An innovative automated flow measuring probe for the measurement of chemical parameters in water based on CHEMFET sensors

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Abstract
An innovative "in-situ" flow measuring probe for the measurement of chemical parameters in water based on CHEMFET sensors is going to be developed under the R&D EC Fifth Framework SEWING project.
The probe demonstrator is the final result of the research activities carried on during the first two years of the project; it is based on the measuring results obtained by other two flow devices used in lab to characterize and test the different types of CHEMFET sensors developed.
The new CHEMFET sensors will allow the measurement of the main chemical parameters in underground and surface water (NH_4^+ and NO_3); these measurements will be compensated by the on-line measurement of K^+ and Na^+ , water temperature and pH.
The analytical part of the new instrument is based upon a novel patented technology named micro Loop Flow Analysis (μLFA); the probe will be equipped with a special near real time software algorithm named ISFETs Source Separation method, which will allow to correct the analytical results for interference of unknown compounds, lifetime and long-term drifts.
The probe will be equipped with specific CHEMFET's conditioning procedure and built-in automatic calibration procedures, both to periodically trim the algorithm but also to provide to the user a reliable and standard way to check the instrument's performance.

Keywords
Analysers, Early warning, Data Transmission, Chemical sensors, Chemical pollutants, Underground water measurements, Water Quality management.

INTRODUCTION

Water, air, soil and sea pollution is a threat for life on our planet. Water is one of the most important elements, as its availability is diminishing, while its pollution is growing. It becomes extremely important to develop systems for measuring, monitoring and early warning, concerning concentration of pollutants in water. The European Fifth Framework Programme for Research and Development (FP5) strongly emphasises the problem of environment protection against pollution. Nine institutions from 7 European countries were granted with the FP5 project SEWING (System for European Water monitorING), which has started on September 2001 and lasts for 3 years.

The main goal of SEWING project is to create a relatively cheap and generally accessible system for in-the-field and in real-time monitoring and early warning of water pollution with non-organic ions. Surface and underground waters were chosen as the object, particularly in agriculture and mining areas, so ammonia, nitrate, calcium, potassium and sodium ions were selected. As ion selective sensors CHEMFETs were chosen, based on ISFETs (Ion Sensitive Field Effect Transistors).

The smart probe, monitoring water in which it is immersed, is composed of a flow-cell with CHEMFETs, pH and temperature sensors, of electronic interfaces, data processing and controller chips, memory, transmitter and power supply. Hydraulic part of the probe is responsible for pumping measured water to the flow-cell, conditioning properly the sensors before the measurement and cleaning them after each measurement too.

The purpose if this paper is to present the prototype of the measuring probe with preliminary results of its verification in real life conditions.

METHODS

CHEMFET sensors

The construction of ISFET is based on a MOSFET transistor. In the case of the ISFET, the gate metal electrode of the MOSFET is replaced by an electrolyte solution, which is contacted by reference electrode (Figure 1). When SiO_2 is used as the insulator, the gate oxide contains OH-functionalities, which are in equilibrium with ions in the sample solutions. The hydroxyl groups at the gate oxide surface can be protonated/deprotonated and thus, when the gate oxide contacts an aqueous solution, a change of pH will change the SiO_2 surface potential.

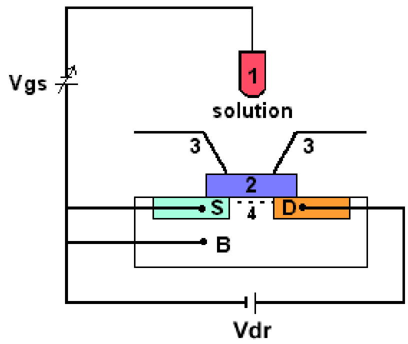

Figure 1: Schematic construction of ISFET

1–reference electrode, 2–gate, 3–insulating resin, 4–channel, S–source, D–drain, B–bulk

The ISFET can be modified with an ion-sensitive membrane, which determines the response of the sensor. One of the approaches has led to a chemically modified FET (CHEMFET), where the deposition of an intermediate layer (polyHEMA) between the ion-selective membrane and the transducer established a reversible electron transfer pair at the ion-selective membrane/ISFET interface, through the immobilized inner solution (Sudholter *et al.*, 1990).

Plasticized PVC membranes were widely used as sensing membranes of CHEMFETs. However, due to their weak adhesion to the FET other polymer matrices are also applied to construct CHEMFETs of enhanced durability. Silicone materials, especially polysiloxanes, offer the greatest possibilities in improving the robustness of the membranes. Moreover, the use of UV-photopolymerizable monomers is advantageous from the point of view of the ultimately desired mass production of the CHEMFETs, which is essentially based on photolithography.

In the SEWING project two types of ISFETs, dedicated for the flow measuring probe, were designed: front-side contact structures (made by LAAS-CNRS and MICROSENS) and back-side contact structures (made by Institute of Electron Technology and Warsaw Univ. of Tech., Poland).

The paper presents the development of “in-situ” flow measuring probe for the measurement of chemical parameters in water and the construction of back-side contact CHEMFETs (ITE/PW) selective to nitrate and ammonium ions.
The performances of the sensors selective to nitrate and ammonium ions were examined in the flow-cell in a solution of the primary ion in the 0.01 mol l^{-1} solution of Na_2SO_4. The automatic measurement stand. was applied to carry out the measurements.

The automatic measuring stand

The full automated measuring stand was designed for fast ISFET sensors characterisation. It can prepare ions bath for sensor tests and collect measurement data from all sensors under test.

The system is equipped with 4 burettes - Metrohom 765 Dosimat, Reglo Digitall (Ismatec) Peristaltic Pump, number of electrically driven valves, and especially designed fast operating thermostat with cooling/heating system (Figure 2). The sensors operating point (U_{DS} and I_D) is set by two 236 Source Measure Units (KETHLEY) type. The canals (sensors) switching is performed by multiplexer of 34970A Data Acquisition/Switch Unit (Agilent) type. The system is controlled by an embedded PC with IEEE 488 Interface Card and Serial 8xRS 232 Card (National Instruments). The control and data acquisition program was developed using Lab Window C VI 5.5 software.

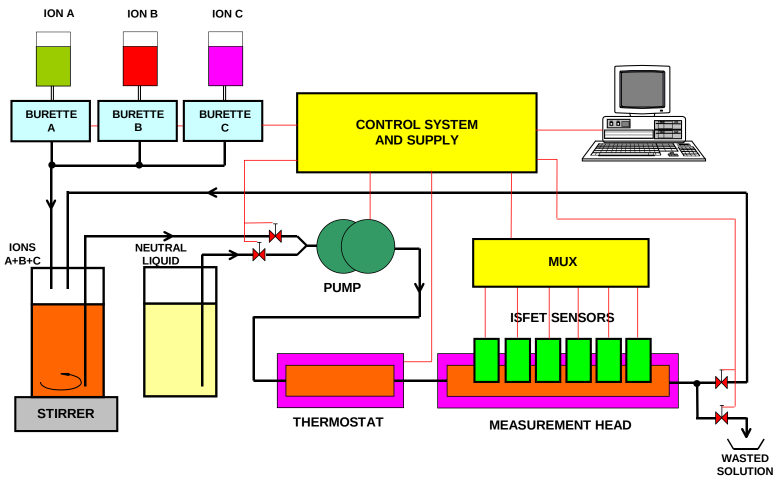

Figure 2: Block diagram of the measurement stand.

<u>General technical data:</u>

- up to 10 ISFET chemical sensors can be tested simultaneously;
- up to 4 different solutions (extendable up to 7) can be added independently into measurement solution (bath) to obtain required ions concentration;
- the ion solution volume, separately injected into bath, can be set in range from 2 µl to 100 ml;
- the bath temperature can be set in range from +5°C to +40°C with accuracy of ±1°K;
- the minimum bath temperature (+5ºC) can be achieved within 12 min. (by chilling) and the highest temperature (+40ºC) within 10 min;
- U_{DS} , U_{GS} and I_D can be defined with error less than 0,25%.

The LFA laboratory test unit

The LFA test unit is a laboratory bench-top analyser, designed to perform automatic measurements, drifts tests and measuring comparisons of two CHEMFET sensors.

The analytical part of the instrument is based upon Loop Flow Analysis (LFA) technology, which is widely used in a variety of chemical analysers for water quality measurements (Gunatilaka *et al.*, 1996); this patented technology ensures a simple and reliable sample handling and measurement and it has reached high levels of analytical automation and instrument miniaturization worldwide.

To allow the automatisation of the measuring method, the standard Loop Flow Reactor (Colosimo *et al.*, 2002) was modified accordingly to the specific analytical method and in particular a two-side flow-cell was integrated to allow CHEMFETs automatic conditioning and measurement.

Figure 3. The LFA laboratory test unit

A second bigger flow-cell is available for the further integration of the FSC CHEMFET sensors too.

The internal electronics and software provide directly output data in concentration unit (mg/l); the benchtop analyser can manage standard additions of a know solution in the sample and two points external calibrations.

ISFET Source Separation (IsfetSS) Algorithm

The nowadays available CHEMFET devices exhibit some problems. They are sensitive to several ions, producing an output signal that must be considered as a real mixture of signals (contributions coming from different ions present in the monitored water). This is the reason why a data processing part intends to separate, in real time, the real and corresponding responses to the different ions. The LFA laboratory test unit and the probe demonstrator are equipped with a smart version of CHEMFET devices, able to facilitate the extraction of relevant information, even in the case of less-sensitive characteristics.

In order to apply IsfetSS algorithm, we need, at least, as many sensors as signals to be detected. Assuming that we can use the Nickolsky equation in order to represent the non-linear analytical relation between parameters and output signals $x_1[n]$, …, $x_m[n]$ corresponding to a non-linear mixture of p source signals $a_1[n]$, …, $a_p[n]$. Expressed in a vector form:

$$\mathbf{x}[n] = (x_1[n] \ldots x_m[n])^T = \mathbf{F}(\mathbf{a}[n])$$

where **F** is a non-linear mixing function, and T denotes transpose. It is implicitly assumed that all the ISFETs in the array are sensitive to the same ion activity a_i and consequently, the other sources are considered as noise. It must be noted that the final system can also provide a measure of the interfering ion activity.

According to the above formulas, the goal of IsfetSS algorithm is to create an inverse of **F** from a set of measurements {**a**[n], **x**[n]} in order to predict ion activities from new input data measurements. The recovery process can be achieved by a p x m separating function **G** which allows an estimation of the source signals {$a_i[n]$, i=1, …, p}through the following reconstruction algorithm,

$$\mathbf{y}[n] = (y_1[n] \ldots y_p[n])^T = \mathbf{G}(\mathbf{x}[n]) \approx \mathbf{a}[n]$$

where **G** must tend to $\mathbf{F}^{-1}$ to obtain a good estimation of **a** with **y**.

The algorithm is implemented using a hybrid neural network approach, with the integration of a linear regression phase into a linear ICA algorithm (Hyvärinen A. *et al.* 2001).

A clear advantage of such an implementation using ICA approach is the possible estimation of linear regressors using a very small set of supervised training samples.

Probe demonstrator analytical technology overview

The primary result of the project until now is the design and the development of the first prototype of a measuring probe (Figure 4), which is going to integrate all the research and the technologies developed during the project. The analytical part of the new instrument is based upon a novel patented technology named micro Loop Flow Analysis (µLFA), which is an evolution of the same technology used to develop the lab benchtop test unit; the main characteristics of this new technology is the extreme compactness (the analytical reactor volume is 5 ml only) and the compatibility to be integrated in submergible measuring devices.

The probe will be able to mount both types of BSC and FCS CHEMFETs, using the linear modular flow-cell already tested in the measuring stand (Figure 5). It will perform the complete electronic management of CHEMFETs, using a customized A/D board designed for this application by other project partners (VTT, Finland; Technical University of Lodz).
The internal software will integrate ad manage automatically the IsfetSS algorithm; to properly manage the CHEMFETs, the probe allows analytical conditioning procedures using ISA buffer,

each measurement to be done using standard addition method, with calibration factors calculated periodically by the system using standard solutions.

Figure 4: Prototype of the measuring probe

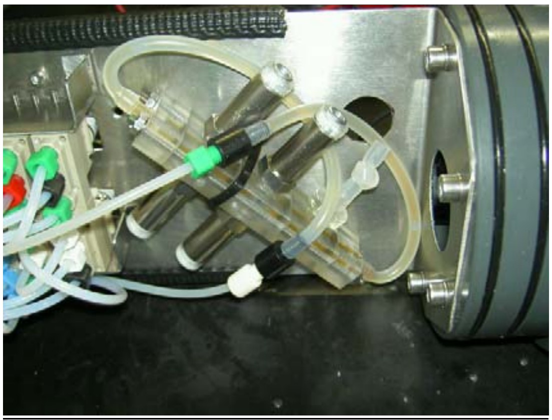

Figure 5: Detail of μLFR hydraulics with the linear modular flow-cell for CHEMFETs

General characteristics:

- Water-proof enclosure, submergible
- Operating temperature range: from +4 to +40 °C, with storage temperature from -10 to +60 °C

Measuring requirements:

- Multiparametric measurements capability: up to 6 parameters measured at the same time
- Fast measurement capability: a complete measurement cycle is performed in less than 5 minutes
- Measuring unattended autonomy: at least one month
- Automatic sample conditioning with ISA buffer solution; automatic cleaning and zero measurement using distilled water
- Standard addition method measurement capability, with automatic compensation for temperature, unknown compounds matrix effect and long term drifts using IsfetSS algorithm for sensor data processing and extraction.
- Periodic automatic calibration procedure using three standard solutions
- Capability to perform fast change of solutions and CHEMFET electrodes and easy maintenance.

Data storage and communication requirements:

- Internal data storage: at least 400 data collected automatically
- Programming and downloading data: locally via RS-232 and external software running on a PC, remotely using an external GSM/GPRS device
- Automatic alarms generation on detection of values over thresholds
- Built-in self diagnostic capability.

Power supply and dimension requirements:

- Low power supply: 12 Vdc, max 10 W during measurement, with sleeping mode capability
- Compact external dimensions: diameter 140 mm, length 900 mm.

The typical applications of the new measuring probe will be:

- underground water control for agriculture purposes;
- rivers and lakes field water pollution measurements
- potable water quality alarm control.

Chemical compounds detected and measured ranges

Table 1 below shows the measured parameters and the actual working ranges, compared with their primary EC emission limits for surface and drinking water.

Parameter	Range (mg/l)	Emission limits (mg/l) EC legislation	
		Surface waters 75/440/EWG	Drinking water 98/83/EWG
Nitrate (NO_3^-)	6-6000	25 / 50	50
Ammonium (NH_4^+)	1.8-1800	0.05-2	0.5
pH	2-12 pH	6-9 pH	6.5-9.5 pH

During the third year of the project we are going to try to lower of a decade the minimum ranges of NO_3^- (down to 0.6 mg/l) and NH_4^+ (down to 0.2 mg/l), in order to better fit with EC emission limits.

RESULTS AND DISCUSSION

All NO_3 sensors worked properly i.e. wide linear range of the responses curves (1÷4.5 pNO_3^-). The detection limit of the calibration curves (10^{-4} mol l^{-1} NH_4^+) of the ammonium-sensitive CHEMFETs was also in good accordance with working parameters of classical NH_4^+-selective electrodes presented in the literature.

The prototype of the probe (fig 4) is going to work in the field by means of SEWING partner IWGA-BOKU in Vienna.

CONCLUSIONS

The measuring probe for non-organic water pollution monitoring, presented in this paper, was an effect of co-operation among all partners of the FP5 project SEWING.

It should be emphasised that the prototype of the probe had to limit the number of ions which are detected or interfering. Within the scope of the project it was impossible to prepare more ion-selective membranes and verify the performance of many different sensors. However, the method is elaborated successfully and at the time the measuring system will be commercialised, more sensors selective for other ions (as Ca^{2+}, K^+, Na^+, Cl^-) will be available.

The authors would like to cordially appreciate collaboration with other partners of the project: Technical University of Lodz (PL), Institute of Electron Technology (PL), LAAS-CNRS (FR), VTT Information Technology (FI), IWGA (AT) and Microsens (CH).

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