SOUTHAMPTON WORKSHOP, 30th MARCH 2009

POSTERS ABSTRACTS

1. Solid-state ion-selective electrodes for flow analytical systems

By W.Woblewski, M. Chudy, E. Malinowska (Warsaw University of Technology, Faculty of Chemistry, Poland), B. Wisocki and J. Taff (Medbryt Sp. z o.o., Poland)

The paper presents the development of solid-state potentiometric microelectrodes based on ion-sensitive polymer membranes and back-side contact transducers – Au and Ag/AgCl miniaturized electrodes (squares 5 x 5 mm, thickness 0.5 mm) – developed using silicon technology or on epoxy-glass laminate support. Solid-state microelectrodes sensitive towards inorganic charged pollutants were obtained by the deposition of polymeric membranes on the surface of Au microelectrodes. Ag/AgCl microelectrodes, developed in silicon technology, have been applied as chloride-sensitive sensors. The responses towards primary ions, selectivity and long-term stability of the developed ion-selective microelectrodes were determined in an automated flow-through system.
After the design of the ion-selective microelectrode prototypes, the process of the sensor industrialisation was realized in a special facility (MEDBRYT) for the semi-industrial sensor fabrication (deposition of the polymeric membranes using an automatic dispenser) and sensor testing. Several sets of industrialised solid-state microelectrodes for the determination of inorganic pollutants: NO_3^-, NH_4^+, K^+, Na^+ have been prepared. The microelectrodes were tested in new modular flow-cells enabling their easy connection and mounting in a measurement loop-flow. The final solid-state microelectrodes will be implemented in a portable analytical device (LFA field test analyzer), developed by SYSTEA, dedicated to on-line water quality monitoring.

2. Novel polymeric chemical sensors for determination of Pb(II) ions

By A.V. Legin, O.V. Mednova, D.O. Kirsanov (St. Petersburg University, Laboratory of Chemical Sensors, Russia) and V.A. Babain (Khlopin Radium Institute, St. Petersburg, Russia)

Novel poly(vinyl chloride) (PVC) plasticized membrane electrodes for determination of lead(II) ions based on N,N'-tetrabutyldiamide of dipicolinic acid as a neutral carrier were developed and studied. The sensors have demonstrated high sensitivity to Pb2+ ions over a wide concentration range 10^{-7} – 10^{-2} mol/L in unbuffered lead solutions with the slope of calibration curves in the range 30-45mV/decade, depending on concentration and the detection limit was about 7.0 pPb^{2+}. The detection limit in buffered solutions was found to be as low as $<10^{-9}$ mol/L (less then 200 ng of lead ions per litre) and the slope was 25 mv/pPb. Selectivity (expressed as logK) in the presence of Cu^{2+}, $Cd^{2+}$and Zn^{+2} ions is about -2, which means that 50-100 excess of interfering ions is acceptable for this Pb polymeric sensor.

3. Heavy metals detection using screen-printed electrodes

By G.Aragay, A.Puig, R.Güell and A.Merkoçi (ICN - Universidad Autonoma Barcelona,Spain)

The last results obtained in the heavy metal detection using batch and flow through system will be presented. The design of the flow through system used along with the results obtained including the stability of the responses to heavy metals will be shown. The developed sensors are applied in both synthetic and real sea water samples achieving detection limits of up to few ppb.

4. Design of a phenol biosensor based on carbon nanotubes.

By M.Guix, M. Sahin, B.Perez, A.Ambrosi and A.Merkoçi (ICN - Universidad Autonoma Barcelona,Spain)

A phenol biosensor based on screen-printed electrodes modified with carbon nanotubes (CNT) and tyrosinase is prepared. Several parameters that affect the biosensor response are optimized. Studies performed by cyclic voltammetry or chronoamperometry clearly show the advantages of CNT. The preliminary results show that the developed biosensor can detect up to 0,86 µM phenol and have a linear range of response from 2.5-75 µM. The application of the developed biosensors in real sea water samples and comparison of the results with standard methods will be also discussed

5. Sensors and devices for water analysis

By M. Zaborowski, D. Tomaszewski, B. Jaroszewicz, P. Grabiec (Institute of Electron Technology, Warsaw, Poland) and J. Taff (Medbryt Sp. z o.o., Poland)

Devices suitable for water analysis have been described in the paper.
A chloride ion sensor has been fabricated in IET using monocrystalline silicon substrate. Both sides of the Si wafer are covered with Cr/Au layers by means of magnetron sputtering technique. Square 1 x 1mm electrodes are patterned and wet etched in a front side of the wafer. Next, a silver layer is electrodeposited and chlorinated to form AgCl layer.
Potentiometric Au electrodes have been also fabricated. They serve as substrates for ion-sensitive layers deposition by WARMER partners. The electrodes are fabricated in process, which is generally similar to the Cl- sensor manufacturing process.
A flow package has been designed by SME MEDBRYT and IET for WARMER needs. The package has been made of ABS. It contains one o-ring sealed sensor chip; the chip could be easy replaced. Each package has been equipped with two gold plated connections. The packages are designed for connection in series in a fluidic system.
The IET is a manufacturer of an ISFET sensor, which has been constructed with source and drain contacts placed in a backside of sensitive area. The hydrogen ion sensitive area (gate of the transistor) is made of silicon nitride layer. ISFET fabrication process has been described elsewhere. The flow package is suitable for this sensor.
A diode thermometer is a new device, which has been developed for fluid examination. Measured temperature is proportional to a drop of tension in p-n junction. The junction has been made by means of boron diffusion to a monocrystalline Si n-type wafer. The device has been fabricated in a Si membrane, which is thinned to 100um. It gives low thermal resistance between p-n junction and an investigated fluid. An oxide layer insulates electrically the device. The thermometer can work in the same flow package as other sensors, connected in serial in the fluidic system.

6. Thick-film Sensors for Analytical and Bioanalytical Applications

By Serena Laschi, Ilaria Palchetti, Giovanna Marrazza, Marco Mascini (Università degli Studi di Firenze, Dipartimento di Chimica, Italy)

Thick-film technology is one of the most used technique for sensor production, since the equipment needed is less complex and costly than other ones; moreover thick-film electrochemical transducers can be easily mass produced at low cost and thus used as disposable. Nowadays disposable thick-film electrochemical transducers are mainly produced by the screen-printing technique. Screen-printing technique allows the production of planar devices by depositing different layers of inks on a plastic substrate. The obtained devices can be applied to environmental as well for clinical or food analysis, and in the field of electrochemical biosensors. Our research group is engaged in the field of sensor and biosensor development using such screen-printed sensors as transducers for analytical and bioanalytical applications. Different kind of inks (graphite, gold) together with different draws are combined in order to obtain sensors and array of sensors suitable for target analytical application. These devices are then coupled with fast and sensitive electroanalytical techniques such as differential pulse voltammetry (DPV), square wave voltammetry (SWV), chronopotentiometry at constant current, or chronoamperometry in order to obtain an accurate analytical result in term of minutes, and this is of great significance when in field analyses are performed

7. Simultaneous determination of heavy metals using an automated electronic tongue

By A. Mimendia, J.M.Gutiérrez, M. del Valle (Sensors and Biosensors Group - Universidad Autonoma Barcelona, Spain) and A. Legin (St. Petersburg University, Laboratory of Chemical Sensors, Russia)

Despite the potentialities of electronic tongue (ET) systems are already known, their application, for example to the environmental field, is still not widely spread. One reason for this could be the time and experimental effort required to obtain the model response of the ET through a calibration stage. In order to overcome this we propose using a flow technique in conjunction with the ET. Besides the time saving, a richer signal can be acquired when the sensors are used in flow conditions. A subsequent data treatment using artificial neural networks (ANN) is then used, to obtain the sought information of content related with metal ions studied and to discriminate the interferences.

8. **Evaluation of the field deployable Loop Flow Analyzer for heavy metal determination in water through extended laboratory experiments**

By R. Allabashi and W. Stach (BOKU - University of Vienna, Austria)

This work presents the evaluation of the system, as the preliminary step to the final evaluation under real conditions in field experiments. An extensive evaluation of performance characteristics like accuracy, stability and sensitivity is performed using synthetic mixtures of heavy metals (Pb, Cd, Cu, Zn). The evaluation criteria are chosen to be a) stability, in terms of precision for calibration slope and control sample, b) accuracy in terms of recovery for calibration slope and control sample concentration and c) sensitivity in terms of limit of quantification (LOQ). Two types of membranes are undergoing the tests, chalcogenide glass for Cu, (Cd) and polymeric thick film for Pb, Zn, (Cd). The influence of measuring conditions, like pH, buffer solution, calibrants and their concentrations, sensor contact time and cross sensitivity on the stability and accuracy of the measured signal is studied during a period of several months. Further experiments are ongoing with potentiometric sensors based on PVC membranes, expected to overcome the problems with cross sensitivities observed before.

9. **Multiparametric microLoop Flow Analyser working with miniaturized Ion selective Electrodes for water quality analysis of chemical parameters**

By L. Opalski, P.Z. Wieczorek (Warsaw University of Technology, Poland), P. Moscetta, L. Sanfilippo (SYSTEA S.p.A., Italy) and M. Malizia (Sysmedia S.r.l., Italy)

Within the frame of WARMER research project SYSTEA developed a fully autonomous µLFA benchtop multiparametric analyzer with controlled water flow conditions capable of measuring K^+, Na^+, $NH4^+$, $NO3^-$, Cl^- (sensors developed by WUT), Cd^+, Pb^+ and Zn^+ (sensors developed SPU), integrated in modular disposable flow-cells. The analyzer can be used for automatic monitoring of potable, surface and ground water. The prototype performs direct or multiple standard addition based measurements using a dedicated version of the micro Loop Flow hydraulics and it is designed to be further integrated inside an in-situ measuring probe. Accuracy/precision of measurements can be enhanced numerically, taking into account on-line characterization of actual selectivity of critical sensors. The prototype developed can be programmed by a scripting language specifically adapted to allow the User to configure and customize the analytical cycle managed by the prototype device.

10. **In-situ voltammetric probe for heavy metal detection**

By P. Moscetta and L. Sanfilippo (SYSTEA S.p.A., Italy), G. Aragay, A.Puig, M. Cadevall, M.Medina, A. Merkoçi (ICN - Universidad Autonoma Barcelona,Spain) and P. Moscetta (Sysmedia S.r.l., Italy)

The successful integration of heavy metal screen-printed sensors (SPE) into the *in-situ* voltammetric probe so as to achieve the required analytical performance is strongly dependent to the flow electrochemical cell as well as the whole flow through and electronic set-up of the system. A new flow through cell that better fits to the developed SPEs ensuring a tight close as well as an easy electrode replacement system has been designed and all the corresponding electrochemical parameters including those of the liquid flow are optimized accordingly. The whole system probe that will ensure the smooth running of all the analytical steps including also its hardware & software is shown. The application of the developed SPEs using the developed *in-situ* probe system represents the final step so as to achieve the objective of WARMER project for voltammetric detection of heavy metals. This work is still in process and the final results will be shown by the end of the project.

11. **Long term operation of the NPA / DPA multi-parametric nutrient probe in a simulated water monitoring station and its evaluation using real surface water.**

By R. Allabashi, A. Pressl and W. Stach (BOKU - University of Vienna, Austria)

The in-situ nutrients probe developed for WARMER project is an innovative automatic chemical analyzer for “in-situ” and continuous measurements, based on a new analytical technology and named µLFA (micro Loop Flow Analysis). The probe allows the automatic analysis of up to four nutrients, by sequential analysis in a single analytical reactor; the parameters to be measured are: ammonia, nitrate+nitrite, nitrite and orthophosphate. An extensive evaluation of system performance characteristics like day-to-day repeatability, short and long term drift, measurement accuracy in real

water matrix belong to the main goal of the field experiments. Real surface water from river Danube is the matrix used for the experiments. An artificial water channel [40cm x 40cm x 150cm] is simulating the river bed, making possible also the adjustment of water velocity and flow rate. The availability of two parallel tanks gives an additional flexibility on experimental design, like water circulation possibility and changing of water quality under investigation, simulating different situations needed for project specific studies.

12. Integrated remote sensing and in situ monitoring for water risk management

By L.H. Pettersson, T. Hamre (Nansen Environmental and Remote Sensing Center, Bergen, Norway), A.R. Allen, B. Sputh and O. Faust (School of Engineering, University of Aberdeen, UK)

The combination of environmental measurements from different sensor equipment improves water quality monitoring and associated risk management. The merging of in-situ and remote sensing data is a prerequisite to efficient monitoring of coastal and marine environments, because of their complementary nature and application areas. Both sensor types can monitor the same phenomena, but remote sensing delivers the overall picture and in-situ measuring provides localized, high-resolution measurements, over a wide range of parameters. The WARMER (WAter RiskManagement in EuRope) system combines remote sensing satellite data with in-situ measurements from multiple sources for water quality risk management applications and delivers products to end-users through a web GIS (Geographic Information System) portal. For the WARMER demonstration campaigns in 2008 a regular provision of satellite Earth observation (EO) based products using data from the European Space Agency's Envisat Medium Resolution Imaging Spectrometer sensor in full resolution (MERIS FR) and Synthetic Aperture radar (ASAR) have been in operations since 1st May 2008 covering southeast UK, including the Blackfield Estuary location. Production lines for near real-time generation of EO data product have been established for each of the satellite sensor data.

13. Conditioning in-situ sensor data for use in remote sensing environmental monitoring

By A.R. Allen, B. Sputh, M.G. Murshed (School of Engineering, University of Aberdeen, UK), T. Hamre, L.H. Pettersson (Nansen Environmental and Remote Sensing Center, Bergen, Norway), D. Vitulli (Sysmedia S.r.l., Italy)

The WARMER system can form the basis of water quality risk management applications. It can provide in-situ sensor data to users via web-based databases such as Zetaced. It can also combine remote sensing (RS) satellite data with in-situ measurements from multiple sources: the resultant products are delivered to end-users through a web Geographic Information System portal (DISPRO). The ADDP (Aberdeen DISPRO Database Proxy) is a key element in the WARMER system, because it conditions in-situ measurements for combination with RS data. This poster details the handling of in-situ data within the ADDP, and its capability to aggregate data from multiple sources. Features such as data polling and synchronization, the spatially-enabled proxy database, and interfacing to the DISPRO portal are described. The ADDP component is designed to be easily modified for other database architectures.

14. Interoperable GMES services for marine pollution monitoring and forecasting

By S. Sandven, T. Hamre (Nansen Environmental and Remote Sensing Center, Bergen, Norway), D. Dunne (University College Cork, Ireland), S. Groom (Playmuth Marine laboratory, UK) and Y. Coene (Spacebel S.A./N.V., Belgium)

The lack of a pan-European infrastructure for uniform access and distribution of environmental data is a severe problem when monitoring and forecasting marine pollution, because situations such as oil spills and harmful algal blooms often have an international dimension. Thus, users in several countries and organisations need access to the same data, including observations, derived parameters and predictions of future conditions. The InterRisk project is developing a pilot system for interoperable GMES services for marine pollution monitoring and forecasting, based on noted GIS and web standards in line with INSPIRE recommendations. The pilot system is being validated by users responsible for risk and crisis management in case of oil spills, harmful algal blooms and other marine pollution events, in Norwegian, UK, Irish, French, German, Polish and Italian coastal waters. InterRisk offers basic services like satellite and in situ data delivery, ocean model simulations,

metadata catalogue access, as well as complex services like oil drift prediction and ecosystem modelling. These services are embedded in the Service Support Environment (SSE) originating from European Space Agency projects. The SSE enables service providers to make their services available to the GMES user community through a common portal. In addition, value-adding companies can develop new services by combining existing ones and deliver these new services through the same portal. End-users are free to choose from all available services, selecting the one(s) best suited for their needs. It is expected that the developed services and SSE components can be used to establish sustainable GMES services.

15. ECOOP Data Management System for in situ observation data

By D. Dunne (University College Cork, Ireland) and Ali Al-Ohtman (CMRC, Ireland)

In order to maximise the value and benefit from existing national and European resources in operational oceanography, existing EU-wide marine observation systems have to be integrated to harmonise the flow of real-time and near real-time observational data. Using well defined standards, the EU FP6 ECOOP (European coastal-shelf sea operational and forecasting programme) project is designing and implementing a European data management system (EDMS) which dovetails with the developments of other EU projects such as SeaDataNet, MERSEA, MyOcean, SEPRISE and InterRisk, taking into account upcoming INSPIRE directive guidelines and GMES (Global Monitoring for Environment and Security) Marine Core Service policy. The data management system also follows key requirements for the European Marine Observation and Data Network (EMODNET) which is part of the Integrated Maritime Policy for the European Union ("The Blue Book"). The EDMS is designed to ensure proper and maximum real-time and near real-time delivery of pan-European observational data including sea temperature, salinity, wave, currents, sea level and river run-off data. The quality of real-time and near real-time observational data is ensured by a series of protocols regulating the operational activity from data collection, transmission, evaluation, and dissemination. The EDMS intends to be a high level service for the exchange of observational data, avoiding the diversity of in-house data management systems and internal processing chains.

16. WARMER second field study planned at the Venice lagoon

By L. Sanfilippo (SYSTEA SpA, Italy)

The deployment of WARMER continuous monitoring platform at the Venice Lagoon will be the second field test (duration of the field test: ca. 3 months) of the project, after the first test conducted in England at Hanningfield reservoir and Blackwater estuary. This study will be conducted with the co-operation of Magistrato alle Acque di Venezia which maintains a continuous monitoring network (SAMANET) with ten stations. The Venice Lagoon with this well established continuous monitoring net, infrastructure with co-operating laboratories, research institutes and universities, all these facilities makes it an ideal location for the field test.
During the field test, WARMER monitoring pontoon will be moored at the following SAMANET stations for a period of 3 weeks at each station, starting from mid April till end of July.

- Ve-4 Fondamenta Nuove; (in the city, by the side of Murano Island; affected by pollution from boat traffic and Murano glass industry)
- Ve-6 Sacca Sessola: (outside the city area in the middle of the lagoon, where spring and summer algal booms are common)
- Ve-5 Porto Marghera: (at the outlet of Porto Marghera industrial area, one of the heavily polluted sites in Italy)
- Ve-7 Dese: (at the outlet of the Dese river; brings point and diffused pollution from watershed).

SAMANET stations are geared to measure number of parameters (pressure, temp., conductivity, salinity, DO, DO%, pH, Redox, Chlorophyll-a, Turbidity) continuously. In addition to above mentioned parameters WARMER pontoon is equipped with a nutrient analyser to measure dissolved nutrients continuously (SRP, nitrite, nitrate and ammonia). During the field test WARMER project intends to test the newly developed sensors for nutrients and metals. Another consideration is Venice Lagoon is a large, eutrophic, turbid water body with successive algal booms during the year. These developments are helpful for some of the remote sensing, tasks under taken by NERSC in attempting to use it as a tool to drive and calibrate models using chlorophyll-a, total suspended solids data and colour spectra.