



Warszawa, December 22nd, 2004

RESULTS OF THE IST-2000-28084 PROJECT SEWING: System for European Water monitorING

1. Introduction.

The objective of the project, formulated in the contract was:

Creating a cheap, flexible and generally accessible system for water monitoring against pollution with non-organic ions.

After 40 months of work the main planned objectives have been achieved. The following 9 partners took part in the project:

1. Politechnika Warszawska (PW), Warsaw, Poland – co-ordinator
2. Institute of Electron Technology (ITE), Warsaw, Poland
3. Technical University of Lodz (TUL), Lodz, Poland
4. Valtion Teknillinen Tutkimuskeskus (VTT), Espoo, Finland
5. Centre National de la Recherche Scientifique (LAAS –CNRS) Toulouse, France
6. MICROSENS S.A., Neuchatel, Switzerland
7. Universitat Polytechnica de Catalunya (UPC), Barcelona, Spain
8. Universität für Bodenkultur, Wien, (BOKU). Austria
9. SYSTEAM, Rome, Italy

The following four main activities were carried on in order to reach the final aim and will be presented in more details below:

1. Fabricating the CHEMFET sensors selective for particular ions, their verification and measurements,
2. Creating mathematical models of these sensors and on that basis creating software for processing of measurement data, including estimation of ion activities in water samples.
3. Building components of the measurement system: computer controlled hydraulics, data acquisition and on-line data processing, remote communication.
4. Final measurements and verification of the system by the representative of end-users.

The project carried some amount of risk concerning reaching the objectives.

Because of that it was decided at the beginning that most crucial elements of the project will be elaborated in more than one version. It was much more probable to reach the success by that means. And so:

- The sensors were fabricated and measured in two versions:
 - Back-Side-Contact (BSC) by ITE and PW (Poland)
 - Front-Side-Contact (FSC) by LAAS-CNRS (France) and MICROSENS (Switzerland).

- The models and software for data extraction were elaborated by 3 partners: PW and TUL (Poland) and UPC (Spain). The models had different complexity, accuracy and software platforms. The software for data extraction is also on different level of complexity and flexibility.

- For the hardware realisation SYSTEA (Italy) became the main responsible partner. VTT (Finland) also was responsible for alternative version of hardware interface between sensors and data processing hardware and for alimentation. TUL created a laboratory version of ASIC interface and made research in transmitting problem.

Partial results were described so far in 67 contributions on conferences and in 6 articles in scientific journals. Most of them are available on the SEWING WEB page:

<http://www.sewing.mixdes.org>. 24 deliverables were presented to the Project Officer.

2. Sensors

Several steps had to be followed in order to obtain CHEMFETs with desired properties.

- Fabrication of back-side contact BSC-ISFETs (ITE)
- Characterization of pH sensitive ISFETs
- Industrial deposition of the polyHEMA on ISFETs
- Final composition of the ion-sensitive membranes (polymer materials: PVC and polysiloxane) (Politechnika Warszawska- PW- Poland)
- Deposition of K^+ , Na^+ , NH_4^+ and NO_3^- ion-sensitive membranes and in this way realisation of CHEMFETs.

Fabrication of back-side contact BSC-ISFETs (ITE)

Back-Side-Contact (BSC) ISFETs were fabricated in the Institute of Electron Technology (ITE), Poland. They have source and drain contacts on the bottom of the chip, while on the upper side the open gate is available. Figure 1 shows the photographs of the wafer of BSC ISFETs and of the chips from bottom and upper sides. Figure 2 shows the drawing of cross section of the BSC ISFET.

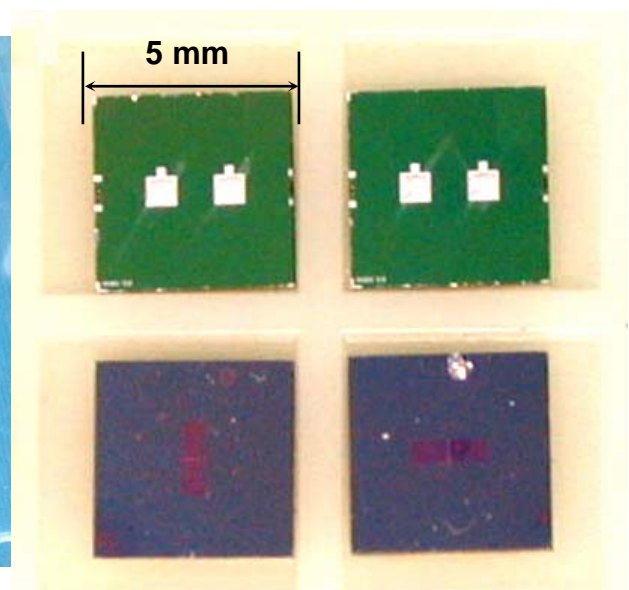
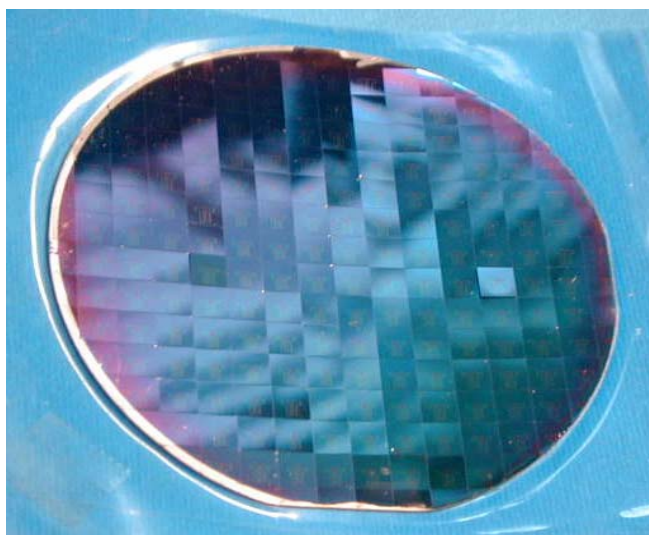


Figure 1

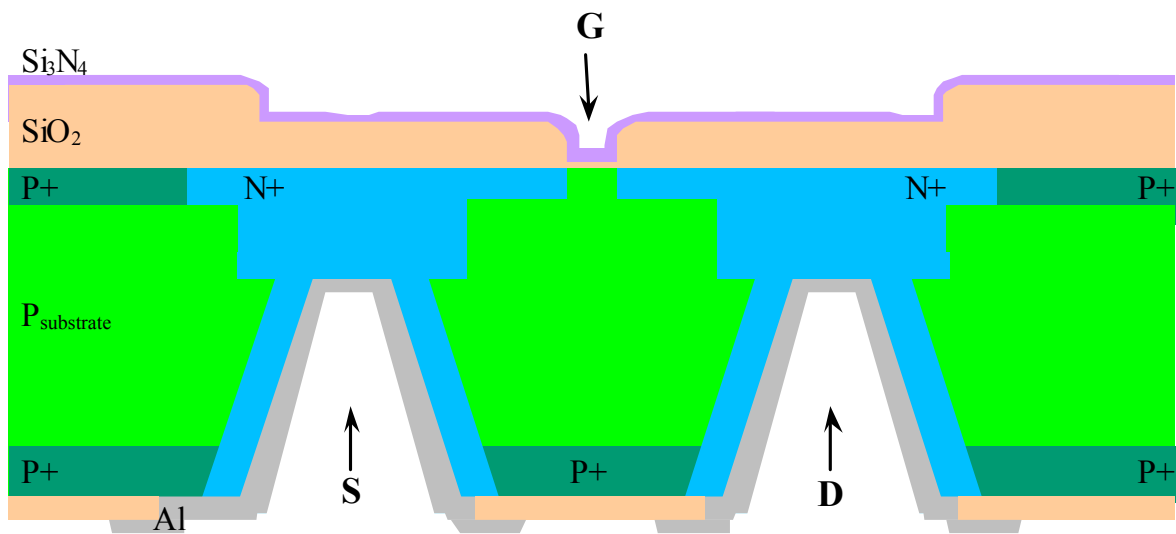


Figure 2

Characterization of pH sensitive ISFETs

Back-side contact BSC-ISFETs have been tested as pH-sensitive sensors and they showed theoretical slopes and good reproducibility (Figure 3) that is crucial for further their applications as basic transducers for Chemically Modified Field Effect Transistors (CHEMFETs), selective for other ions.

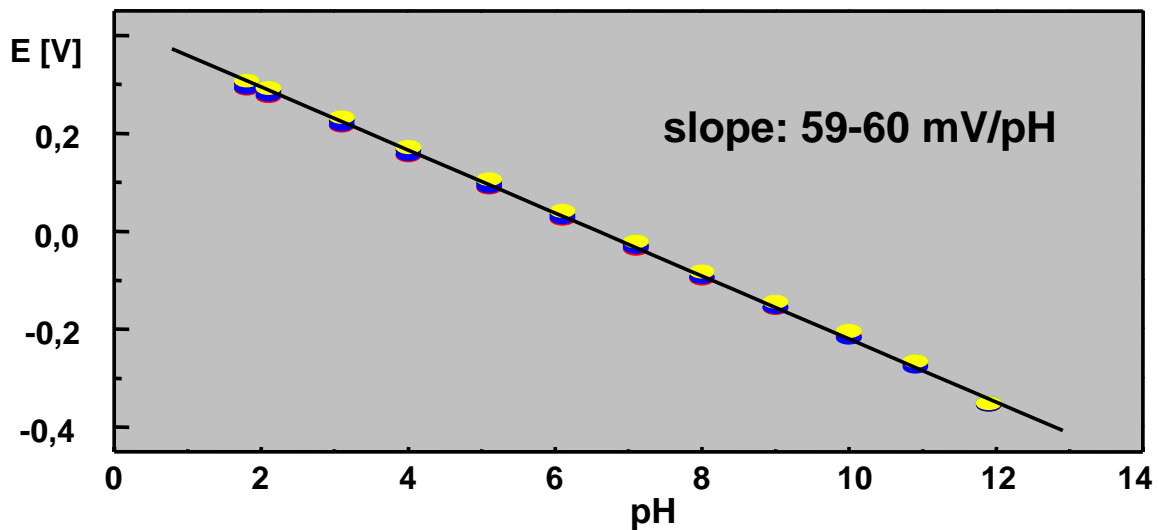


Figure 3.

Industrial deposition of the polyHEMA on ISFETs

In order to obtain reproducible CHEMFETs there was a need to deposit intermediate layer between gate and final ion-sensitive membrane. This intermediate layer, based on pHEMA polymer, plays role of buffered solid electrolyte of the sensors. Industrial deposition of the polyHEMA layer on ISFETs has been done in Institute of Electron Technology in Warsaw applying spin-coating technique and radical, in situ polymerization.

Deposition of ion-sensitive membranes

Ion-sensitive membranes selective for K^+ , Na^+ , NH_4^+ and NO_3^- were carefully optimized in WUT based on two polymeric matrices: plasticized polyvinylchloride (PVC) and polysiloxane. The final composition of optimized membranes have been deposited applying automated dispensing unit (see Figure 4). The unit allows depositing 5 microliter volume of liquid polymeric membrane with high reproducibility (Figure 5).



Figure 4.

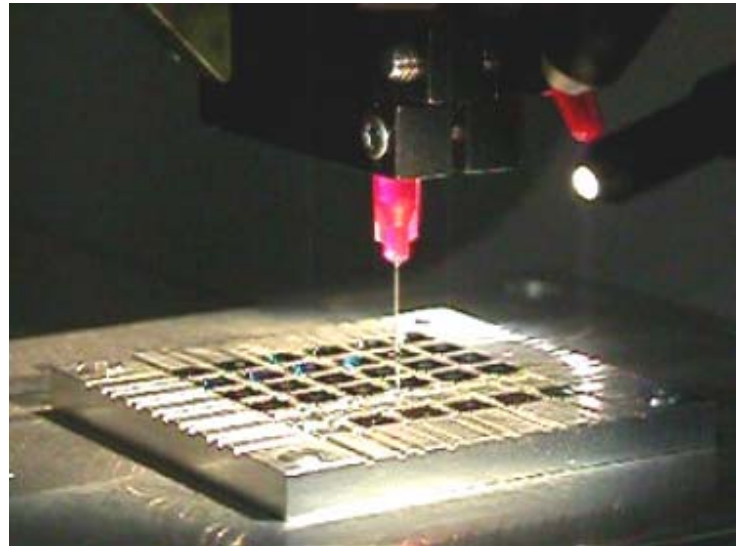


Figure 5.

Figure 6 shows a set of CHEMFETs with ion-selective membranes deposited by automated dispensing unit.

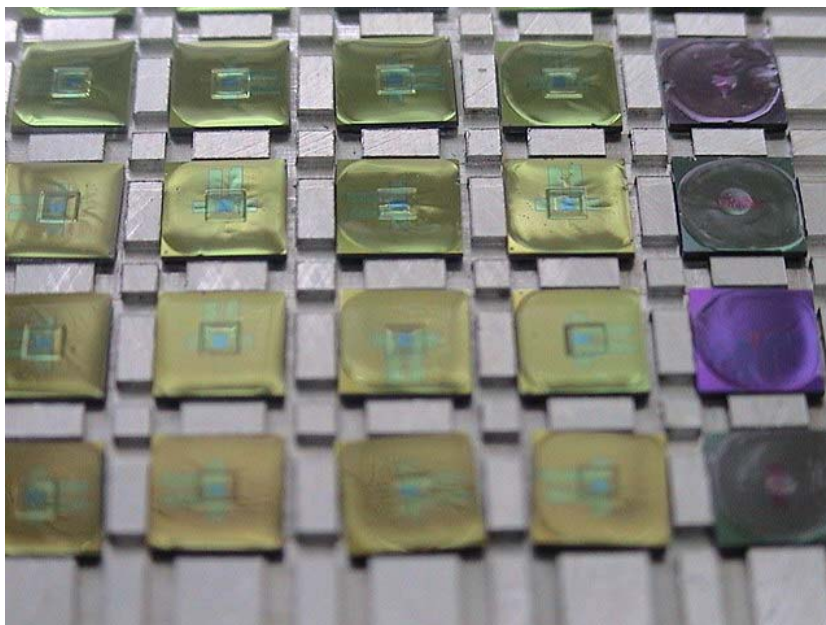


Figure 6.

It took many months to get finally the BSC CHEMFETs with good properties. These properties are the following:

- Reasonable production yield,
- Expected sensitivity and selectivity for selected ions,
- Life-time of at least 3 months,
- Time drift in reasonable limits, allowing automatic calibration before each measurement.

Exemplary responses of CHEMFETs selective for NH_4^+ ions (figure 7) and NO_3^- ions (figure 8) are presented below.

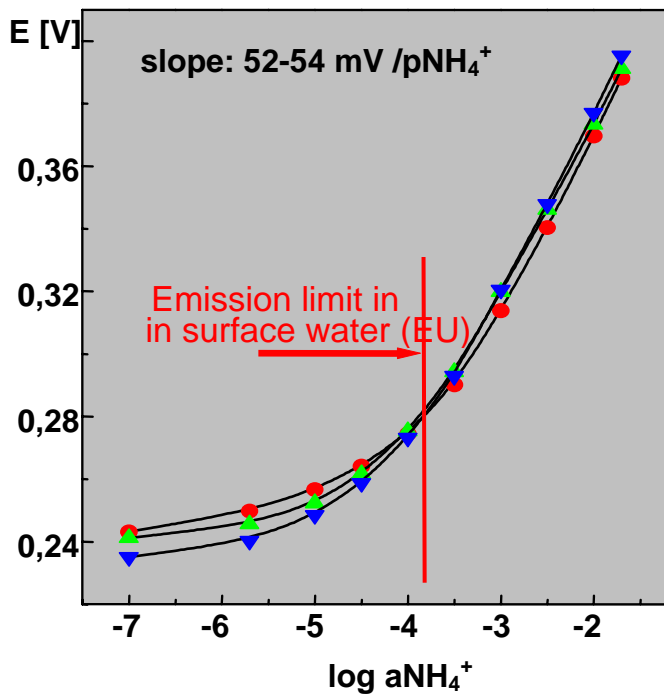


Figure 7

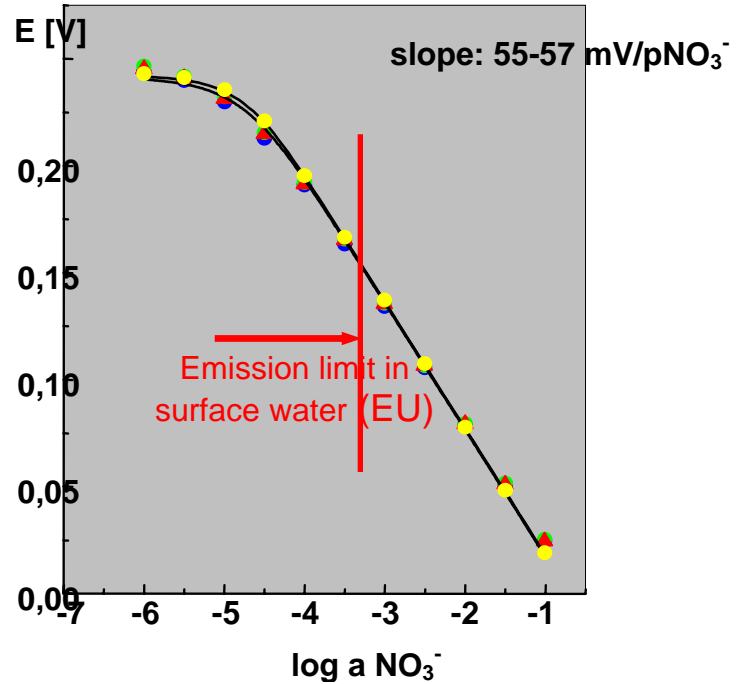


Figure 8

Table 1 shows performance parameter of the final CHEMFETs designed and fabricated in WUT in collaboration with ITE.

	Measuring range [mg/l]	Long-term stability
pH	2 – 12 pH	~ 1 year
K^+	2 – 3 900	at least 3 months
Na^+	2.3 – 2 300	
NH_4^+	1.8 – 1 800	
NO_3^-	6 – 6 000	

At the same time in LAAS-CNRS in France and in MICROSENS in Switzerland created the Front-Side-Contact (FSC) ISFETs. Fig. 9 shows the FSC sensors before and after encapsulation.

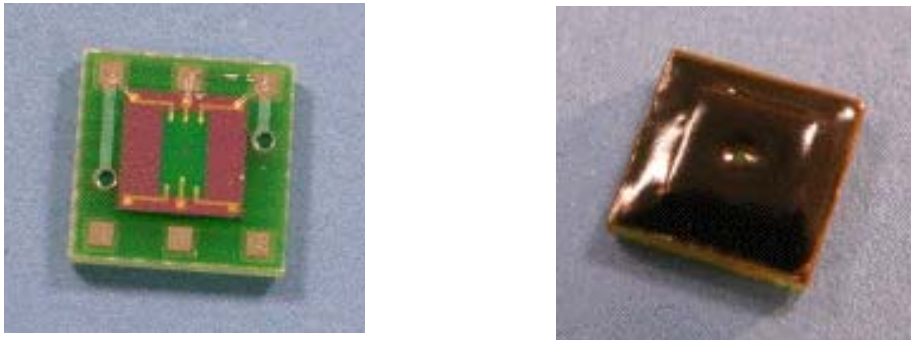
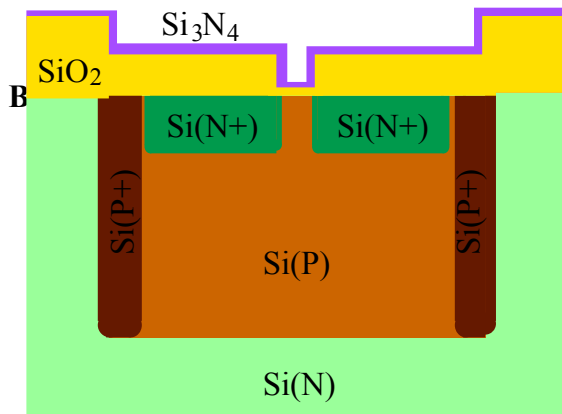


Figure 9

Fig 10 is a drawing of cross-section of FSC ISFET. Here the source and drain contacts are on the top, as the gate window, and connections must be done to the PSB, being the base of the sensor.



The FSC sensors are ready to use in alternative versions of the SEWING system. More, they are prepared for realisation of Calcium selective sensors. In the prototype prepared at the end of the project, BSC CHEMFETs are used.

Figure 10

Ion-sensitive membranes based on polysiloxane as a polymer matrix has been deposited applying spin-coating technique. Figure 11 shows spin coater and figure 12 – UV aligner.

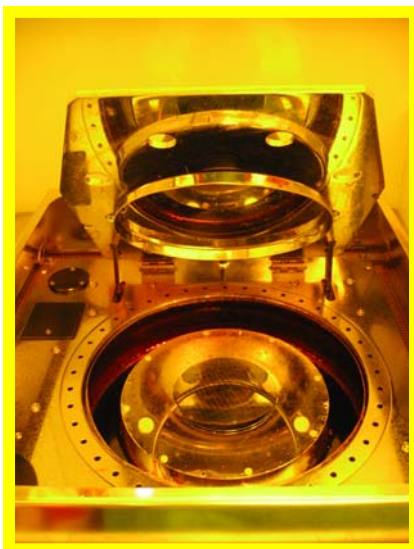


Figure 11



Figure 12

Figure 13 shows a fragment of wafer with polysiloxane membranes deposited by spin coating technique and the membrane deposited on the single chip.

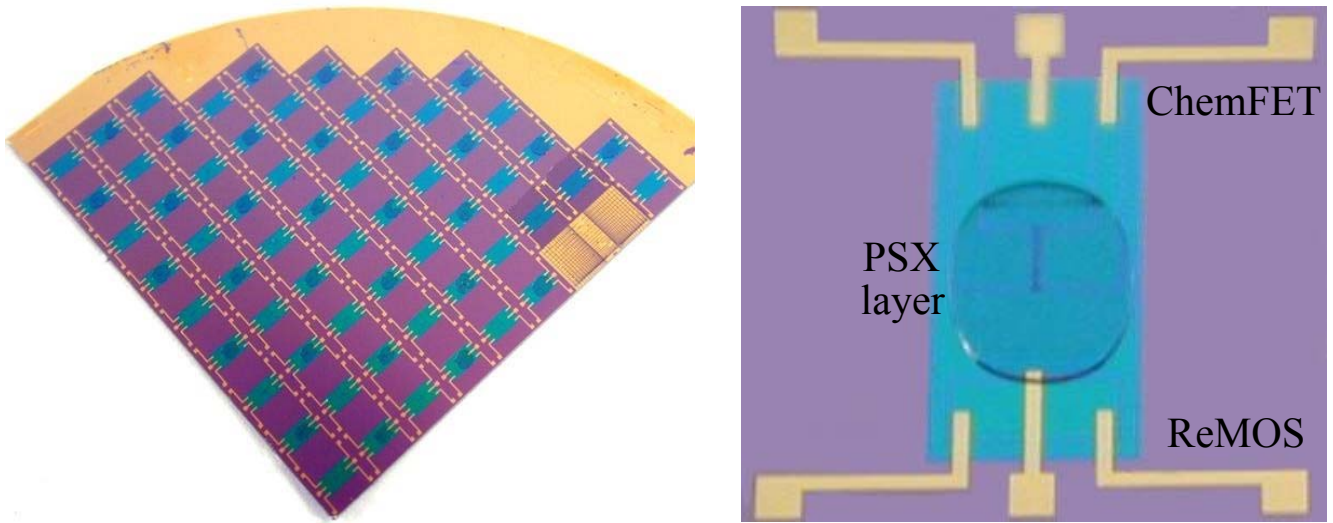


Figure 13

The sensors based on back-side contacts (BSC) were thoroughly measured, by the partners fabricating and using them. In the fig 14 the automatic stand for measuring sensors is shown. Its main purpose is to verify the quality of sensors and to find the values of their model parameters, necessary for further investigations on the system SEWING. Fig 15 shows the functional diagram of the measuring stand.



Figure 14

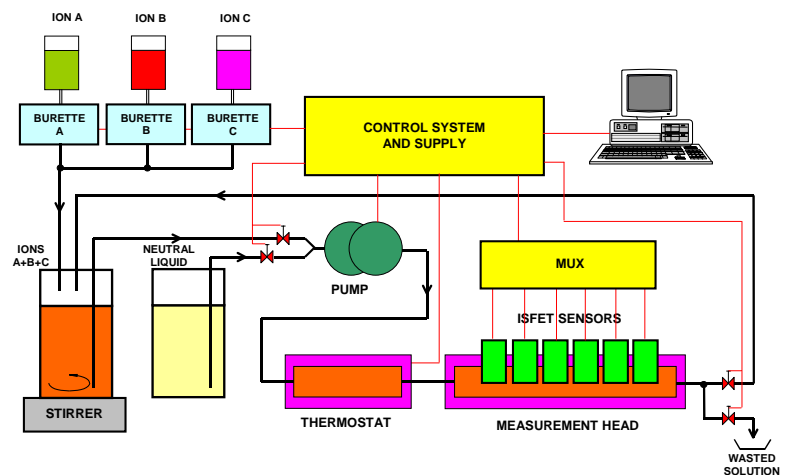


Figure 15

The sensors based on front-side contacts (FSC) were measured and evaluated by the automatic stand developed in LAAS (France) – Fig. 16.

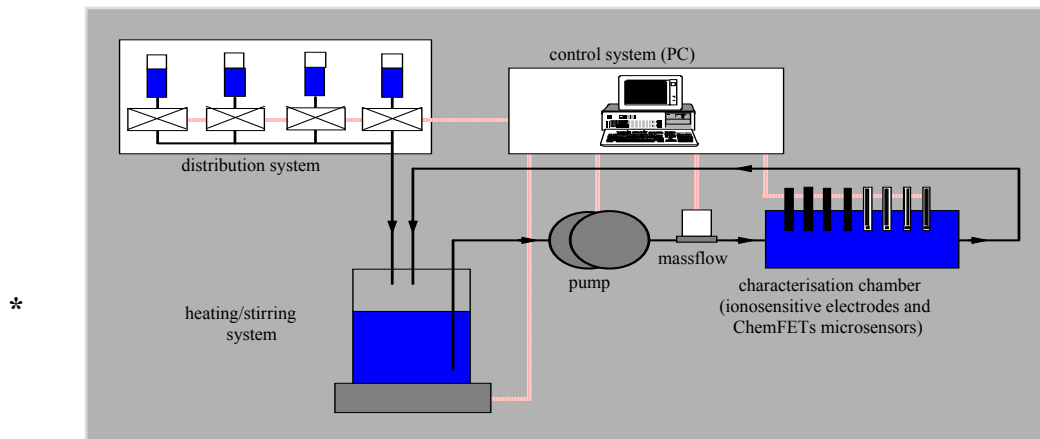


Figure 16.

3. Mathematical models of sensors and software for measurement data processing

Three groups of activities have been performed in order to develop methods, algorithms and software for measurement data processing in the final SEWING prototype.

- Measurement data acquisition (at an automatic measurement stand shown above), storage, retrieval, characterisation and visualisation of sensor parameters and properties.
- Modelling for sensor characterisation and design,
- Development of measurement method and algorithms for estimation of ion concentration in water samples with compensation of nonlinearity, finite selectivity, drift and ageing.

In the framework of the first activity - a specialised software tool **CEDaR** (Chemfet sensor Evaluator for Design and Research) has been created to assist researchers in measurement data processing (storage, query, retrieval, analysis and visualisation), sensor modelling and characterisation. An example plot from a data analysis is shown in Fig.17: it visually proofs dependence of a K-sensor response on the operating point.

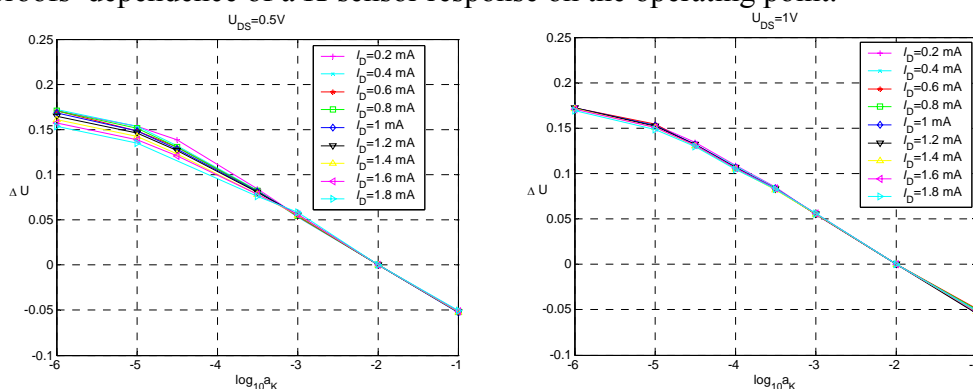


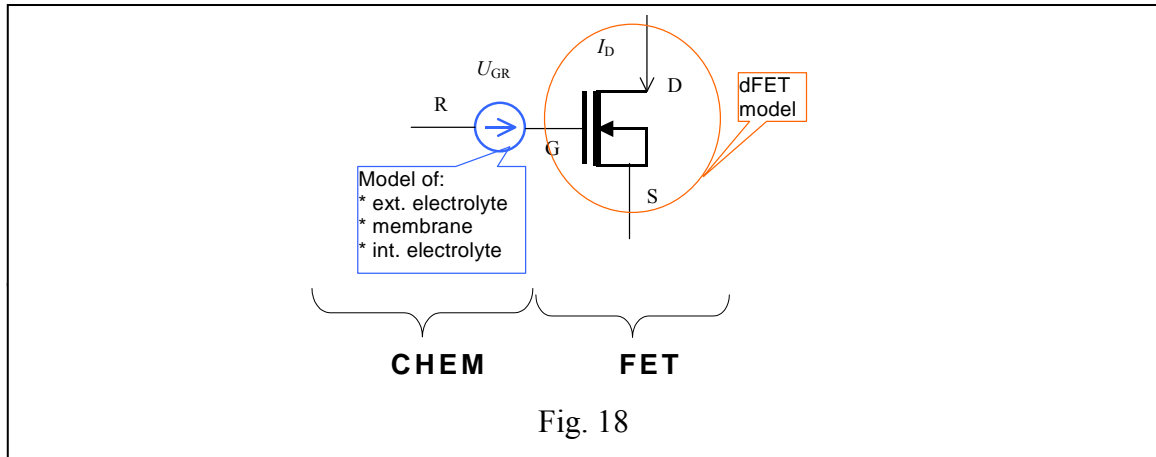
Figure 17

Numerous measurement sessions have been used to validate sensor models and estimate values of their parameters. Knowledge of dependency of sensor properties on the operating point was used to design measurement setup circuitry. Analyses of sensor model properties were influencing design of the most appropriate on-line data processing algorithm to be used in the final SEWING prototype.

The second activity – sensor modelling, had several goals in mind. Models are very useful, when designing measurement setup circuitry. Model characterisation allows for comparison

of devices from different manufacturing batches and estimation of variability. Finally, models have to be used in measurement data processing software, that is to compensate for sensor non-idealities.

Most of the models, that have been considered in SEWING research, assumed separability of the CHEMFET two-domain (electrical-chemical) device model into two parts: chemical and electrical, as shown in Fig 18.

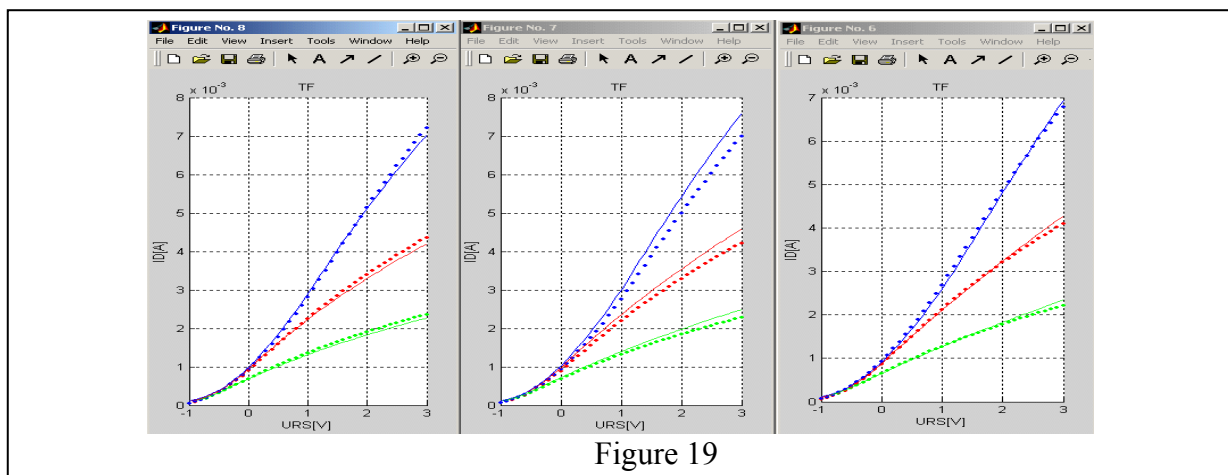


Three main versions of the chemical sub-model have been considered for CHEMFETs:

- Nikolski-Eisenmann (**NE**) model – standard, semi-empirical, limited in accuracy,
- Van den Berg (**VDB**) model – physics based, complicated, implicit, but accurate,
- Super-Nikolski-Eisenmann (**SNE**) model – simplified VDB, physics based but still simple (created by PW).

The electrical sub-models were adaptations of known FET models for circuit simulation programmes. The models were specially tailored for the needs of accurate modelling of particular silicon structures used for the SEWING project (e.g. depletion mode FETs from ITE).

Mathematical models and appropriate automatic characterisation software (**CEDaR**) have demonstrated possibility of pretty accurate prediction of CHEMFET behaviour in wide range of conditions: electrical (operating point), chemical (ion concentration in the sample) and environmental (temperature). Fig. 19 presents an exemplary comparison of CHEMFET measurements (dotted curves) and model responses (solid lines) for 3 temperatures (10, 20 and 30 centigrades) for very wide biasing range of the sensor.



Validation of CHEMFET models and parameter extraction software enabled design of an on-line data processing software for the final SEWING demonstrator (the third software-related activity).

CHEMFET sensors are known to have the following non-idealities:

1. Nonlinearity: → region of quasi-linear response depends on activity of interfering ions
2. Finite sensor selectivity towards interfering ions: → One-sensor-at-a-time measurements can be very inaccurate
3. Drift of sensor responses and ageing

Software was assumed to compensate for the first two non-idealities, why selection of the data acquisition scenario addressed the third problem.

Three different measurement data processing methods were created in the framework of the SEWING project. They were called, respectively:

1. **Data Fusion (DF, created by PW),**
2. **Inverse modelling Problem Algorithm (IPA, created by TUL),**
3. **Blind Source Separation of stochastic responses of an array of sensors (BSS created by UPC).**

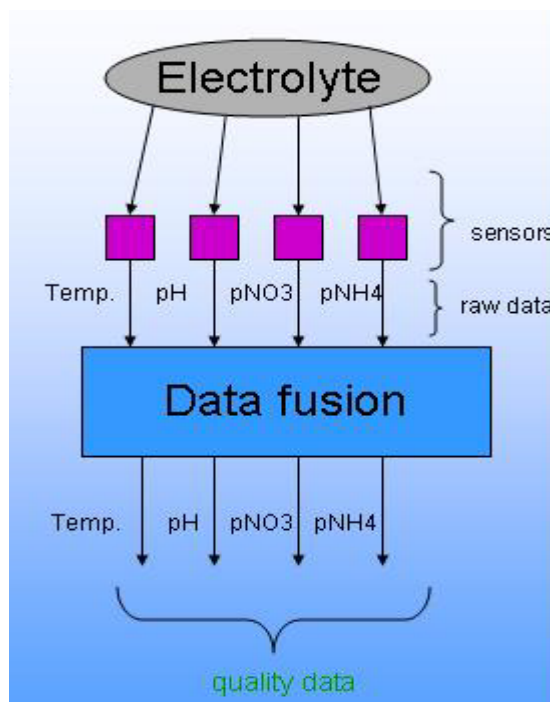


Figure 10

The general principle of Data Fusion (DF) algorithm is shown in fig 20. DF combines “raw” information from several sensors of limited selectivity (could be even of different type), taking into account accurate models of non-ideal sensors, so as to improve on quality of output data (e.g. ion estimation accuracy).

The DF principles were used for design of an on-line data processing software that was embedded in the final SEWING principle. To reduce influence of sensor drift and to reduce so called matrix effects, i.e. influence of interfering ions that are not directly measured in the sensor matrix - multiple standard addition measurement scenario was implemented. As sketched in Fig. 21 - water sample is stored in the measurement chamber (reactor), and pre-treated with an Ionic Strength Adjuster (ISA). After that, read-outs from all sensors are stored in memory.

Then a precisely controlled amount of a standard solution (containing precisely controlled type and concentration of selected ions) is injected into the read-outs from all sensors stored again. Injections can be repeated with the same or different standard solutions.

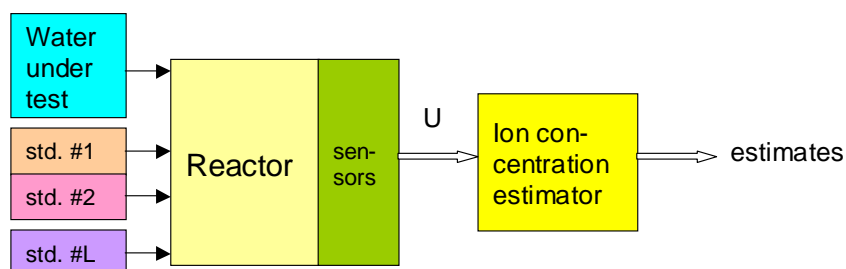


Figure 21

For n sensors, m ions and R standard additions there are $N=n*(R+1)$ measurements $U_{j,r}$. Selection of the number and content of the standards depends on the number and type of sensors used, number of important ions and range of ion activities in the sample. Generally all the N measurements and individual models of each sensor are used to solve a system of nonlinear equations w.r.t. all model parameters and ion concentrations. To give an idea about nature of a single equation from the set – here is a generic form of the equation, assuming Nikolsky-Eisenmann model of each sensor:

$$U_{j,r} = U_{0,j} - N_j \cdot \frac{kT_r}{qz_j} \cdot \ln \left[\gamma \cdot \tilde{c}_{j,r} + \sum_{l=1, l \neq j}^{m-1} K_{l,j} (\gamma \cdot \tilde{c}_{l,r})^{z_j/z_l} \right]$$

$$\tilde{c}_{j,r} = \beta_r \cdot c_j + (1 - \beta_r) \cdot c_{std,j,r}; \quad j = 1, \dots, n; \quad r = 0, 1, \dots, R$$

c_j and z_j denote molar concentration and valency of the j -th ion, and $c_{std,j,r}$ – molar concentration of the j -th ion in the r -th standard solution. $U_{0,j}$, N_j , $K_{l,j}$ denote parameters of the j -th sensor, β_r – denotes a dilution coefficient due to the r -th injection, and γ – the activity coefficient (assumed constant – due to ISA). T_r denotes temperature of the sample (in reactor) and $U_{j,r}$ – the output voltage from the j -th sensor after the r -th addition of a standard solution. Similar equations are automatically setup by software for other models.

The number and contents of the standards determine solvability of such a set of equations. For **over-determined** set of equations the solution can be found e.g. in the minimum least squares sense. For **under-determined** systems some a priori knowledge has to be added in a form of an equation (for regularisation purpose). For the final probe the well-determined or over-determined case was assumed. It is important to add, that using current measurement scenario and solution algorithm there is an extra possibility of filtering-out measurement noise. It is sufficient to repeat („over-sample”) sensor read-outs at each step of the measurement scenario (without change of the contents of the reactor). This feature has not actually been field tested.

There were two other approaches to ion estimation in the framework of the SEWING project. They both assumed an alternative measurement scenario: calibration + estimation – as sketched in Fig. 22. The algorithms have not been implemented in the final probe but lab tested.

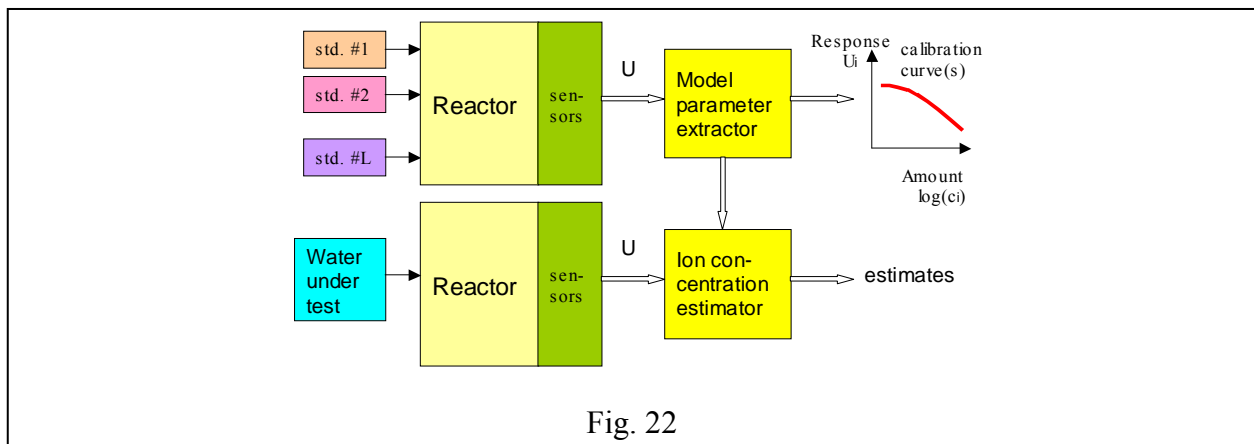


Fig. 22

The Inverse Problem Algorithm (IPA), developed in TUL, assumes the following sensor model (Nikolsky-Eisenmann model for univalent ions):

$$U_i(t_n) = V_T \ln \left[a_i(t_n) + \sum_{j \neq i} k_{ij} a_j(t_n) \right]$$

Its equivalent form is linear w.r.t. unknown activities a_i :

$$a_i(t_n) + \sum_{j \neq i} k_{ij} a_j(t_n) = \underbrace{\exp\left(\frac{U_i(t_n)}{V_T}\right)}_{\Delta V_{i,n}}$$

If the samples are taken at time points t_n , and the following matrix notation is used:

$$A = [a_i(t_n)]_p \quad \Delta V = [\Delta V_{i,n}]$$

the IPA solves the following set of equations w.r.t all ionic activities at all time points:

$$A = K^{-1} \cdot \Delta V$$

where K is a matrix built of selectivity coefficients k_{ij} of all sensors. When ionic activities change slowly, as compared to sampling rate – IPA can be used to filter-out measurement noise. The calculations can be performed recursively by IPA, and so can be implemented as a digital filter. The digital filter approach makes possible design of an ion concentration monitoring unit, containing a digital filter implementing the function specification algorithm and some additional logic circuitry, which can even be integrated within a single IC ASIC, upon user demand. The IPA is applicable for univalent ions, when separate sensor calibration is available and sensor drift is sufficiently small, to justify filtration of stochastic measurement noise.

The Blind Source Separation (BSS) based method, developed at UPC, is a learning algorithm that treats each response from a sensor as a mixture of the exact information about the main ion (the ion the sensor is selective to most) and stochastic noise from disturbing ions. The proposed ion activity estimation method uses signal processing BSS technique to separate sources of information, i.e. information about main ions for each sensor. BSS can recover the shape of the original signals for calibrated sensors. The method has been developed so far in laboratory version, but can be implemented in a measurement probe on the end-user demand.

The block diagram of data processing in the final SEWING prototype is shown in Fig. 23.

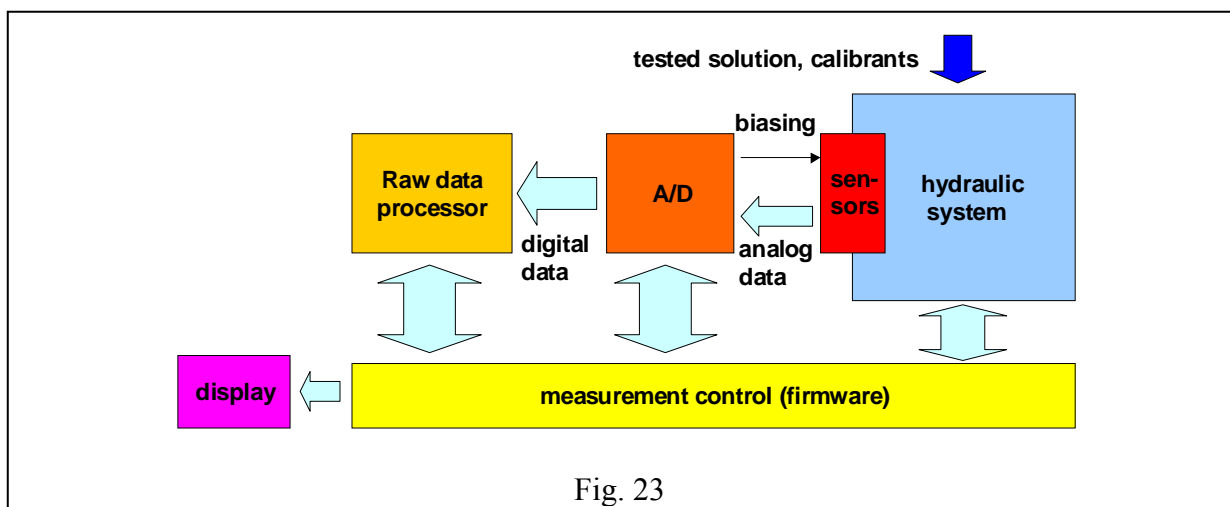


Fig. 23

For the final SEWING prototype the standard addition based measurement scenario and the DF based data processing algorithm were selected, as they were best suited for the prototype and delivering good results.

The following minimum size plan of measurements was selected such, that selectivity of all cation-selective sensors w.r.t. **the main interfering ion** (i.e. potassium) could be estimated and used for increase of estimation accuracy of other cation concentrations

	NH ₄	NO ₃	K	Na
Sample+ISA	-----	-----	-----	-----
std. #1	low	low	low	low
std. #2	-----	-----	high	-----
std. #3	high	high	-----	high

The two levels (denoted: low and high in the table) of ion concentrations in the standard solutions were selected based on measurement range of the probe and actual selectivities of CHEMFET sensors used.

To reduce computational effort and increase reliability of **on-line** data processing - the following ion estimation strategy was implemented.

- **NO₃** calculations are performed separately (no interferent measured)–
- **NH₄** and **K** sensors have mutually low sensitivity ==> calculations performed together
- **Na** calculations are separate, but take into account the main interferent (K)

Each calculation involved solution of a set of nonlinear equations. A **special-purpose** box-constrained nonlinear optimiser algorithm has been developed in WUT, that can also automatically estimate good initial approximation of the optimum solution (i.e. parameters of sensor and concentration of the ions involved). The resulting ion estimation software is flexible, in that it should work for arbitrary number of ions, sensors, standard solutions, but has been tested (in lab, in field, and in off-line calculations) for the particular selection of 4 ions and 4 CHEMFET sensors – as assumed for the final SEWING probe.

Firmware code that controls the hydraulic and electric components of the final prototype, provides remote access and calls the DF based data processing algorithm - has been written by Sys-media Company (a Systea sub-contractor).

Overall software developed for the SEWING project met well the expectations and enabled successful design of the final prototype.

4. Technological realisation of the prototype

All elements of the system were verified in successive approaches of the prototype. The first one was the LFA (Loop Flow Analysis) unit built by SYSTEA, very flexible equipment, in which all elements could be checked in working conditions and adjusted for best performance. It is shown in fig 24.



Figure 24

All the parameters can be easily changed on the key-board and the results are printed by the internal printer. Digital display allows controlling the measurement process. The next approach was the micro probe, shown in fig 25, also built by SYSTEA.



Figure 25

The hydraulic and controlling part of the system was implemented there, but finally it was decided that a different, more flexible prototype is constructed (by SYSTEA), called Micro-Mac-1000, shown in fig 26. Fig 27 shows the inside of the prototype.



Figure 26



Figure 27

The following are the main properties of the prototype:

- Portable/on-line, multisensors measuring device, with intrinsic automatic calibration capability,
- possibility of integration of both type of BSC and FSC Chemfet sensors,
- extensively tested by BOKU partner.

When building the prototype integration of PW DF calculation algorithm and development of a new dedicated PC remote interface program was done. In that way the results of water sample measurements can be visualised.

LFA test unit was retrofitted to work with the same new firmware and hardware configuration developed for the final prototype, to allow parallel FSC sensors tests and parallel future works of different partners of the project.

The most expensive part of the prototype is the programmed hydraulic system, which performs the following activities:

- calibrating the sensors with standard sample,
- introducing the measured sample,
- introducing samples according to standard addition method,
- washing the sensors and embedding them in standard liquid.

The sensors are inserted in a specially designed flow-cell, where reference electrode and temperature sensors are also inserted. Part of the hydraulic system and the flow-cell are shown in figs. 28 and 29.



Figure 28



Single module for FET sensor

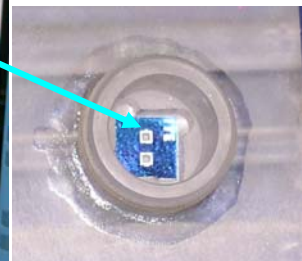


Figure 29

The prototype described above gives the starting point for future works leading to industrial implementation of the system. The following adaptive works are to be done:

- Based on the same LFA technology adopted in two prototypes, a new generation of cheaper on-line measuring devices will be designed and developed,
- Standard Systema hardware and Chemfet electronics will be redesigned to achieve a more compact size,
- Standard firmware and I/O interfaces will be easily upgraded based on the extensive software developments and integrations done under the project,
- Additional sensors could be easily added on the actual configuration using the same technological solutions already developed and tested under the research.

To finalise this point it should be pointed out that some alternative hardware solutions are also done in laboratory form, to be eventually used in future industrial solutions. These are:

- Interface circuitry based on voltage rather than current measurement of the sensor signal, realised by VTT,
- The IPA and BSS software implemented in PCB form realised by UPC and TUL,
- An ASIC circuit realising the $\Sigma\Delta$ a/d converter, realised by TUL.

The first two realisations are shown in fig 30, while the last in fig 31.



Figure 30

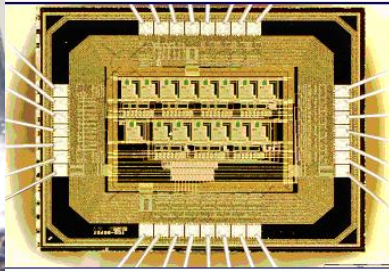
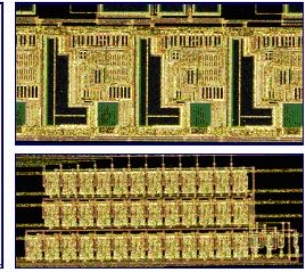


Figure 31



5. Final measurements and verification of the system

Final measurements were done by the Austrian partner BOKU. The following properties were checked:

- System stability by means of calibration slope
- Limit of Quantification (LOQ)
- Accuracy & Precision by means of control samples
- Accuracy by means of real samples (comparison with reference methods)
- Sensor conditioning time (manually imposed)
- Sensor life time and homogeneity (manually imposed)

Preliminary measurements were done on the LFA unit, while the last, most important, on the prototype. Emphasis was put on the sensors behaviour, particularly comparison was done between different technologies and chemical versions of ion-selective membranes. The measurements were as follows:

LFA test unit

- Nitrate sensor: PVC membrane, with polyHEMA layer, manually imposed,
- Ammonia sensor: RMS membrane, without polyHEMA layer, manually imposed.

Final prototype

- K, Na, NH₄ sensors: PVC membrane, with polyHEMA layer, semi-industrial imposed,
- Nitrate sensor: PVC membrane, with polyHEMA layer, manually imposed.

The most interesting for final evaluation are the last measurements, where the DF software with all correcting algorithms is used and final accuracy Limit of Quantification (LOQ) can be found.

Definition: ...the limit of quantification (or limit of determination) is regarded as the lowest limit for precise quantitative measurements, as opposed to qualitative detection. [Miller et al.] Strong improvement was found, thanks to new improved sensors and proper data processing by DF algorithm.

Figs 32, 33 and 34 show the final accuracy measurements. The equation on the top of each diagram shows the offset (should be zero) and slope accuracy (should be 1).

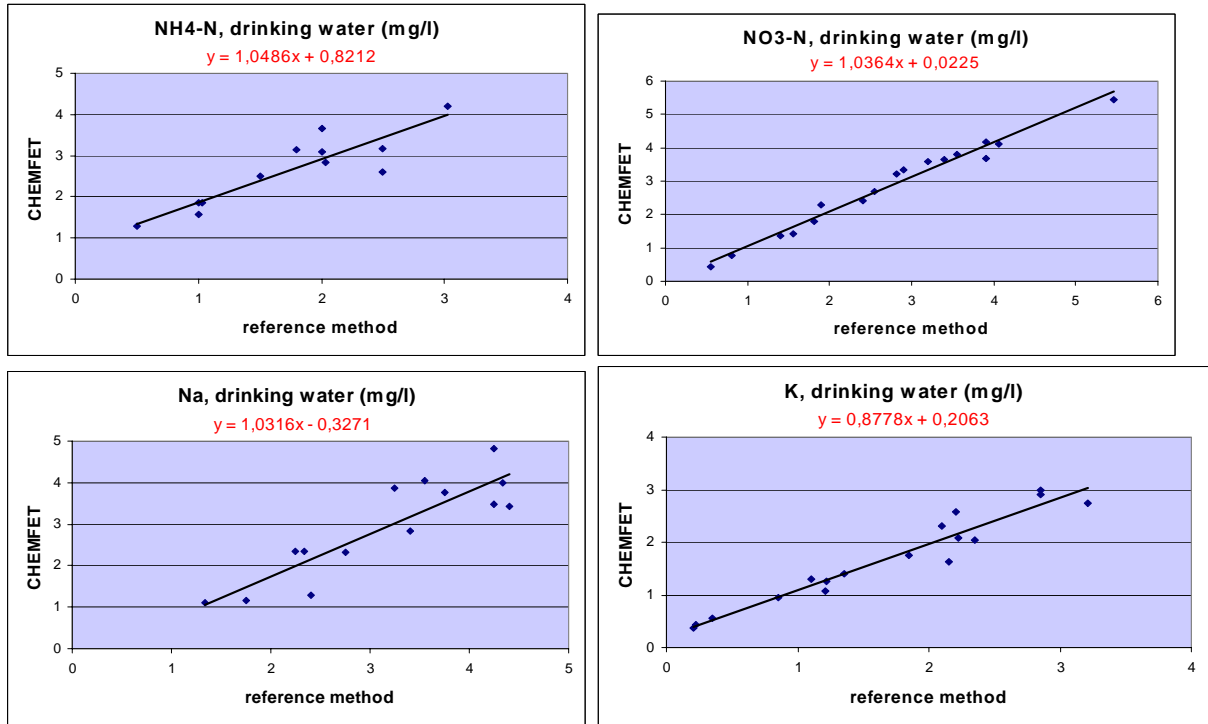


Figure 32

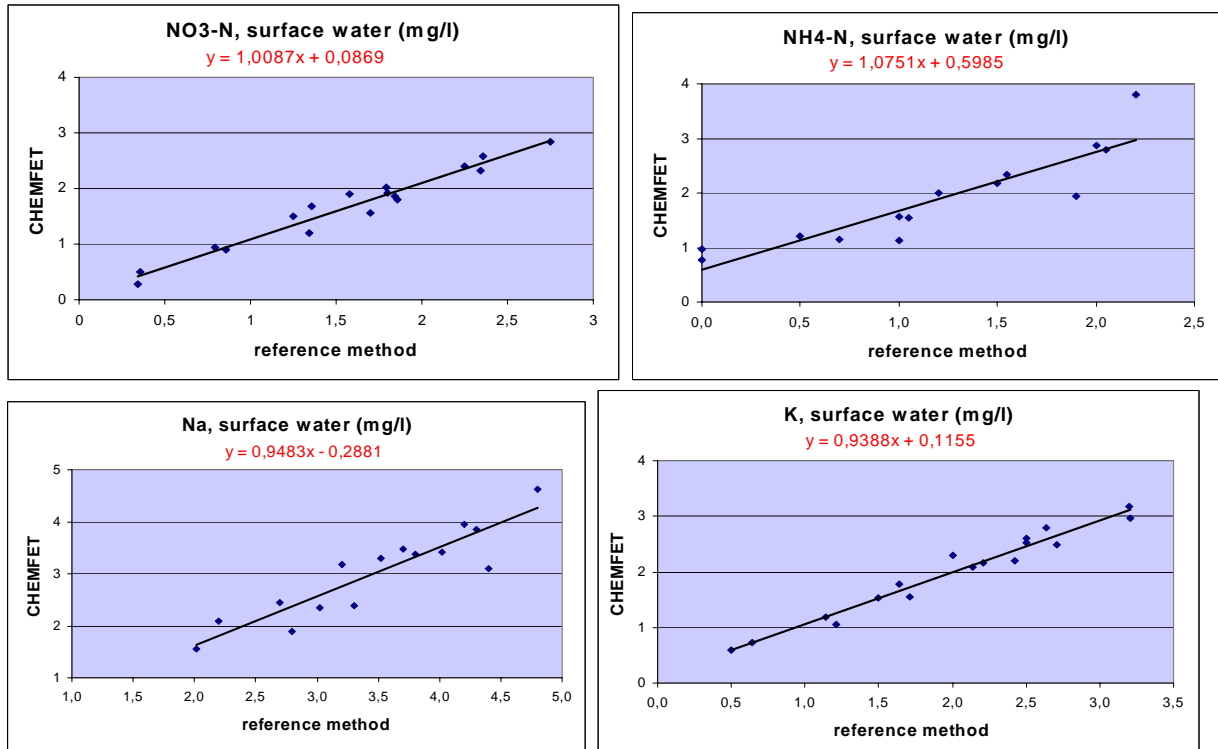


Figure 33

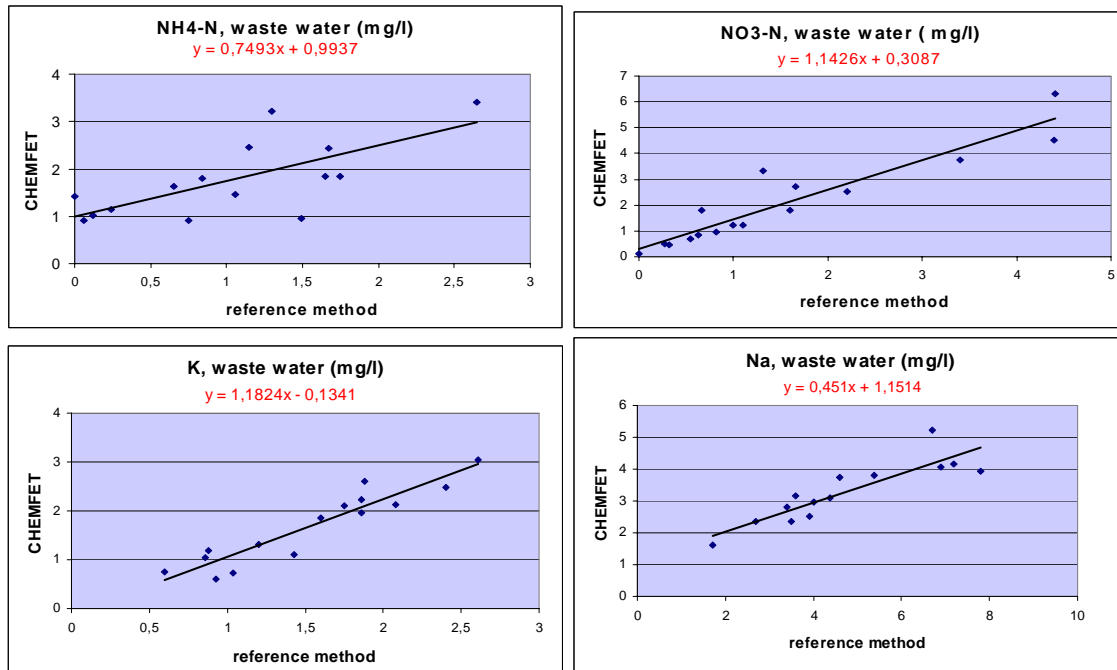


Figure 34

These results show that improvements should be done for waste water monitoring. In the present state, results for drinking and surface water are highly satisfactory.

The final conclusions are as follows:

- ▶ The mechanical / hydraulic system of the LFA unit and the final prototype is a well designed and a rugged one,
- ▶ The computation software developed by SEWING partners manage the automatic measurement sequences and the data processing very well,
- ▶ The two-sides back-planed ISFET measuring flow cell make possible the simultaneous using of up to eight sensors (one reference electrode),
- ▶ Additional ions can be measured in order to compensate their interference to the main ions in real samples.
- ▶ All sensors tested by the final prototype (NO₃, NH₄, K, Na) work very accurate and precise at the defined working range. The precision is improved strongly by the automated production of the sensors.
- ▶ The limit of quantification is improved during the period of the project (NO₃, NH₄), but further improvement is needed, especially for ammonium, to better fit to the EC emission limits.
- ▶ The sensors give excellent results for real samples like drinking and surface water. In spite of the developed algorithm for compensating interferences from K and Na, the results for ammonium in waste water are not very satisfactory, but this was not the aim of this project.

6. Future industrial implementation

Results obtained with the SEWING project and its prototype show clearly what are the possibilities of future industrial versions of the system.

- At least two versions: portable and on-line measuring device
- Actual main applications: automatic measurements of drinking, surface and underground waters,
- Future improvements: tests and adaptations to measure on outlet of waste water treatment plants,

- Future improvements: integration of other compact “chip sized” sensors, even based on different measurement technology (potentiometric, biosensors),
- Price target: comparable with a conventional high-level multiparametric measurement probe.

The existing prototype can be used "as is" for some applications. But the results of the project SEWING are much broader and flexible, enabling creating different versions of the system, according to end-user demand. To do that further investigations are needed, adapting the existing solutions to industrial implementation.

One of the crucial problems is the preparation of sensors for industrial production. Sensor in mass production should be inserted in flow-cells, conditioned and certified. This should be done by a SME, existing or spin-off, using the know-how obtained in realization of SEWING project.

The software for data processing would be updated according to end-user demand, eventually using alternative solutions described above.

SYSTEVA, industrial SEWING partner, is designated for market production of the system.

Application for a STREP project is under consideration, which would give funds for further adaptive works.