purified scrubbing water from waste incineration plant and river water and have proved to provide very good long time stability (Skogvold & Mikkelsen, 2008).

Solid silver amalgam electrodes

Silver amalgam electrode is an alloy electrode, containing silver powder and liquid mercury at 1:1 ratio by weight (mole ratio 1.85). In this alloy, mercury is bound up as stable solid Ag_2Hg_3 alloy, being non-toxic for analytical purposes. The construction of the silver amalgam electrodes is fast and inexpensive. The technique for constructing this type of electrodes is very similar to the technique as used by dentists for constructing dental amalgam. Typically, 2.5 g fine silver powder and 2.5

g of analytical grade mercury is used for electrode fabrication. This mixture is transferred into a mixing capsule by first introducing mercury and then silver powder. The capsule is then installed in a dental amalgam mixer and mixed for 12 seconds and centrifuged for 3 seconds. Immediately after this process the amalgam paste is filled into the electrode holder and copper wire is inserted in the upper part as electrical conductor. The amalgam is solidified after some minutes but it is kept for at least one day before polishing to a mirror-like surface (Mikkelsen & Schrøder, 2003).

The silver amalgam electrode has been found to act similar to bare silver electrode but with much higher overvoltage towards hydrogen. Solid silver amalgam electrode combines some of the properties of the bare silver electrodes with some of the properties of the mercury electrodes. Silver amalgam material is a solid electrode and solid deposits are formed. On mercury electrodes, liquid mercury amalgams are formed. The formations of intermetalic compounds may be observed in greater extent than for liquid mercury, but use of chloride solution prevents this problem (Mikkelsen & Schrøder, 2003).

The high overpotential to hydrogen evolution reaction allows measurements of trace metals at a sufficiently negative potential to determine zinc, cobalt, nickel and iron (Mikkelsen & Schrøder, 2000a; Mikkelsen & Schrøder, 2000b). The combination of a higher overpotential towards the hydrogen evolution reaction and a better stability for such electrodes extends greatly the range of analytical applications. The non-toxicity and long time stability renders the possibilities for using this type of electrodes for in-situ field measurements.

The production of the solid silver amalgam electrodes have opened up more possibilities for detection of a wide range of metals and in-situ long time metal monitoring. The solid silver amalgam electrode has been successfully used in field applications for online measurements of metals in natural water and waste water. Solid silver amalgam electrode has been applied successfully for long time monitoring for iron and zinc in sea water (Mikkelsen et al., 2005), zinc, iron and copper in river water (Mikkelsen et al., 2005; Mikkelsen et al., 2007), zinc in drainage water, zinc and iron in waste water (Mikkelsen et al., 2007), zinc, iron and copper in groundwater (Østebrød et al., in prep.), manganese in river water (Lesven et al., 2009), zinc and lead in wines (Mikkelsen et al., 2004), zinc, lead, cobalt and nickel in the samples from metallurgical nickel industry (Mikkelsen et al., 2003*)*. A general disadvantage of the silver amalgam electrodes is the limited potential window in the positive direction.

Silver amalgam electrode (silver amalgam paste electrode), constructed and developed by other researches has a slightly different construction. It is a solid silver electrode with platinum wire for electric contact and with mercury layer or mercury meniscus as the active part of the electrode in the earlier versions, then with amalgam paste in the newer versions (Yosypchuk & Novotny, 2001). These types of electrodes are reported to combine the properties of solid metal electrodes with those of paste electrodes. High hydrogen overvoltage allows measurements of compounds such as p-nitrophenols, ascorbic acid, adenine and cysteine with good reproducibility (Yosypchuk & Sestakova, 2007). The useful potential range is limited by the oxidation of electrode material in relatively low positive region. The negative aspects of this type of electrodes are formation of intermetallic compounds and the difficulty to achieve the stability of the active electrode layer.

Silver germanium and silver antimony electrodes

Silver germanium and silver antimony electrodes are new alternative solid metal alloy electrodes. They are made of silver and germanium or antimony and may be added a third or fourth metal such as bismuth or mercury. The electrodes exhibit a very wide potential window to allow measurements of different metals, such as magnesium, zinc, cadmium, lead, and copper. Very good sensitivity for cadmium has been observed. Silver germanium electrode, coated with protective Nafion layer, was used for long time monitoring of zinc in river water and has shown reasonable stability for 12 days (Strasunske et al., 2010).

1.3. APPLICATION OF VOLTAMMETRY

Voltammetry has been an important and widespread analytical technique. Since 1950 to 1980 it was the dominating analytical method for determination of several important trace metals and important organic compounds. Although the range of organic and inorganic compounds that can be measured by voltammetry is very broad, the major type of application is analysis of metal ions (Buffle & Tercier Waeber, 2005). Some of the most important applications of voltammetry are reviewed in the following sections.

1.3.1. Determination of Metals in Various Samples

The remarkable sensitivity, broad scope and low cost of stripping voltammetry have led to a wide application. Over 30 trace elements can be measured in various matrixes by the various versions of stripping analysis. Some of the many examples include useful determination of numerous trace metals in environmental (Desmond et al., 1998; Lau & Cheng, 1998; Locatelli & Torsi, 2000; Locatelli & Torsi, 2001; Wang et al., 1992), food (Brainina et al., 2000; Brainina et al., 2004; Galeano Diaz et al., 2006; Sancho et al., 2001; Qiong et al., 2006), industrial (Maali & Hady, 1998; Maali et al., 2000) and clinical (Brainina et al., 2009; Kajic et al., 2003) samples.

1.3.2. Determination of Complexicity Properties

Determination of complexing properties is another important laboratory application of voltammetry. The speciation of metals is much related to the presence of organic complexing groups. Therefore, the study of metal-ligand interactions to determine stability constants, total ligand concentrations of model or natural complexants is the subject of many studies over years. Various methods of data treatment, obtained from experimental voltammetric measurements, coupled with metal titrations, based on mathematical transformation, partial linearization and optimization calculation have been developed. These techniques are aimed to define complexing properties of natural samples regarding trace metals. Some of the examples include natural waters (Buffle, 1988; Cuculic et al., 2005; Garnier et al., 2005; Mota & Correia dos Santos, 1995), sediments and soils (Correia dos Santos et al., 2001; Pacakova et al., 2000).

1.3.3. Speciation studies

Another application area of voltammetry, rapidly expanded during the last years, is the use of ASV in a speciation analysis. Speciation analysis provides valuable information about different fractions of metal in a water sample and about the likely transport of that metal in a natural water system (Florence, 1984).

There are two main reasons for studying the speciation of elements in waters – to understand either biological or the geochemical cycling of the elements. Biological cycling includes bioaccumulation, bioconcentration, bioavailability and toxicity and geochemical cycling involves the transport, adsorbtion and precipitation of the element in the water system. Now it is well established that no meaningful interpretation of either biological or geochemical cycling can be achieved without speciation information (Borgmann, 1983; Florence, 1983; Turner, 1984). Each different physico – chemical form of an element has a different toxicity, so an analysis of water sample for total metal concentration alone does not necessarily provide sufficient information to predict toxicity (Florence, 1986). Due to their toxicity, even at low concentrations lead, cadmium, arsenic, mercury, aluminum, chromium are the key elements, while copper, zinc, nickel, cobalt and selenium are important because they play a vital or a toxic role, depending on their concentrations and the physico-chemical form. The measurement of specific species is therefore essential.

Trace element speciation in natural water requires specialized techniques for the collection, filtration, storage and analysis of the samples, because there is a constant risk of contamination, changes in equilibrium or trace element losses when working with such low concentrations. Electrochemical techniques have an important advantage, that the sample requires much less handling and is in contact with fewer potential sources of contamination than other speciation methods, such as extraction, dialysis or ultrafiltration (Florence, 1986).

Electroanalysis is a powerful technique for the study of trace elements speciation and has been applied to about 30 elements (Batley, 1983; Bond, 1980; Florence et al., 1980). Four metals of prime environmental concern, copper, lead, cadmium and zinc can be determined simultaneously and with great sensitivity. Of all trace metal speciation methods, available at present, electroanalysis appears to provide the best opportunity for providing empirical data for experimental modeling of the bioavailability of elements and their complexes with organic and inorganic ligands. ASV is therefore the most widely applicable electrochemical technique for trace element speciation in waters (Achterberg & Braungardt, 1999; Azenha & Vasconcelos, 2000; Bond, 1980; Buffle & Tercier Waeber, 2005; Jakubaa et al., 2008; Kiptoo et al., 2004; Louis et al., 2008; Salaun et al., 2007; Wang et al., 1987; Wang & Chakrabarti, 2008).

1.3.4. On-line Monitoring in Natural and Industrial Waters

Environmental monitoring of metals is of great importance for environmental assessments as well as for understanding the circulation of pollutants in nature. The Water Framework Directive (WFD) of the European Union (EU) includes a wide range of measures aimed at achieving good quality status in all waters (Buffle & Tercier-Waeber, 2005; European Commission, 2007; European Commission, 2008; Gonzalez et al., 2007; Roig et al., 2007). Therefore, water monitoring is necessary and this could be achieved either by frequent sampling and laboratory analysis or by in-situ monitoring.

As it has been mentioned earlier, ICP-MS and GF-AAS are sensitive sophisticated analytical laboratory methods (Chen & Teo, 2001; Holliday & Beauchemin, 2004; Jimoh et al., 2004; Saracoglu et al., 2003; Skoog et al., 1996; Ulrich et al., 2004), but with a limited range of use for in-situ monitoring. Using these methods, samples have to be collected manually and brought to laboratories for analysis. This gives an undesired time lag from the appearance of an accidental or illegal pollutant to the detection of it. Additionally, contamination of the sample and metal loss due to adsorbtion on a bottle walls is an issue. A great advantage therefore is to carry out the measurements on-line and automatically with remote transfer of the results via Internet.

However, because concentrations of the actual metal ions are very low, sensitive and sophisticated instruments are required, rarely being suitable for remote operations in field. The only suitable on-line analytical method being sufficiently sensitive in the low µg/L range for this purpose is voltammetry. The advantages of in-situ use of voltammetry are low cost and no or minimal sample change, since the sample is taken automatically and analysis is performed immediately without a need to collect a sample manually risking contamination and metal loss. Automatic monitoring is essential to record the natural variations of metal concentration in natural water sample and registration of accident due to natural or anthropogenic reasons. Automatic instrumentation gives a possibility to monitoring, detection and warning.

Recent developments of in-situ approaches to monitor metals in aquatic systems include reviews of voltammetric in-situ profiling systems (VIP). The VIP is a submersible probe that has been developed for in-situ continuous trace metals monitoring in natural waters (Buffle & Horvai, 2000). The instrument allows simultaneous determination of several metals without sample pretreatment. It combines a rapid trace metal analysis with automated in-situ operation, data acquisition and transfer. The VIP has been applied to monitor the temporal and spatial distribution of trace metals in natural waters (Belmont et al., 1998; Tercier et al., 1998), lakes (Tercier Waeber et al., 1998; Tercier Waeber et al., 1999), surface water, ground water and sediment interface (Tercier Waeber et al., 1999), river waters (Tercier et al., 1995; Tercier Waeber et al., 2005), coastal and estuarine waters (Howell et al., 2003; Braungardt et al., 2009).

Earlier prototypes of this type of systems were limited to a short term application of in-situ measurements (Tercier et al., 1990; Wang et al., 1995; Wang et al., 1998). The new VIP systems have extended a capability of trace metal measurements. Those systems are based on voltammetric microsensors, consisting of multiple amounts of gel integrated microelectrodes (Tercier Waeber et al., 2005).

Another approach to in-situ metal monitoring is on-board systems. Those systems are mobile monitoring stations, mounted on board in a ship and considered very close to real time in-situ monitoring systems. The system typically includes a submersible pump for continuous sample collection; pretreatment steps include filtration and often UV digestion for breakdown of surfactants and natural metal complexing ligands (Achterberg et al., 2001). The pretreated sample is then analysed using mercury drop electrode as a working electrode. The underwater pumping system in combination with near real time metal analysis enables close investigation of spatial and tidal metal concentration variations. This type of monitoring has been performed in estuarine and coastal waters for determination of dissolved metal concentration (Achterberg, 2000; Braungardt et al., 1998; Braungardt et al., 2009; Howell et al., 2003; Whitworth et al., 1998), labile concentrations and metal speciation in marine waters (Achterberg & Braungardt, 1999; Achterberg & van den Berg, 1996; Bowie et al., 1998; Colombo et al., 1997; van den Berg, 1991; van den Berg & Achterberg, 1994).

The introduction of solid silver amalgam electrode (Mikkelsen & Schrøder, 2000a, Mikkelsen & Schrøder, 2000b; Mikkelsen & Schrøder, 2004) have resulted in more environmental friendly possibilities for continuous in-situ trace metal monitoring. Trace metals were monitored continuously for long time in river water (Lesven et al., 2009; Mikkelsen et al., 2005; Mikkelsen et al., 2007), sea water (Mikkelsen et al., 2005), industrial water (Mikkelsen et al., 2003*)*, drainage and waste water (Mikkelsen et.al., 2007) and ground water (Mikkelsen et al., in prep.). The monitoring stations described there consist of submersible pump supplying the systems with water sample, a filtration unit and an electroanalysis unit with a solid silver amalgam electrode as a working electrode. The work reported there has been aimed to detect electrolabile concentration of metals in the low μg/L level. An important point has been to establish a better and more complete analytical procedure for environmental monitoring by reporting both labile fraction and total amount of the metals by use of two analytical methods – voltammetry in field and ICP-MS for laboratory analyses.

The challenges of in-situ monitoring is complex analyte matrix, containing surface active compounds, that may interfere to analysis and suspended particles that may cause fouling of the tubes and filtration units and fouling of the electrode surface due to adsorbtion of natural organic or inorganic matter, in addition to interference from the dissolved oxygen. Other challenges considering the equipment being in field for long time are technical properties of the equipment, resistance to harsh environment conditions (humidity, extreme temperatures), availability to data transfer communications and access to maintenance.

1.4. CHEMICAL MODIFICATION OF ELECTRODES

Surface active compounds, present in a sample, may interfere to direct metal determination. Adsorption of organic matter onto the working electrode may hinder the diffusion of metal ions and thus diminish or eliminate the diffusion current and cause a non linear relationship between stripping current and deposition time. This may have a significant effect on the ASV response (Bhat et al., 1981). In addition, adsorbtion-desorbtion processes can yield “tensammetric” peaks when pulse voltammetric techniques are used (Batley & Florence, 1976; Jacobsen & Lindseth, 1976). These substances may also adsorb on the electrode surface and disturb deposition of the analyte (Economou & Fielden, 2003; Jia et al., 2007; Sagberg & Lund, 1982; Wang & Luo, 1984). This is one of the most serious interferences in practical application of DPASV because the adsorption of surface active compounds on the electrode surface causes fouling and results in loss of sensitivity. As a result, lower and broader peaks are observed. Such surface fouling is a limitation in direct ASV application in environmental samples and a big challenge considering use of solid electrodes in long time monitoring stations in field.

This problem may be solved by applying a protective polymer film layer to decrease the adsorption of surface active compounds. The polymer film mechanically blocks the surfactant species from reaching the electrode surface, while small metal cations can diffuse through the film and reach the electrode surface. Several compounds have been tested for this purpose and are described in the following sections.

Chemically modified electrodes (CME) represent a modern approach to electrode systems. These rely on the placement of a reagent onto the surface, to impart behavior of that reagent to the modified surface. Such deliberate alteration can thus meet the needs of solution to many electroanalytical problems.

There are various ways in which the CME can benefit analytical applications. These include the acceleration of electron transfer reactions, preferential accumulation or selective membrane permeation. Such steps can impart higher sensitivity, selectivity or stability (Baldwin & Thomsen, 1991; Murray et al., 1987).

One of the most common approaches for incorporating a modifier onto the surface is coverage of the electrode with an appropriate polymer film. Polymer modified electrodes are often prepared by casting a solution containing the dissolved polymer onto the surface and allowing the solvent to evaporate, or via electropolymerization in the presence of the dissolved monomer. Other useful modification schemes include bulk modification of composite carbon materials, covalent chemical attachment, sol-gel encapsulation, physical adsorbtion and spontaneous chemisorbtion. Some of the different modifications of the electrodes are reviewed in the next sections.

1.4.1. Agarose gel

Agarose is obtained from agar, which is extracted from the cells of marine red algae. The gel layer works as a small separation/reaction chamber, with fast transport by diffusion. The advantages are as follows: it acts as a dialysis membrane to separate most of the fouling components (usually negatively charges colloids and macromolecules) by size and charge exclusion; it forms a layer in which transport is controlled exclusively by molecular diffusion; it stabilizes the electrode mechanically; it forms a "reactive" chamber where specific reactions/processes can be performed and thus improves the selectivity or enlarges the field of application of the electrodes. One of the main problems of its use is the thickness of the gel layer, which is in the order of several hundreds of micrometers. Consequently, the response time of the covered electrode is longer compared to the response time of the bare electrode and before measurement, a time period is needed to permit the species to diffuse in the gel (Buffle & Tercier Waeber, 2005). In addition, as the convection cannot be established near the surface of the electrode, agarose is mainly reserved to microelectrodes.

An agarose gel, with thickness varying from 0.4 to 0.9 μm is used as an inert membrane and allows the diffusion of small metal ions and molecules and retains colloidal molecules. Mercury plated, iridium based microelectrodes, covered with a protective agarose gel membrane has been used for determination of lead and cadmium by SWASV in river water samples, containing high amount of suspended particles and surfactants (Tercier & Buffle, 1996). An array of 100 mercury plated, iridium based microelectrodes, coated with an agarose gel membrane have been used for in-situ analysis of low concentrations of lead and cadmium by chronoamperometry and SWASV in natural waters. Good reproducibility, low detection limit and protective effect of the gel have been reported (Belmont-Hebert et al., 1998). Gel integrated microelectrode array was used for a simultaneous determination and speciation of zinc, cadmium, lead and copper by SWASV in river water. Gel protective properties and reproducibility have been reported (Pei et al., 2000). A voltammetric probe, based on gel integrated 64 mercury plated iridium based microelectrodes array have been used for real time concentration profile measurements of trace metals at well controlled liquid – liquid and liquid – "solid" interfaces (Pei et al., 2001).

1.4.2. Cellulose acetate

Cellulose acetate (CA) is one of the most useful materials for the electrode coating due to its excellent membrane-forming properties (Kesting, 1985). Coating the working electrode surface with permselective CA membrane has been reported to prevent organic interferences in ASV. The coating of the electrode is done either by mounting a preformed bulk membrane directly in contact with the electrode or by casting the membrane in-situ on the electrode surface, usually followed by suitable conditioning (Wang & Hutchins - Kumar, 1986; Høyer & Jensen, 1996).

The general drawback of CA membranes is their thickness that can to some extent interfere with the mass transport of the analyte. The time, required for equilibration with the contacting solution is the same order of magnitude as the duration of the typical ASV measurement and the response time of the electrode can become a limiting factor (Høyer & Jensen, 1995). Moreover, bulk membranes strongly hinder the mass transport of the analyte to and from the electrode surface and cause a reduction of sensitivity in ASV (Aldstadt & Dewald, 1993). In-situ formed membranes can be made much thinner. Electrode modification is carried out by casting a dense CA film and subsequently applying the electrode to base hydrolysis. This treatment breaks the polymer backbone and increases the permeability of the CA membrane. The permselectivity can be controlled via the hydrolysis time. CA membranes, casted in-situ have been reported to protect well against surfactant interferences in a stripping analysis (Wang & Hutchins - Kumar, 1986; Wang et al., 1987) and are used for a selective detection of low molecular weight species in amperometric detectors (Wang & Hutchins, 1985; Hutchins-Kumar et al., 1986). However, poor stability and reproducibility of CA membranes, prepared in this manner have also been reported (Dam et al., 1995) which may be a result of polymer degradation in hydrolysis step (Kuhn et al., 1989).

An alternative way of controlling permeability of CA membranes is achieved in the phase-inversion (PI) process, in which a pore former or swelling agent is added to the casting solution (Kesting, 1985). When the casting solvent has evaporated, the membrane is immersed in a non-solvent gelation bath, where the polymer precipitates. The porosity of the resulting membrane depends on the composition of the casting solution, the pore former (swelling agent) used and the experimental conditions in the casting procedure. Generally, anisotrophic membranes are produced with a dense skin layer and a permselective porous sub-layer (Kesting et al., 1965; Kesting, 1985). This method has two advantages: first, the process does not involve any degradation of the CA polymer; second, the main diffusional barrier is the skin layer and the inhibition of mass transport of the analyte caused by the coating is therefore minimized. PI CA membranes, prepared in this manner have been used for detection of cadmium and lead by DPASV in the presence of albumin (Høyer & Jensen, 1995).

The permselectivity and reproducibility of the PI CA membrane can be improved by allowing complete evaporation of the solvent in a controlled humidity environment before the membrane is gelated. Using cadmium and lead as test ions it has been reported that interferences from albumin, lysozyme, gelatin and polyethylene glycol were significantly reduced. The permselectivity of the membrane can be controlled by varying the amount of magnesium perchlorate in the casting solution and relative humidity during pro-gelation step (Høyer & Jensen, 1996). The CA improved procedure has been further developed by the same researchers. Reproducibility has been improved and interferences from polyethylene glycol were reduced using ultrathin CA coating, deposited by electrostatic spraying of a solution, consisting of CA, acetone and aqueous magnesium perchlorate as a pore former. After conditioning in constant relative humidity, the CA deposit resolvated in a chamber, containing a saturated acetone vapor and the membrane structure was formed by applying ice water to the coating while remaining in the acetone chamber (Høyer et al., 1999). CA coating on mercury film electrode is reported to eliminate severe adsorbtion interferences from humic acid when determining lead by DPASV, seen at the conventional MFE (Christensen & Høyer, 2000). CA coated MFE has been applied for the determination of lead in sewage samples and reported to be advantageous compared to bare MFE (Dam et al., 1995).

1.4.3. *Nafion*

Nafion has been widely used as an electrode modifier because it is stable and easy to prepare. A film, formed by Nafion on the electrode surface, is electroinactive, chemically inert and hydrophilic. It has exceptional properties of super selectivity and facile cation transport. Moreover, it can preconcentrate a wide variety of cations while rejecting anionic interferences. These properties are due to the microstructure of Nafion that looks like segregated domains of fluorocarbon and clusters of hydrated sulfonate sites. Cations travel across the membrane through interconnected hydrated domains (Martin et al., 1982; Yeager & Steck, 1979).

The Nafion film can be deposited on the electrode surface by spread–coating (Høyer et al., 1987), dip-coating (Harrison et al., 1988), spin-coating (Zen & Lee, 1993), electrochemical plating (Brazell et al., 1987), electrostatic spraying (Høyer et al., 2001) or by applying a drop of diluted Nafion solution directly to the electrode surface (Kefala et al., 2004; Kefala & Economou, 2006). The thickness of the Nafion layer is directly proportional to the concentration of Nafion in the coating solution. The thickness of this film has a profound effect on the stripping response. Too thin Nafion layer has no or very little desired properties, and too thick layer is very likely to hinder mass transport to the electrode surface. The optimal Nafion film thickness is considered to be less than that of the diffusion layer and therefore does not appreciably restrict the mass transport to the electrode surface. It is often reported to be produced from the 0.5% Nafion solution (Høyer & Florence, 1987; Kefala et al., 2004; Kefala & Economou, 2006; Torma et al., 2008; Xu et al., 2008). Nafion coatings have been studied in combination with glassy carbon electrodes (Crowley & Cassidy, 2002; Szentirmay & Martin, 1984), glassy carbon bismuth film electrodes (Kefala et al., 2004; Kefala & Economou, 2006; Wang et al., 2001; Xu et al.,. 2008), glassy carbon mercury film electrodes (Capelo et al., 1995; Dam et al., 1995; Dam & Schrøder, 1996;

Høyer & Florence, 1987; Hurst & Bruland, 1987; Høyer et al., 1987; Høyer & Jensen, 1994; 2005 Wang & Luo, 1984), solid silver amalgam electrodes (Strasunske et al., 2010).

In most of these contributions an increased electrode sensitivity and better resistance to surface active compounds are reported. The increased sensitivity is believed to arise from several reasons. The polymer film helps to confine the stripped species close to the electrode surface where repetitive replating – stripping cycling occurs resulting in signal amplification during the anodic stripping by using the differential pulse sweep (Høyer et al., 1987; Kefala et al., 2004). Further, the negatively charged sulfonate groups in the Nafion film help the film to act as a cation exchanger and facilitate a non-faradaic preconcentration of metal cations (Dam & Schrøder, 1996; Xu et al., 2008). In addition, the enhancement of DPASV signal is due to the protection of the electrode surface by Nafion film to slow down any formation of passive or non-conducting oxide layers.

The practical application of Nafion coated electrodes has been tested for the determination of metals in tap water and white wine (Kefala et al., 2004; Torma et al., 2008), plant extracts (Legeai & Vittori, 2006), vegetable (Xu et al., 2008), body fluids (Høyer & Florence, 1987; Høyer et al., 1987), waste water (Dam et al., 1995; Zen & Ting, 1996), estuarine water (Hurst & Bruland, 2005) and river water (Strasunske et al., 2010).

1.5. SUMMARY OF THE PAPERS INCLUDED

1.5.1. Paper I

Determination of Zinc and Iron in Waste Water by Anodic Stripping Voltammetry

Differential pulse anodic stripping voltammetry have been used to determine trace metals in waste water and applied in an on-line monitoring station for long time monitoring of trace metals in a waste water treatment plant (WWTP). Zinc and iron have been monitored continuously every 30 minutes for 7 months using solid silver amalgam electrode as a working electrode. The electrode has shown good stability over a long time and a good linearity (r^2_{avg}=0.98). Manual maintenance like polishing of the working electrode and cleaning the cell system has been carried out once every 5 days.

For comparison, verification and to provide a better insight into the complex waste water matrix manual samples have been taken regularly and analysed with ICP-MS. A speciation study have been performed from combination of ICP-MS and voltammetry. It was observed, that concentration of metals varied a lot during the whole measurements period. The variations are assumed to be related to water treatment cycle in WWTP, processes in industrial organizations, which discharges their effluents to WWTP, seasoning, precipitation, temperature, pH, concentration of suspended particles and other.

1.5.2. Paper II

Automatic Voltammetric System for Continuous Trace Metal Monitoring in Various Environmental Samples

This paper describes an automatic voltammetric system for continuous monitoring of trace metals in various environmental water samples. Three different monitoring stations are presented in this paper. River water, drainage water and waste water represent three different but very common environmental matrixes. Solid silver amalgam electrode was used as a working electrode in all monitoring stations. The systems were fully automated to measure the labile concentrations of trace metal for a long time monitoring and to store the collected data. Manual maintenance was performed to calibrate the systems and to clean the electrodes. Additionally, random samples were collected manually and analyzed by ICP-MS for the total metal concentration for data verification and getting better insight into the sample matrix.

The automated monitoring station in river water was set up in the polluted river Leirelva (Trondheim, Norway) to measure zinc and iron concentrations. Leirelva flows through an industrial area of the city and enters Nidelva, which is a very important river for salmon in the area. The average labile iron concentration, measured by voltammetry was about 25% of the average total iron, measured by ICP-MS. The average labile concentration of zinc, measured by voltammetry is very similar to the average total concentration of zinc, measured by ICP-MS. Results from calibration are also reported, showing a linear regression curve for both metals with $r^2_{avg}=0.99$.

The automated monitoring station in drainage water was set up in Odenskog (Østersund, Sweeden) to monitor zinc in drainage water originated from a nearby industrial area. The system monitored zinc concentration every 60 minutes. In addition to voltammetric measurements, external analyses by ICP-MS were carried out on manually collected samples. The average zinc concentration, found by both two analytical methods corresponds very well, indicating that almost all zinc was present in labile form.

The automated monitoring station in waste water was set up at Høvringen waste water treatment plant to measure concentration of zinc and iron in the waste outlet every 30 minutes. Field experiments have been performed to measure the concentration of trace metals in the effluents (outlet to the sea). For data verification manual samples were collected regularly and analyzed by ICP-MS. Comparing results obtained from these two analytical methods it has been found that a big part of zinc exists as colloidal and solid complexes and 22-54% zinc is in dissolved form. It has been found that 2-24% iron is in dissolved state, other iron complexes exist in colloidal and solid state. Only about 3 % iron of total iron was found to be in most bioavailable and toxic state. Calculations show that free zinc ions and weak complexes varied from 2% to 40% of total Zn concentration.

1.5.3. Paper III

Continuous Monitoring of Heavy Metals in Ground Water as a Tool for the Detection and Verification of Earthquake Precursors

This paper describes an automatic monitoring station, installed in Husavik, Northern Iceland, for monitoring of trace metals in a ground water source. The monitored concentration of metals clearly indicated changes in the ground water prior the earthquake. The results revealed increased electrolabile concentrations of zinc, iron and copper 7-8 days before to the earthquake. The increased concentrations lasted until the occurrence of the earthquake and were possible to monitor by the ATMS. Solid silver amalgam electrode was used as a working electrode.

Ground water in Husavik is affected by changes in ground water fluxes. Basalt is the dominated type of rock there. The equilibrium between water and basalt at high temperatures shows that some metals will leak into the water. An increase in heavy metal concentrations before an earthquake is believed to be related to changed flow patterns in ground water. Increased concentration of heavy metals in ground water is the result of leakage of water with higher temperature and higher concentration of heavy metals into a ground water source.

The monitoring station, described in this paper, worked automatically since September 2006 and monitored concentrations of zinc, iron and copper every 30 minutes. On the 1st of November an earthquake occurred, measured to (M) 4.5 on Richters scale. Continuous measurements showed visible changes in the electrolabile metal concentrations 8 days before the earthquake. No metals were visible 30 days before the earthquake, but several metals were detected in the ground water 8 days before. The observed change in metal concentrations agrees with literature describing changes in water in equilibrium with basalt when the temperature rises. In addition to increased metal concentrations, a decrease in pH and thus acidic environment has also been observed, indicating the leakage of warmer water into the ground water source.

The automatic monitoring station for determination of heavy metals, installed in the actual site showed the possible application of such systems. The testing of the station by the real earthquake showed the possibility of an early warning indications of changes which could occur prior to earthquakes. The results, presented in this paper, are based on one earthquake only and the method is still under development for further validation for earthquakes prediction. The results are promising for such application, taking into account the former observations and the new observations reported here. The changes measured by voltammetry were more distinctive than the changes detected by ICP-AES. These preliminary results strongly indicated that with further development of the method, it may in the future be used as a warning system for earthquakes in the areas where basalt is the dominating type of rock.

1.5.4. Paper IV

Solid Alloy Electrodes in Voltammetry

This review paper gives a short overview of the solid amalgam electrode and some alloy electrodes, which during the last 10 years have been reported to be suitable alternative electrodes to liquid mercury, especially for an environmental monitoring. The choice of working electrode is of outmost importance in voltammetry in order to fulfill needed demands and criteria.

Recently, the voltammetric methods have proved to have a great potential within environmental monitoring, demanding for additional electrodes, specifically suited for such purpose. Primary goals are therefore to find solid electrodes which passivate slowly, are non toxic, and have as broad as possible working window. Since several interesting trace and heavy metals undergo redox reaction in the range from 0 to -1.5 V it is a specific goal to make electrodes which suppress the formation of hydrogen gas in this area.

As the electrochemical techniques have shown to have a large potential in environmental monitoring in field applications, an intensive research activity during the past years has been carried out in order to develop useful solid electrodes, favourable for field use. However, the main problems are that most solid metal electrodes have a relatively low overvoltage towards hydrogen evolution, limiting their working windows to only around - 0.5 V in the cathodic area, which makes them unsuitable for analyses of several important metals like nickel, cobalt, zinc, iron and cadmium. Further, using solid metals which actually possess high overvoltage towards HER are also limited due to fast passivation through formation of non-conducting oxide layers.

Of special importance is the dental amalgam electrode, which is a real solid silver amalgam electrode, compromising silver powder and liquid mercury in a 1:1 ratio. The main problem with mercury film electrodes on metal substrates are the difficulties to achieve a stable base line and reproducible measurements, due to continuous reaction between the mercury layer and the bare metal electrode since such electrodes are not in an equilibrium state. The combination of a higher overpotential towards the hydrogen evolution reaction and a better stability for such electrodes extends greatly the range of analytical applications and renders the possibilities to using these electrodes in field. Additionally, solid amalgam electrodes are easy and cheap to construct and are stable over a reasonable time up to several weeks.

The idea for introducing the dental amalgam electrode was to overcome this main problem with 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 favorable since silver itself has a relatively high overpotential towards HER. Additionally, silver oxidize close to mercury and this gives a maximum working window also in the positive direction. Finally, the amalgamation between silver and mercury is particularly strong and stable when brought out under optimum conditions, using the same techniques as used in dental practice.

1.5.5. Paper V

Nafion Coated Silver Amalgam Electrode for Determination of Trace Metals by Anodic Stripping Voltammetry

This paper describes characterization and application of Nafion coated solid silver amalgam electrode for the determination of trace metals by differential pulse anodic stripping voltammetry (DPASV). The effect of surfactants has also been studied and described in this paper. Triton X-100, sodium dodecyl sulphate, dodecyl pyridinium chloride and bovine serum albumin were chosen as representatives of surface active compounds. It has been found that a Nafion coated electrode is useful in surfactant containing samples, although it is also affected by all four surfactants. Moreover, the long time use of Nafion film has been tested by the use of DPASV in polluted river water sample and has shown to work optimally.

The performance of the Nafion coated silver amalgam electrode was investigated and compared to the uncoated silver amalgam electrodes. The modification of the electrode yields higher sensitivity. It has been demonstrated here that Nafion coating increases the sensitivity of silver amalgam electrodes by 156 % for zinc, 57 % for lead and 52 % for cadmium compared to the uncoated electrode when metals are present in aqueous samples.

The influence of model surfactants on a trace metal determination was investigated on a solid silver amalgam and Nafion coated silver amalgam electrodes by DPASV. Common surfactants such as Triton X-100, sodium dodecyl sulphate, dodecyl pyridinium chloride and bovine serum albumin have a significant effect on DPASV response of silver amalgam electrodes. Signal suppression is observed even when small amounts of surfactants are present. The effect depends on the specific surfactant, its concentration, target metal and its concentration as well. The results demonstrated that Nafion coating increased sensitivity for all measured metals in aqueous samples containing surface active compounds by reducing ability of surfactants to block the electrode surface.

The practical application of the Nafion coated silver amalgam electrode was tested by applying the electrode for a long time monitoring of metals in a natural water sample. Results showed good stability of measurements for the monitoring period of

14 days. Nafion coated silver amalgam electrode proved to be suitable for the determination of trace metals in the real sample.

1.5.6. *Paper VI*

Silver germanium and silver antimony electrodes for determination of trace metals by anodic stripping voltammetry

Mixed silver-germanium and silver-antimony alloy electrodes have been investigated for determination of trace metals by differential pulse anodic stripping voltammetry. The electrodes have a wide potential window to allow measurements of different metals. Zinc, cadmium, lead, and copper were measured in ammonium chloride solution. A good linearity was found for all metals in all the measured range. It has been found, that mixed silver-germanium alloy electrodes were especially advantageous for determination of cadmium.

One of the most important properties of an electrode material, used in voltammetry is the range of the potential window. One of the most attractive properties of HMDE is the high overvoltage towards the hydrogen evolution reaction, extending the working window significantly in the negative direction, what enables to measure compounds appearing in the more negative potential range even in relatively acid solutions. In this paper, the potential window of several mixed electrodes consisting of silver with different amounts of germanium added has been investigated. One of the drawbacks with bare silver electrodes is relatively low overvoltage towards HER. Silver amalgam electrodes exhibit a wider potential window. Addition of small amounts of germanium or antimony or both to the silver electrode material extends potential window even more.

All silver-germanium and silver-antimony electrodes have been tested for detection of low concentrations of cadmium. It has been observed that all the tested electrodes exhibit very good sensitivity to cadmium. Cadmium was measured in ammonium chloride (0.02 M) solution down to 0.5 μg/L concentration with a good linearity (r^2=0.966) in the tested range 0.5 - 4 μg/L. It has been observed, that additions of small amounts of germanium or antimony or both to a silver electrode material increased sensitivity. This is very interesting feature, since bare silver electrodes are relatively less sensitive to cadmium.

The practical application of silver-germanium and silver antimony electrodes was tested by applying electrode for long time monitoring of metals in natural sample. Zinc was measured in polluted river water for a period of 12 days. Results show good stability of measurements. Moreover, a protective Nafion film on the electrode surface was applied and proved to be helpful. Thus, silver-germanium alloy electrodes, coated with Nafion can be successfully applied as trace metal sensors in natural samples with the presence of surfactants by giving protection on surface fouling. This opens up new possibilities for direct measurements of trace metals in complex natural samples, such as sea water, river water and industrial effluents.

1.6. CONCLUSIONS

The aim of this work has been to test the silver amalgam electrode for application in natural and environmental water samples for use in a long time on-line monitoring in field. The papers included in this thesis prove successful applications of these electrodes in different environmental matrixes.

Automatic voltammetric monitoring systems, using solid silver amalgam electrode as a working electrode, have been tested. In the experiments described there it has been focused on testing the practical applicability of this type of electrode. The results provide positive evidence about the ability of voltammetry in combination with solid silver amalgam electrode (and solid silver amalgam electrode modified with Nafion) as a working electrode to be employed in automatic monitoring of trace metals in polluted water with minimal sample pretreatment and minimal maintenance of the system. The possibility to monitor trace metal concentration continuously is a great advantage comparing to random data received from manual sampling and measurements in laboratory. The aim of this work has also been to establish a better and more complete analytical procedure for environmental water monitoring by reporting both the labile fraction and the total amount of metals. Therefore, more complete analysis received through combined measurements is crucial to get information about the toxicity levels of metals in aquatic systems. The successful use of solid silver amalgam electrode in different water samples for a long time monitoring with a good stability over a reasonable period of time demonstrates a wide range of application and opens new possibilities for environmental monitoring in complex water samples.

The voltammetric system in combination with solid silver amalgam electrode fulfills the requirements to be used for automatic and remote monitoring of trace metals in various natural water samples. The use of silver amalgam electrode allows avoiding the use of toxic mercury in voltammetric analyses, and offers an environmental friendly alternative suitable for use in field.

Several experimental projects at different locations and in different water samples (river-, sea-, ground-, drainage- and waste water) have shown sufficient long time stability without the need for physical presence for maintenance. The possibility to monitor trace metal concentrations every 30 minutes is a great advantage comparing with a data received from routine analyses of manual sampling which are usually performed by municipalities once a week in laboratories. Automatic monitoring stations at different locations in different water samples functioned sufficiently during all the period of measurements. Electrolabile fractions of trace metals were detected simultaneously with minimal sample pretreatment, only using electrolyte solution and filtrating suspended particles. Those results strongly indicate that with further development of the method, it may in future be used as a commercial warning system for environmental pollution accidents.

The performance of the silver amalgam electrode coated with Nafion film has also been investigated. It has been observed, that the modification of the electrode improves sensitivity. The influence of model surfactants on a trace metal determination has been investigated on a solid silver amalgam and Nafion coated silver amalgam electrodes by DPASV. The results demonstrate that Nafion coating increases sensitivity for all measured metals in aqueous samples containing surface active compounds by reducing ability of surfactants to block electrode surface.

The practical application of Nafion coated silver amalgam electrode has been tested by applying the electrode for a long time monitoring of metals in natural water sample. The results showed good stability of measurements. Nafion coated silver amalgam electrode is suitable for the determination of trace metals in the real natural water sample.

Silver amalgam electrodes, coated with Nafion can be successfully applied as trace metal sensors in natural samples with the presence of surfactants by giving the protection on surface fouling for silver amalgam electrodes. This opens up new possibilities for the direct measurements of trace metals in complex natural samples, such as sea water, river water and industrial effluents.

Mixed silver-germanium and silver-antimony alloy electrodes have been investigated for determination of trace metals by differential pulse anodic stripping voltammetry. The electrodes have a wide potential window to allow measurements of different metals. Zinc, cadmium, lead, and copper were measured in ammonium chloride solution. A good linearity was found for all metals in all the measured range. It was found, that mixed silver-germanium alloy electrodes are especially advantageous for determination of cadmium, which is interesting, since sensitivity towards cadmium in general is less on bare silver electrodes.

The practical application of silver-germanium and silver antimony electrodes was tested by applying electrode for long time monitoring of metals in natural sample. Zinc was measured in polluted river water for a period of 12 days. Results show good stability of measurements. Moreover, a protective Nafion film on the electrode surface was applied and showed to be advantageous.

The results presented in this thesis show that solid silver amalgam and other mixed metal electrodes are suitable for use in automatic field equipment for long time automatic in-situ monitoring. The application in various matrixes demonstrates a wide range of applications. Due to ease to use, non-toxic fabrication materials, wide cathodic potential window, long time stability, and good sensitivity these electrodes can be applied for continuous online monitoring in various environmental and industrial solutions. They are also easy to modify and this extends application even further.

1.7. FUTURE ASPECTS

Results presented here indicate great possibilities for optimal in-situ monitoring, but there is a long way to go to commercial monitoring systems. Long time stability of the working electrode is one of the most important factors and should be investigated further.

Nafion membrane, described here, offers a great protection in addition to sensitivity enhancement. Although, it is worth noting that it cannot eliminate all organic interferences in DPASV. Even if the interfering species are prevented from reaching the electrode surface, they may still deposit on the outside of the membrane and affect the mass transport. For the repetitive DPASV analyses of samples with surface active compounds electrode regeneration after a certain period of time should be considered. Additionally, influence of pH and addition of casting solvent to Nafion solution may be investigated.

Development of modified electrodes may be another research area. Other electrode modifiers, such as cellulose acetate or agarose gel membranes in combination with solid silver amalgam electrode and other solid metal electrodes are worth to investigate.

Other types of solid metal electrodes may be further investigated. Determination of some rare metals (such as arsenic) may be an interesting task. In-situ long time monitoring of metals in natural water sources shall be considered. Some challenging environmental matrixes such as sea water or polluted water due to the high content of organic or biological matter may be an interesting choice of application too.

Miniaturisation is a growing trend in electrochemistry. Development of microelectrodes, nanoelectrodes and electrode arrays for the determination of very low concentrations of metals is another interesting research area. Application for a long time in-situ monitoring in various water sources as well as other environmental samples may be considered.

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II. PAPERS I - VI

2.1. Paper I

Kristina Strasunskiene, Øyvind Mikkelsen, Knut H. Schrøder, Marion Rydningen

Continuous monitoring of trace metals in waste water effluents using voltammetric system.

Young researchers 2006, 279-286. IWA publishing, London, UK.

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2.2. Paper II

Øyvind Mikkelsen, **Kristina Strasunskiene**, Silje M. Skogvold, Knut H. Schrøder, Camilla C. Johnsen, Marion Rydningen, Patrik Jonsson, Anders Jonsson

Automatic voltammetric system for continuous trace metal monitoring in various environmental samples.

Electroanalysis, 2007, 19, 2085-2092.

Is not included due to copyright

2.3. Paper III

Øyvind Mikkelsen, Silje M. Skogvold, Tonje B. Østerbrød, **Kristina Strasunske**, Knut H. Schrøder, Lillemor Claesson, Alasdair Skelton.

Continuous monitoring of heavy metals in groundwater as a tool for the detection and verification of earthquake precursors

Under preparation

Is not included due to copyright

2.4. Paper IV

Øyvind Mikkelsen, **Kristina Strasunskiene**, Silje M. Skogvold, Knut H. Schroder

Solid alloy electrodes in stripping voltammetry.

Current Analytical Chemistry, 2008, 4, 202-205.

Solid alloy electrodes in stripping voltammetry

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Abstract

In voltammetry, the choice of working electrode is of outmost importance to fulfil needed demands and criteria. Heyrovsky's invention of the polarographic method started in 1922 and granted with the Nobel Prize in 1959, was a pioneer work within the field of electroanalytical chemistry. In polarography, the working electrode is normally a liquid mercury drop electrode, possessing several advantageous properties for this purpose. Recently, the voltammetric methods has proved to have a great potential within environmental monitoring, demanding for additionally electrodes specifically for such purpose. This review gives a short overview of the solid amalgam electrode and some additionally alloy electrodes, which during the last 10 years has been reported to be suitable alternative electrodes to liquid mercury, especially for environmental monitoring.

Key words: solid silver amalgam electrode, alloy electrodes, voltammetry, trace metals

Introduction

Previous to the introduction of the liquid mercury electrode, early work within the field of electrochemistry was actually carried out by use of solid electrodes [1 - 3]. Some of the first work actually dealing with limiting current was carried out by Wilson and Youth [4], and Gladsstone and Reynolds [5, 6] in the period 1920 to 1930. However, of real interests are the work carried out by Laitinen and Kolthoff [7, 8], Zlotowski [9], and Rogers [10] which all worked on limiting current at solid electrodes.

Of crucial importance within the field of voltammetry is the overvoltage towards the hydrogen evolution reaction (HER) on the working electrode surface. This is because this reaction greatly limits the range of application for such sensors. The complicated process resulting in measurable hydrogen overpotential at metal electrode surfaces has challenged electrochemists for more than a century. Famous scientists like Tafel, Heyrovsky, and Volmer are inseparably connected with the important field of electrode kinetic [11].

During the past decades the dominant role of hydrogen in heterogeneous catalysis, energy storage technology, and metallurgy has become widely evident. Consequently, there has been an increasing interest in the study of elementary processes that occur on or within surfaces, and especially the hydrogen, but also the oxygen evolution reactions.

Mechanistic studies of the hydrogen evolution reaction in the past have suggested that there are two pathways for the reaction [12]. In the first, protons discharge onto the surface sites (Volmer reaction), and there is a consecutive chemical reaction in which adsorbed H atoms diffuse to each others across the electrode surface and undergo a chemical reaction to form H_2 (g), known as the Tafel reaction.

In the second pathway, the same proton discharge occurs on empty sites (Volmer reaction), but the desorption reaction consist of a second discharge reaction of protons, this time on the top of the adsorbed H produced by the first proton discharge (Heyrovsky reaction). The kinetics of the hydrogen evolution reaction at *e.g.* Hg and Ni or Pt cathodes are characterized by widely differing values of the exchange current density, i_0, and also by the extent of H coverage [13-16]. Empirical relations between the exchange current densities, i_0, and metal properties were investigated by Ruetschi and Delahay [17]. Major further advances were made by Parsons [18], Conway and Bockris [19] during the fifties and sixties. In this work the volcano plot showed that "volcano-type" curves forms when log i_0 values for a series of metals are plotted against the standard Gibbs energy of chemisorptions of H. The connection of HER to the G_H^0 was a particular important contribution, and through this work and work of Gerischer [20] the catalytic activity of different single metals for the Volmer-Tafel and the Volmer-Heyrovsky mechanisms were correlated to the strength of chemisorbed hydrogen.

Within the field of analytical electrochemistry, the mercury drop working electrode has been of especially importance due to the unique properties of mercury. The high overvoltage towards the hydrogen evolution reaction extends the working window significantly in the negative direction, enabling to measure compounds appearing in the more negative potential range even in relatively acid solutions. Another advantage using mercury is that diluted, liquid amalgams are formed with many metals during the reduction process, which is important in stripping techniques and contributes to better-defined voltammetric curves. The third advantage appears to the possibility to restore a new and clean electrode surface unaffected from any previous scan, simply by knocking off the old drop and by forming a new one. Well known drawbacks with the mercury drop electrode in polarography is the easy oxidation of mercury occurring from about 0 V, difficulties to install in automatic systems, and the scepticism to use mercury in field systems due to claimed toxicity aspects [21].

As the electrochemical techniques has shown to have a large potential in environmental monitoring in field applications, initiated through early work of Zirino and co-workers [22], an intensive research activity during the past years has been carried out in order to develop useful solid electrodes [23-31] favourable for field use. However, the main problems is that most solid metal electrodes have a relatively low overvoltage towards hydrogen evolution, limiting their working windows to only around - 0.5 V in the cathodic area, which makes them unsuitable for analyses of several important metals like nickel, cobalt, zinc, iron and cadmium. Further, using solid metals which actually possesses high overvoltage towards HER are also limited due to fast passivation through formation of non-conducting oxide layers. Primary goals are therefore to find solid electrodes which passivate slowly, are non toxic, and have a broad as possible working window. Since several interesting trace and heavy metals undergoes redox reaction in the range from 0 to -1.5 V it is a specific goal to make electrodes which suppress the formation of hydrogen gas in this area.

In 1947 Airey [32] observed that the negative potential range for platinum electrode, as well as for a silver electrode, was extended from -0.3 V to -2.1 V by plating a mercury film onto the surfaces of the wires. In addition to platinum and silver, also other metals has been used for making liquid mercury film electrodes, including iridium [33, 34], gold [35] and carbon in different forms [36]. Extensive work for in situ measurements has been performed by Luther III and co-workers [37-42], using solid gold microelectrodes plated with mercury.

Another interesting approach for in situ studies is worked out by Buffle and his group [43-48], using a micro array system, with an iridium matrix plated with mercury. Recently, Novotny and co-workers proposed an alternative to electroplating of the mercury film, simply by repeatedly dipping metal electrodes directly in liquid mercury [49, 50].

Our group demonstrated some years ago that the overpotential for HER on noble metals can be altered significantly by adding a second compound which possesses a high overvoltage for hydrogen formation reaction. Even additions of a few percent of the second metal possessing high hydrogen overvoltage were shown to result in a significant increase in the overvoltage towards HER. For instance, by alloying small amounts of mercury or bismuth in a silver electrode, it was shown that the working window was significantly extended in the negative area [51 - 53]. Later, in [54] it was shown that adding from 0 to 15 % of bismuth to the silver, the hydrogen formation reaction is shifted from -0.3 V to -1.2 V.

The observed increase in overpotential towards HER (shown in Figure 1) follows a nearly straight line, however somewhat larger increase is seen in the start for the smallest additions. The observed increase in overpotential is actually around – 59 mV in average if a straight line is drawn as the trend line, which is of particular interests since this incidentally coincides with the Nernst factor. In the same work reviewed above, the increased overpotential towards HER was also demonstrated through scanning electrochemical impedance measurements.

Of special importance is the dental amalgam electrode [55], which is a real solid silver amalgam electrode, compromising silver powder and liquid mercury in a 1:1 ratio. A main problem with mercury film electrodes on metal substrates are the difficulties to achieve a stable base line and reproducible measurements, due to continuously reaction between the mercury layer and the bare metal electrode since such electrodes are not in an equilibrium state.

The idea for introducing the dental amalgam electrode was to overcome this main problem with 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 favorable since silver it self has a relatively high overpotential towards HER. Additionally, silver oxidize close to mercury and by this gives a maximum working window also in the positive direction. Finally, the amalgamation between silver and mercury is particularly strong and stable when brought out under optimum conditions, using same techniques as used in dental practice as described in [52].

The production of the solid silver amalgam electrode and the alloy electrodes, have open up for detecting a wide range of metals [51 - 65], which some are summarized in Table 1. For instance, a unique sensitivity for bivalent iron in the ng/L rage was demonstrated in [58, 63], and successfully used for analyzing real samples from rivers and seawater with a minimum of sample treatment. The reduction from iron (II) to iron has a very high over-potential at the traditional mercury drop electrode, a phenomena well known for metals that are insoluble in mercury. This results in a reduction wave that coincides with the hydrogen wave, and therefore a low sensitivity at the mercury drop electrode. However, at the solid amalgam electrode the stripping peak for iron occurs around – 0.75 V vs. Ag/AgCl/KCl (3 M) reference electrode.

An evaluation of different solid electrodes for detection of several metals in process water from industry and waste water with use of solid ally electrodes was demonstrated in [59, 65]. For instance nickel and cobalt was detected in the low μg/L range using adsorptive cathodic stripping voltammetry (AdCSV) after complexing the metals with dimethylglyoxime. In [60] a simple method for detection of zinc and lead in wine by using potentiometric stripping analyses (PSA) and the solid silver amalgam electrode was introduced. The use of application was demonstrated in 10 different wines, both red and white without matrix effects.

The successfully implementation of the solid silver amalgam electrode in field applications for online measurements of metals in natural water and waste water has been given in several recent publications [59, 61, 62, 64, 65]. The possibility to implement such solid alloy electrodes in online voltammetric systems are of especially importance. Within the field of environmental monitoring, unattended in-situ measurement in a significant extent has up to now been limited to a few parameters like pH, some anions like nitrate and phosphate, conductivity and temperature. Voltammetry combined with the use of solid alloy electrodes, renders interesting possibilities for continuously measurements of important organic and inorganic environmental toxicants.

Conclusions

Liquid mercury has for almost 100 years been the most used working electrode material in voltammetry, due to its favorable properties *e.g* like the high overvoltage for hydrogen formation reaction which significantly extending the actual potential working window. Because of the fact that voltammetry is very suitable technique for field and remote monitoring, issues concerning the use of mercury electrodes in environmental analyses have led to considerable research effort aimed at find alternative materials with acceptable performance and low toxicity. Solid alloy metal electrodes have been proved to be such alternatives. In particular, solid amalgam electrodes and silver added bismuth are very promising, with acceptable low toxicity to be allowed for field measurements. Further, the increase in overpotential makes it possible to detect several metals occurring in at the more negative potential, like *e.g* manganese, zinc, cobalt, nickel, cadmium and lead. This has been shown through findings by cyclic voltammetry, impedance measurements and differential voltammetric techniques in the above reviewed papers. The combination of a higher overpotential towards the hydrogen evolution reaction and a better stability for such electrodes extends greatly the range of analytical applications and renders the possibilities to using these electrodes in field. Solid amalgam electrodes are easy and cheap to construct and are stable over a reasonable time up to several weeks.

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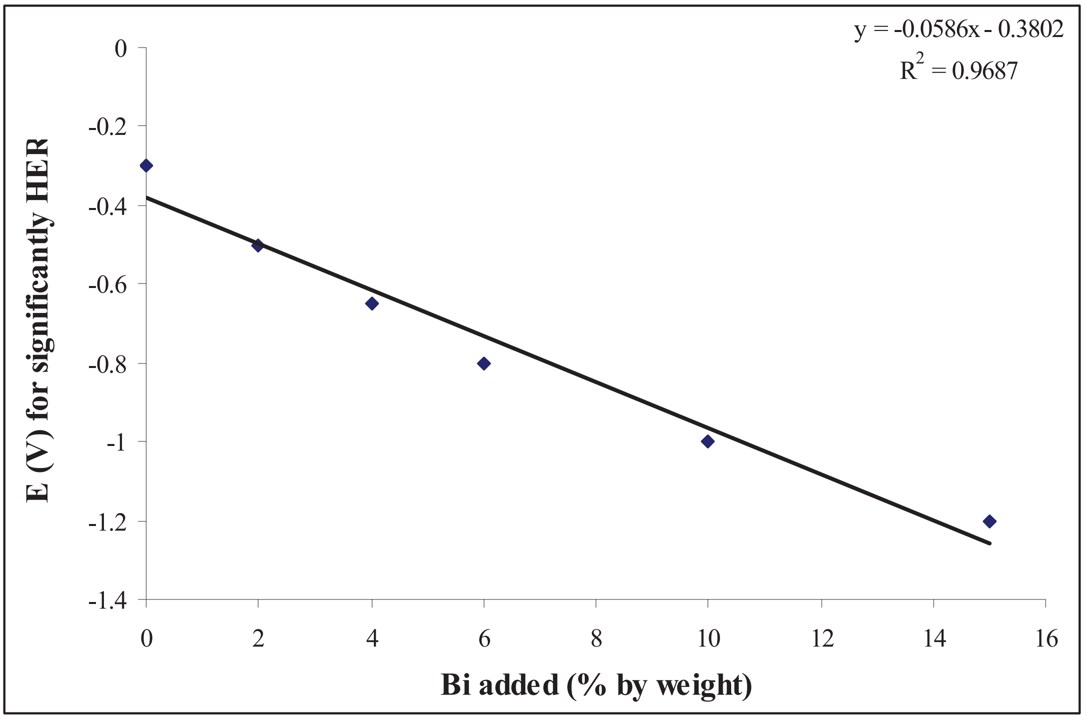

Fig. 1 Increase in overpotential towards HER for a silver electrode added increasingly amounts of bismuth. Measurements carried out by use of cyclic voltammetry in HNO_3 (0.1 M) solutions. Scan rate was 100 mV/s.

Table 1. Overview of some metals detected with the solid silver amalgam electrode, using Anodic Stripping Voltammetry (ASV), Adsorptive Cathodic Stripping Voltammetry (AdASV), or -Potentiometric Stripping Analyses (PSA). Peak potentials vs. Ag/AgCl/KCl (3 M).

Metal	**Solution**	**Supporting electrolyte**	**Peak pot.**	**Ref.**
Mn	River water	NH_4Cl (0.05 M)	-1.55	-
Zn	River water	NH_4Cl buffer pH=6.4	-1.10	61
Zn	Wine	NH_4Ac (0.05 M)	-1.05	51, 60
Zn	Waste water	NH_4Cl	-0.39	64, 65
Zn	Seawater	No chemicals added	-1.15	63
Co	Natural water (AdCSV)	NH_4Cl buffer pH=11.0, added DMG	-1.13	53
Co	Waste water (AdCSV)	NH_4Cl buffer pH=11.0, added DMG and 8-hydroxyquinoline	-1.15 / -1.14	53, 59
Ni	Natural water and waste water (AdCSV)	NH_4Cl buffer pH=11.0, added DMG	-0.10 / -0.98	53, 59
Cd	Natural Water	NH_4Cl / HCl buffer pH=6.4	-0.63	53
Cd	Waste water	NH_4Cl (0.05 M)	-0.68	55
Cr	Natural Water	NH_4Cl (0.05 M)	-0.70	-
Fe	River water (pH 5)	Ammonium oxalate (0.1 M)	-0.65	58
Fe	River water	NH_4Cl (0.02 M)	-0.75	61
Fe	Seawater	Ammonium oxalate (0.1 M)	-0.85	58
Pb	River water	NH_4Ac buffer pH=6.4	-0.45	53
Pb	Wine	NH_4Ac (0.05 M)	-0.52	51
Tl	Natural water	NH_4Ac buffer pH=6.4	-0.60	53
Cu	River water	NH_4Ac (0.02 M)	-0.27	61

2.5. Paper V

Kristina Strasunske, Øyvind Mikkelsen, Gabriel Billon.

Nafion coated silver amalgam electrode for determination of trace metals by anodic stripping voltammetry.

Electroanalysis, 2010, 22, 501-507.

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2.6. Paper VI

Kristina Strasunske, Øyvind Mikkelsen, Eve Petroix, 2010.

Silver germanium and silver antimony electrodes for determination of trace metals by anodic stripping voltammetry.

Submitted, 2010, *Electroanalysis*.

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