Electrochemical stripping analysis, a powerful technique for real-time controlling of environment pollution from heavy metals

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Abstract: The real-time controlling of environmental pollution from heavy metals is of great importance. Although several instruments and technologies are already available for laboratory use up to date there is not still any fast and low cost device that can solve such a problem fulfilling all the necessary criteria for the in-situ and long-term monitoring of heavy metals in waters. The application of electrochemical stripping analysis for heavy metal analysis using a flow through system will be shown. The detection system is based on screen-printed electrodes (SPE) which allow an easy electrochemical stripping ensuring a high sensitivity in detection of heavy metal traces and allowing an \textit{in-situ} control of water pollution. The results obtained for the measurements of lead, cadmium and copper including the response stability will be shown. Concentrations up to few ppb have been possible to be detected with SPEs immersed up to a 2 week monitoring period. The mentioned electrochemical detection system is under further development for its future integration into a complex microanalyser that aims to be with interest in the future for water risk management in Europe in the framework of WARMER, a FP6 European project.

Keywords: Heavy metals; Lead; Cadmium; Copper; Electrochemical Stripping Analysis; Screen-printed electrodes; Flow through analysis; WARMER.

1. WATER POLLUTION AND MONITORING SYSTEMS

Since many years modern civilisation has become concerned about the water quality from all rivers, lakes, underground waters, as well as in waste waters. Nowadays, society brings very severe danger of degradation for our environment not only through catastrophes (hard risks), but also through such called “soft risks”, which involves the slowly degradation of the environment leading to disaster.[1, 2] For this reason on-line chemical analyses for water quality measurements, are considered as very important. Water monitoring tools must be adapted or improved to face new objectives, such as investigation, surveillance and operation. Given that the needs for monitoring are increasing within resource limits, the emerging tools for water-quality monitoring are being based on new principles and techniques, giving either quantitative or qualitative information. For instance, ion-selective electrodes (ISEs) have been employed as a tool for process control monitoring, measuring concentrations of many ions in drinking and other types of water. [3] Although ISEs are applied in a number of fields in flow through systems, such as clinical or environmental, they have some limitations concerning the detection limits and their low selectivity.[4] Sensors based on electrochemical stripping analysis are an alternative to ISEs. The
application of this emerging technology in connection to the use of screen-printing electrodes (SPE) for water-quality monitoring is the main objective of this paper. Monitoring systems should be built by developing small and easy-to-maintain smart sensors, being able to detect a large spectrum of pollutants, typical for monitored region. The Water Risk Management in EuRope (WARMER) is an FP6 EU project that aims to create an extended system for on-line water monitoring with main purpose of risk management, integrating mixed technologies in the areas of semiconductors, analytical chemistry, micro-mechanical fluidic systems, ICT technology, remote sensing and extensive networking of environmental water monitoring data. The system will be ready to be connected in a large network with terrestrial “in situ” sensors and satellite remote sensing of data, capable of creating risk maps for the region. This will lead to have permanent control of water resources in Europe.

Several detection techniques ranging from optical to electrochemical will be integrated into the water monitoring system. This paper will show the latest advances in the design and application of electrochemical stripping based sensors for heavy metal analysis.

2. ELECTROCHEMICAL STRIPPING ANALYSIS FOR HEAVY METALS.

Heavy metal pollution is a growing environmental problem which requires immediate attention in terms of fast, low cost and effective devices for in-situ control. Several techniques for heavy metals detection are being used. Nowadays, the most common methods used for the analysis of heavy metals are flame atomic absorption spectrometry, graphite furnace-atomic absorption spectrometry, inductively coupled plasma-atomic emission spectroscopy and inductively coupled plasma-mass spectrometry.[4,5] These techniques have high sensitivity, accuracy and reproducibility. They are commonly used for measuring trace metals in laboratories but they are not suitable for in-situ measurements due to their complex set up. Because health concerns and legal restrictions of contamination by heavy metals, it is critical to have probes that can provide rapid on-site evaluation of heavy metal contents. Towards this goal, electrochemical methods offer several advantages related to cost and simplicity. Electrochemical stripping analysis (ESA) has proved to be a powerful technique for the determination of trace heavy metals in environmental, clinical and industrial origin samples.[6-9] ESA enhances selectivity and sensitivity by combining heavy metal separation, pre-concentration and determination in one step.

ESA has a first step that consists of the electrodeposition of the heavy metal ions at constant potential for the purpose of their preconcentration onto the surface of a working electrode, normally in a stirring solution. The second step is a linear potential sweep in the anodic direction to reoxidize or strip out the plated metals after a known and measured time. The concentration of the metals onto the electrode surface is higher than in the solution achieving by this way lower detection limits.

Square Wave Anodic Stripping Voltammetry (SWASV) is the most used ESA method for heavy metals. SWASV offers several advantages including a more rapid determination step and the fact that the necessity to remove dissolved oxygen from solution is avoided.

The focus to further improvements of ESA is mainly directed to the choice of the working electrode material. Traditionally, mercury has been used as working electrode material for heavy metals analysis in ESA due to its ability to form an amalgam with the metals. It is well known that mercury is highly toxic and the increased risks associated with its use and manipulation have caused a trend for more environmentally friendly materials. [10]. The use of bismuth instead of mercury is also reported due to its properties to form alloys with different metals but at the same time its lower toxicity in comparison to mercury. Gold-based SPE have also been used for trace measurement of heavy metals in connection to potentiometric stripping analysis.[11]

3. SCREEN-PRINTED SENSORS AND THE MEASURING SYSTEM

Screen-printing technology is a well known alternative for making patterns on various substrates (i.e., paper, plastic, wood, glass, ceramics, etc.). It offers the possibility of mass and inexpensive production of the screen-printed electrodes (SPE) to be used for several applications including the ESA of heavy metals.[6-8] SPEs (Ecobioservices & Researches s.r.l., Italy) have been used in this study (see Figure 1).
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Figure 1. Image of the hand held device system used for ESA of heavy metals. The principal components are the Palmsens potentiostat; a pocket PC and the SPE the details of which are shown in the right side: a reference electrode (R), a working electrode (W) and a counter electrode (C). They consist in three electrodes (working, W; reference, R; counter C, electrodes) in a single strip. W and C are based on graphite ink while R is a do-reference electrode based on a silver ink (see Figure 1). The graphite working electrode is modified with a cellulose-based membrane using a solution containing 100 mg of mercury acetate, 100µL of acetic acid in 10 mL of H₂O. To 1.5 mL of this solution, were added 3.5 mL of H₂O and 12.5 mg ml⁻¹ of Methocel® 90HG. The 5µl of this solution were cast onto the surface of the working electrode, dried in the air at room temperature.[12] It is well known that the electrodes configuration and the graphite based inks used for printing significantly affect the electrochemical performances of the printed strip sensor being the composition of the working electrode the most important.

The measuring system used is a PalmSens potentiostat, battery powered that offers future possibilities to be integrated in the automatic analyser. The SPEs used in metal detection have been checked in both batch and flow through measuring systems.

4. HEAVY METAL MEASUREMENTS

The measuring system (see Figure 2a) consists of a peristaltic pump used for pumping the measuring solutions to the flow cell where the SPE is integrated. The SPE is connected through the PalmSens potentiostat which is at the same time connected to the Pocket PC that control the applied potential and measure the currents giving the final Square Wave Voltammetry (SWV) curves used for heavy metal quantification.

The measuring SWV parameters are: potential range for stripping was between -1.1 and -0.15 V. The square wave waveform has a step potential of 3 mV, a pulse amplitude of 28 mV and a frequency of 15 Hz. A conditioning step to clean the electrode from residual heavy metals, applying a potential of -0.15 V
for 60 s, is used. The next step is the deposition step, where a potential of -1.1 V is applied to the working electrode. First two steps (conditioning and preconcentration) were performed in flow通过 conditions with a flow rate of 300 µL/min combined with stirring conditions. An equilibration step of 30 sec. is applied after the preconcentration step in quiescent solution (stop flow and not stirring). A pre-treatment step for the sensors is needed when the electrode (SPE) is used for the first time. It consists of applying a potential of -1.1 V during 300s and it is a necessary step to activate the mercury film of the SPE.

The flow cell used consists of a cylindrical flow cell of 10 mL of volume (Figure 2b). The advantage of this flow cell is that it avoids the risk of bubbles forming as well as the dryness of the sensor while operating during a long measuring period (up to 2 weeks). However this cell has the drawbacks of the use of stirring conditions as well as of the high amounts of sample required for measurements.

An external reference electrode (immersed in the same flow cell) has been used due to the fact that the medium did not contain chloride ions necessary for the internal reference electrode (pseudo reference electrode) to work normally.

For the batch system the measurements were performed by immersing the SPE in an acetate buffer 0.1M (pH 4.75) containing 100 ppb of lead. An external reference electrode was immersed in the same solution and was used instead of the internal one. Conditioning and deposition step have been performed under stirring conditions but equilibration step and square wave scan were performed in quiescent solution. No oxygen removing was performed. A stand-by potential of -0.15V was applied when the sensor was not used. The SPEs was immersed in the measuring solution during the whole measuring period.

For the flow through life-time measurements, the external RE was not used. Measurements were performed by immersing the SPE in a solution of 100 ppb of lead in HCl 0.1M (so the external RE was not needed). Acetate buffer 0.1M (pH 4.75) was used to perform the activation of the electrode and for stand-by conditions to avoid the damage of the electrode.

Figure 4 shows the stability of the responses during a 2 weeks measuring period under the mentioned conditions.

Figure 4a shows the trend for 100ppb concentration of lead in the batch measurements with the described parameters. There is a good stability (rsd about 10%) in the measurements performed within the same day and also during the two weeks. In the flow through system (figure 4b) the measurements are less reproducible but the peak height is higher showing that the efficiency of the stripping analysis is higher.
due probably to the combined flow and stirring conditions. In both cases it can be affirmed that the SPE has a lifetime of at least two weeks being the electrode immersed in the measuring solution (acetate buffer 0.1M pH 4.75). Some parameters including the pH of the measuring solution are still being studied so as to improve the reproducibility of the measurement.

Some tests with real sea water samples have been already performed in both systems showing good responses for different concentrations of heavy metals. Test were performed spiking real sea water samples from Mediterranian sea (Mataro area), North sea, Cantabria sea and Mar Menor lagoon in a heavy metal range from 5 to 100 ppb. Fresh water, contaminated with heavy metals, from different sources in Catalonia were also analysed for lead contamination. The results were compared to the standard method of heavy metals determination in sea water (Hang Drop Mercury Electrode HDME) giving rise to good results with no significant differences (results not shown).

5. CONCLUSIONS.

The designed flow through system and the flow cells presented in this paper show good response for heavy metals determination using SWASV as the selected ESA technique. A linear response to Pb, Cd and Cu at 10 to 100 ppb has been observed being the measuring system stable during a 2 weeks measuring period. The developed detection system will open the way for the fast, low cost and in-situ simultaneous analysis of trace heavy metals.

Modifications of the SPEs so as to improve the analytical performance and avoid the use of mercury are still in process at our laboratories with the aim to integrate these in an automated microanalyser for field use. Home made electrodes (mercury-free) versus mercury based electrodes are being evaluated in terms of analytical performance. The home-made SPEs have been modified with bismuth, an environmental friendly material that substitutes mercury due to its possibility to form alloys with different metals. In addition to the SPE improvement, other flow cells designs are being considered. The use of a thin-layer wall-jet, including a lab-on-a-chip platform and new modifications of the SPEs are being considered and will be object of future publications.

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REFERENCES