THE FP5 EUROPEAN PROJECT ***SEWING***
"**S**YSTEM FOR **E**UROPEAN **W**ATER MONITOR**ING**"

COORDINATOR**:**
Warsaw University of Technology
Nowowiejska 15/19
00-665 Warszawa, Poland
Professor Andrzej Filipkowski
tel. (48-22) 660 7744, fax +(48-22) 825 2300
e-mail: filip@ise.pw.edu.pl

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To: **Mr Antonios Barbas**
EUROPEAN Commission –
DG INFORMATION SOCIETY MV/kv
Office: BU31 4/16
B-1049 Brussels
Belgium

Dear Mr Barbas

Enclosed please find the Final Report of the project SEWING, covering the period 01.09.2001 – 31.12.2004. It presents also the deliverable 24 "Final Report".

Sincerely

	SEWING ***IST-2000-28084*** ***System for European Water monitorING***

Final Report (Deliverable 24)

Covering period 01.09.2001 – 31.12.2004

Report Version:	1st
Report Preparation Date:	15 February 2005
Classification:	for public
Contract Start Date:	01.09.2001
Duration:	40 months
Project Co-ordinator:	Politechnika Warszawska, Poland
Partners:	Politechnika Warszawska - PL, Instytut Technologii Elektronowej - PL., Technical University of Lodz - PL., Valtion Teknillinen Tutkimuskeskus - FI, Centre National de la Recherche Scientifique - FR, MICROSENS - CH, Universitat Politecnica Catalunya - ES, Institut fuer Wasservorsorge, Gewaesserekologie und Abfallwirtschaft - AT, SYSTEA- IT.

Project funded by the European Community under the "Information Society Technology" Programme (1998-2002)

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1. Project overview

The project SEWING was concluded on time on December 31, 2004. The results were presented on the Annual Review on November 29, 2004 in Brussels and were positively evaluated by the reviewers.

The following main achievements can be listed:

1. Creating the theoretical basis for modelling of ISFET sensors,

- The models of ISFETs met in literature were not adequate for SEWING purpose. New models and their libraries have been created.

2. Creating technology and production of two kinds of ISFET sensors: BSC (Back-Side-Contact) and FSC (Front-Side-Contact,

- Sensors are the crucial elements of the system. They were subject of several deliverables and their final version was made available near the end of the project. Their behaviour is fully satisfactory. Two versions of sensor allow choosing one of them for a given application.

3. Measurement and extracting model parameters of sensors,

- Based on the theoretical models of CHEMFETs and their measurements the model parameters could be extracted and be used in further software works.

4. Creating the software for acquisition of data obtained from sensors sensitive for different ions in presence of interferences (three versions),

- Adequate processing of signals obtained from the sensors give the final information about the concentration of polluting ions in measured water. Model parameters are essential for this stage of work. Digital, analogue and neural versions of data processing was created, to use the best for given application

5. Creating the hardware for realisation of this software in the final instrument,

The algorithms created for data processing are then introduced in hardware. This can be a commercial chip or ASIC produced specially for that purpose. The choice depends on application.

6. Creating the hydraulic system for water measuring, sensor calibration and maintenance,

- This very crucial part of the project allows making a programmable hydraulic system for automatic taking of measured samples, sensor calibrating and washing.

7. Creating the system for data transmitting and visualisation,

- Several solutions are theoretically prepared, but in the prototype typical versions are used.

8. Assembling selected elements of the project in one final prototype,

- The prototype uses selected versions of particular parts of the system prepared during running the project. It shows that the idea of SEWING was well invented and useful.

9. Verification of the prototype in real-time measurement,

- The numerous measurements show, how the prototype behaves in different real-life conditions.

10. Creating the vision of future industrialisation of the system,

- On the basis of these results visions of different versions of the system, depending on end-user demand, is created.

The consortium was composed of 9 partners from 7 European countries. Here is the list with their role in the project, by pointing the numbers of the results, listed above.

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

8. Universität für Bodenkultur, Wien, (BOKU). Austria (9)
9. SYSTEA, Rome, Italy (5, 6, 7, 8, 10)

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.

A working prototype is the final effect of the project. The selected, most suitable versions of particular achievements were used in it, other are ready to use in the industrialised versions of the system.

2. Project objectives

The objective in the annex 1 to the Contract was:

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

This objective was reached in most of its details. The final prototype can be evaluated as *relatively cheap* as it has many sophisticated elements enabling more accurate measuring of water pollution. The selected ions are now available for monitoring: NO3, NH4, Na, K and additionally pH.

The prototype can be used in the field measurement in real-time, being remotely controlled and sending the results of monitoring to the central computer by means of GMS. This fulfils most of the objectives listed in the Annex 1 to the Contract.

3. Approach

The approach chosen in the project SEWING was based on the following assumptions:

a. As the deficit of clean water becomes more of a problem in Europe, there is a need to develop easily accessible, cheap and reliable Microsystems, which could be used for water pollution monitoring and early warning of many water resources in Europe. The equipment available so far is mostly of laboratory type and measures water samples inserted to the measuring device.

b. Creating an integrated equipment combining sensors for a possibly large choice of polluting ions with data processing, storing and transmitting and with hydraulic system for programmed measurements was therefore chosen as the objective of the project.

c. The consortium including specialists in electronics, chemistry, information technology, environmental engineering and semiconductor technology, having also an industrial partner, was therefore created to work on the problem.

4. Project results and achievements

4.1 Introduction

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 and using them in the realisation of a prototype.
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 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. 23 deliverables were presented to the Project Officer.

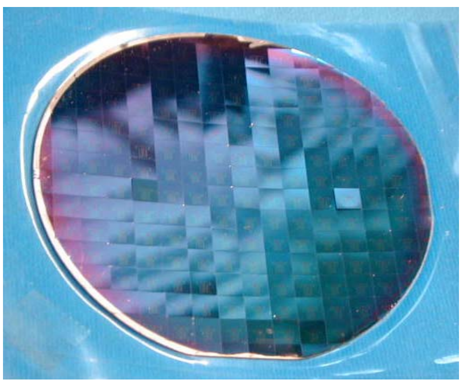
4.2. Sensors

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

- Fabrication of back-side contact BSC-ISFETs (ITE) – used in the final prototype
- Fabrication of front-side contact FSC-ISFETs (LAAS-CNRS)
- 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+, NH4+ and NO3 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.



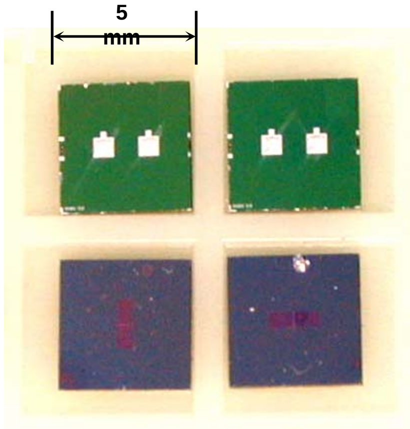


Figure 1

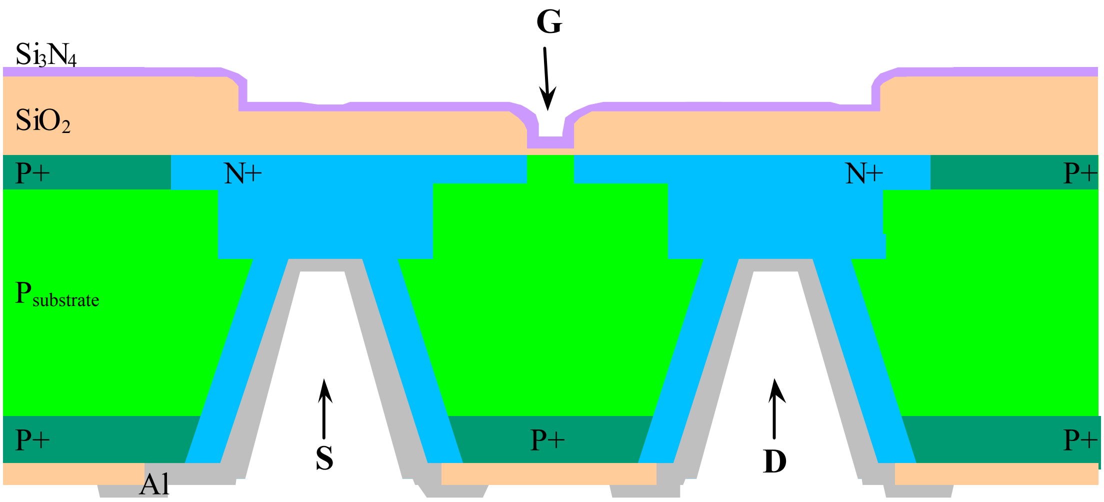


Figure 2

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.

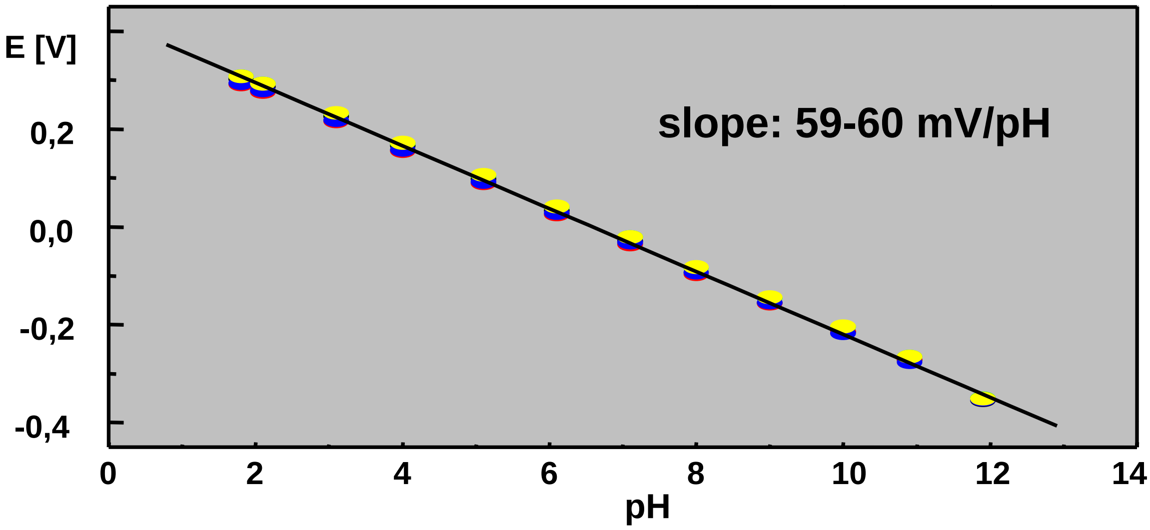


Figure 3.

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+, NH4+ and NO3$^-$ 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.

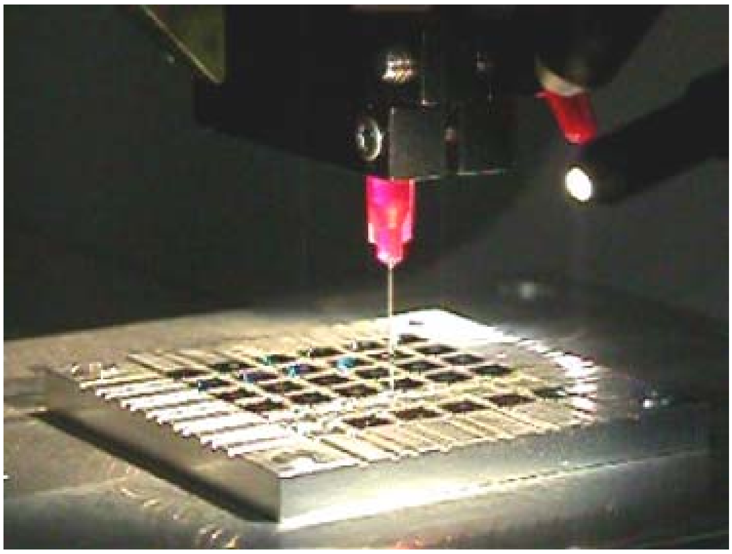


Figure 5.

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

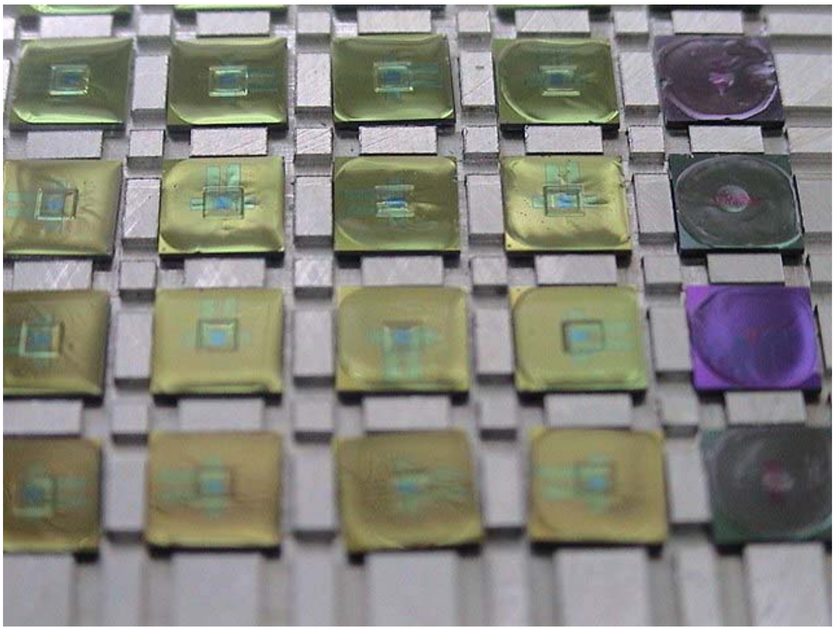


Figure 6.

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.

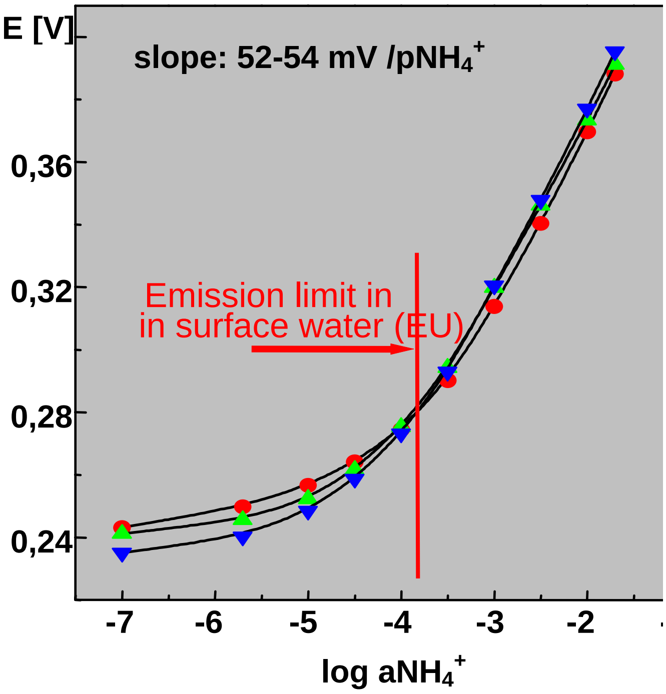


Figure 7

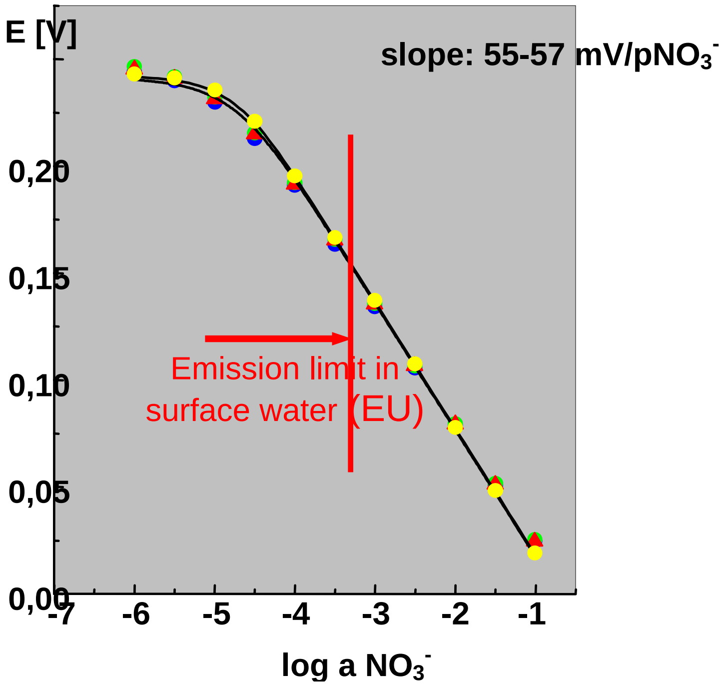


Figure 8

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, front-side-contact (FSC) ISFETs were fabricated in LAAS-CNRS in France and in MICROSENS S.A. in Switzerland. Compared to the BSC design, the FSC one uses a simpler fabrication technology but requires a packaging process to be adapted to the flow-cell concept. Fig. 9 shows these FSC sensors before and after encapsulation.

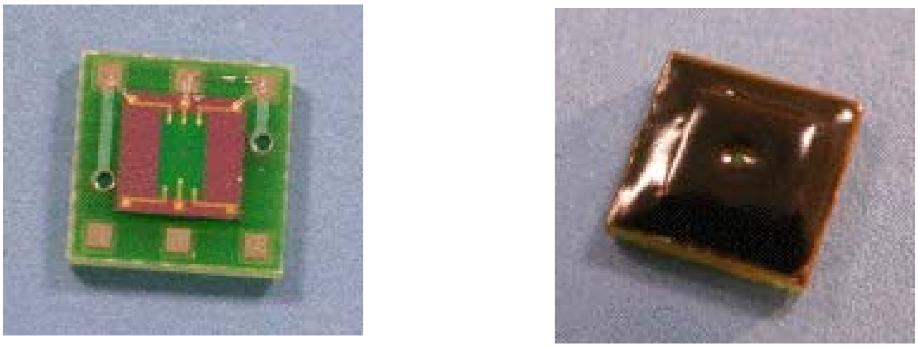


Figure 9

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 a back-side contact printed circuit board (BSC-PCB), being the base of the sensor.

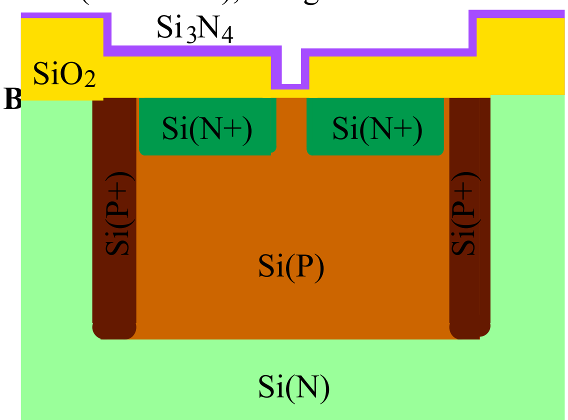


Figure 10

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.
Front-side-contact FSC-ISFETs have been tested as pH-sensitive sensors. They showed good accuracy and reproducibility of measurement as well as theoretical pH-sensitivity (Fig. 11), that is crucial for their adaptation to the detection of others ions thanks to ion-sensitive polymeric matrices.

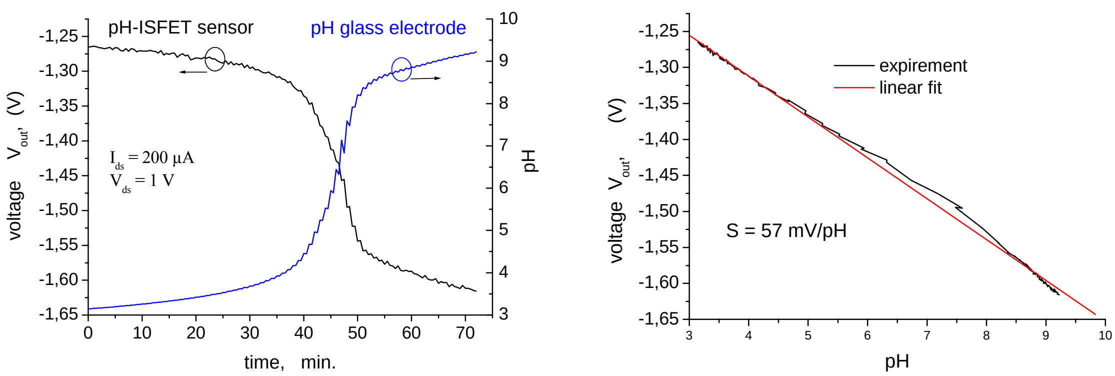


Figure 11

Ion-sensitive membranes based on polysiloxane (PSX) as a polymer matrix has been studied and developed for the detection of the ammonium NH_4^+ ion. Special attention was applied to the mass fabrication of polysiloxane patterns using spin-coating and photolithography techniques. Figures 12 and 13 show the standard equipments, i.e. the spin-coater and the UV aligner, used for these developments.

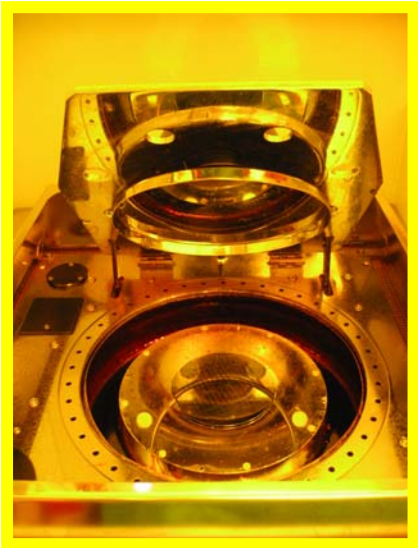


Figure 12

Figure 13

Figure 14 shows a quarter of wafer with polysiloxane ion-sensitive layers deposited by spin-coating and patterned by UV photolithography, as well as a detail of the PSX membrane on a the FSC-ISFET gate.

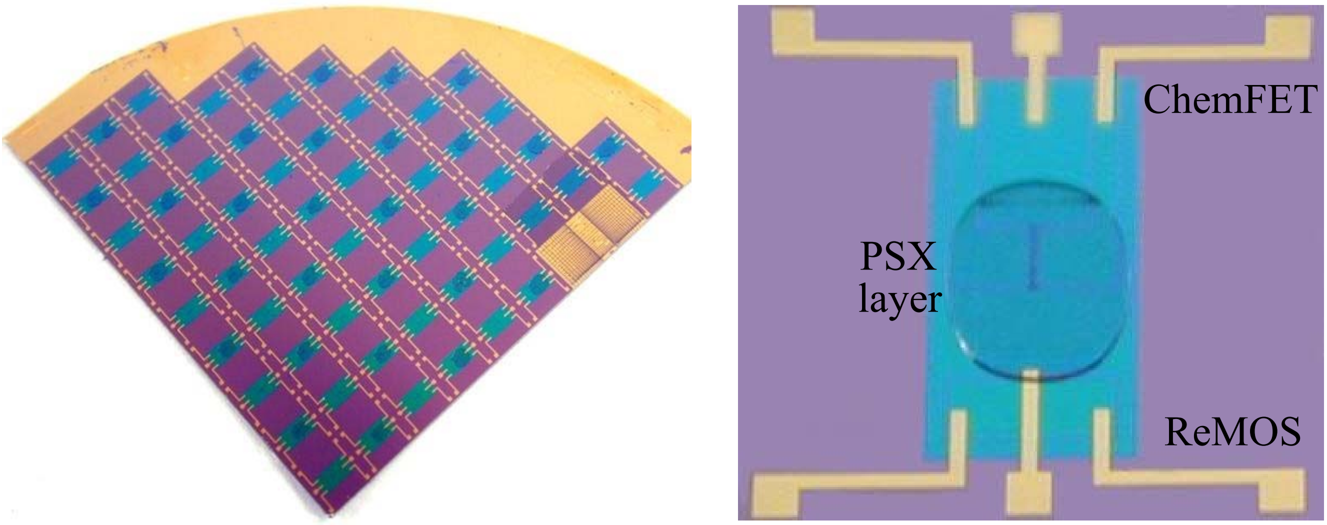


Figure 14

The whole technological process has to be further improved in order to have a better definition of the PSX membrane characteristics. Nevertheless, the FSC-ChemFETs shows good properties:

- Reasonable production yield
- Expected sensitivity and selectivity for the selected ions
- Life-time around three months
- Time drift in reasonable limits, allowing automatic calibration before each measurement

Figure 15 presents typical responses of the FSC-ChemFETs selective for NH_4^+ ions.

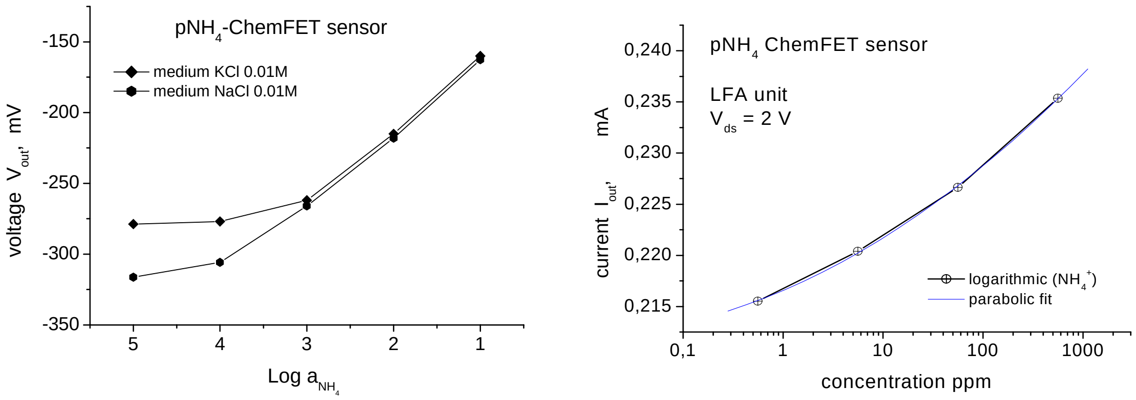


Figure 15

The sensors based on back-side contacts (BSC) were thoroughly measured, by the partners fabricating and using them. In the fig 16 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 17 shows the functional diagram of the measuring stand.

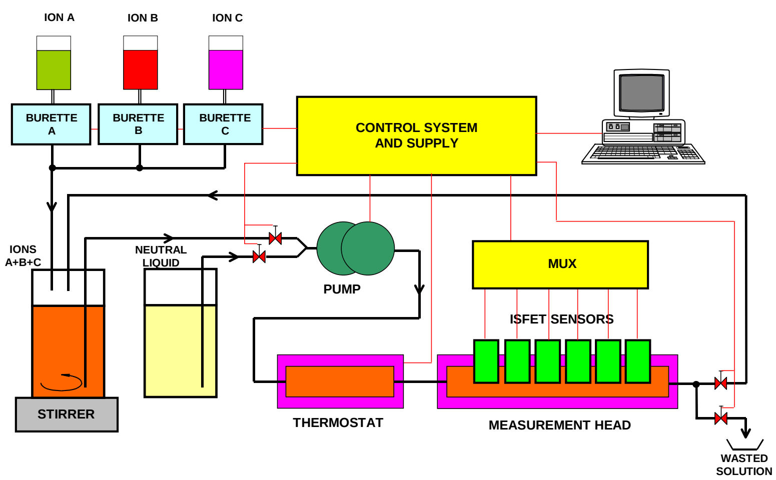


Figure 16 Figure 17

The sensors based on front-side contacts (FSC) were measured and evaluated by the automatic stand developed in LAAS (France) – Fig. 18.

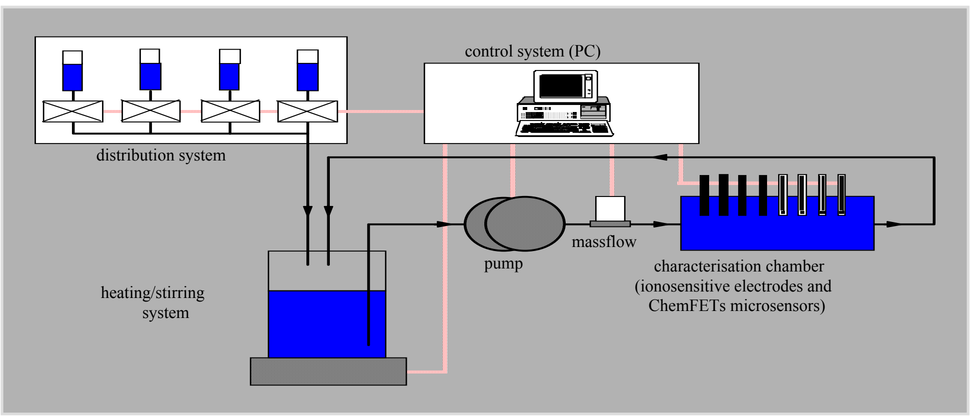


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Figure 18.

Finally the BSC CHEMFETs fabricated by ITE and PW were used in the prototype.

4.3. 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** (**C**hemfet sensor **E**valuator for **D**esign **a**nd **R**esearch) 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.19: it visually proofs dependence of a K-sensor response on the operating point.

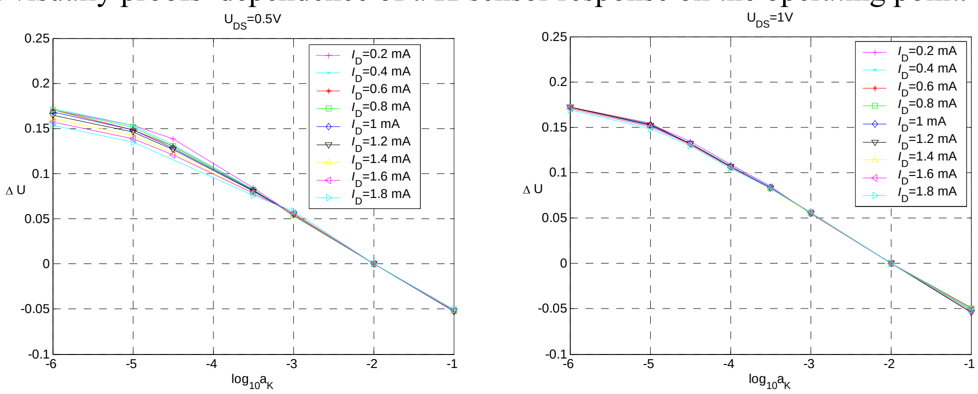

Figure 19

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 20.

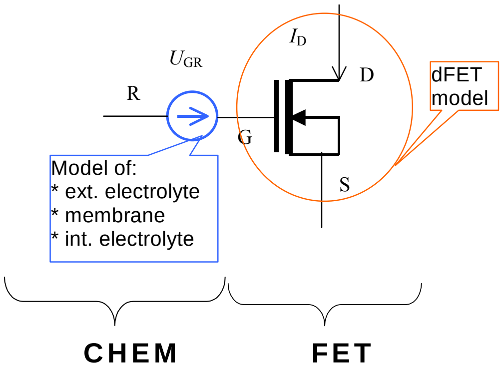

Fig. 20

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. 21 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.

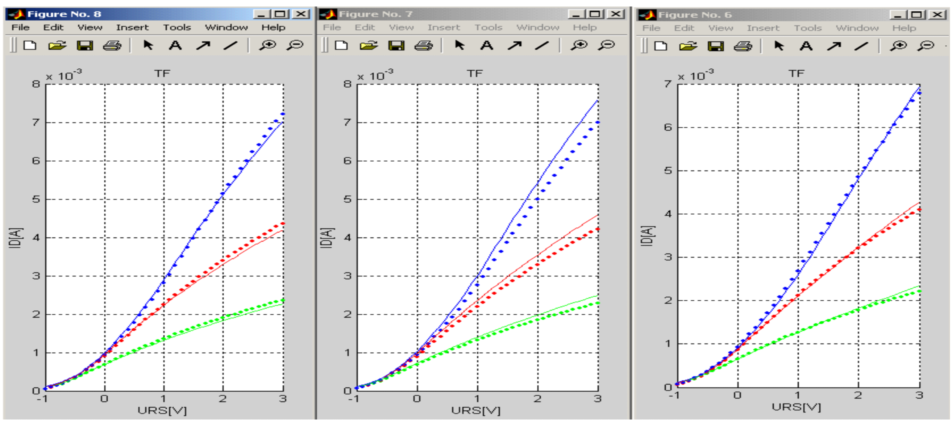

Figure 21

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. **D**ata **F**usion (**DF,** created by PW),
2. **I**nverse modelling **P**roblem **A**lgorithm (**IPA**, created by TUL),
3. **B**lind **S**ource **S**eparation of stochastic responses of an array of sensors (**BSS** created by UPC).

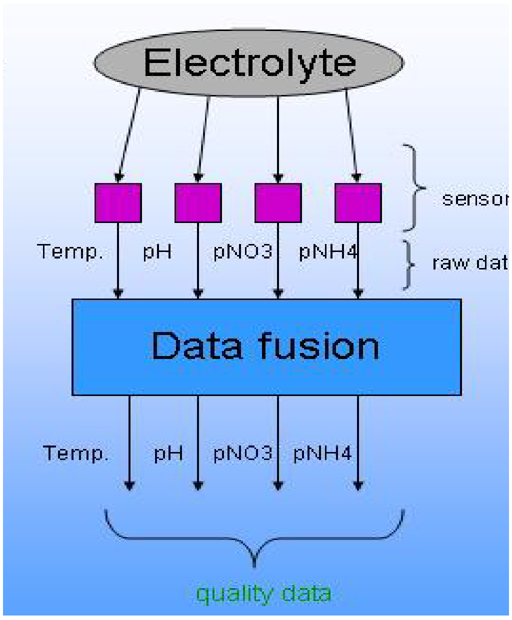

Figure 22

The general principle of Data Fusion (DF) algorithm is shown in fig 22. 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 senor matrix - multiple standard addition measurement scenario was implemented. As sketched in Fig. 23 - 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.

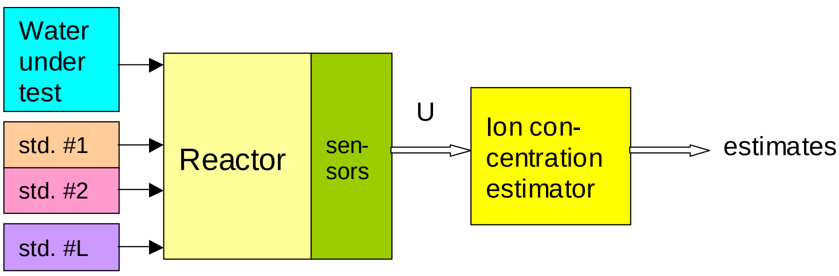

Figure 23

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.

For n sensors, m ions and R standard additions there are $N=n*(R+1)$ measurements $U_{j\gamma}$. 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:

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

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_{0j}, N_j, K_{lj} 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_{jr} – 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. 24. The algorithms have not been implemented in the final probe but lab tested.

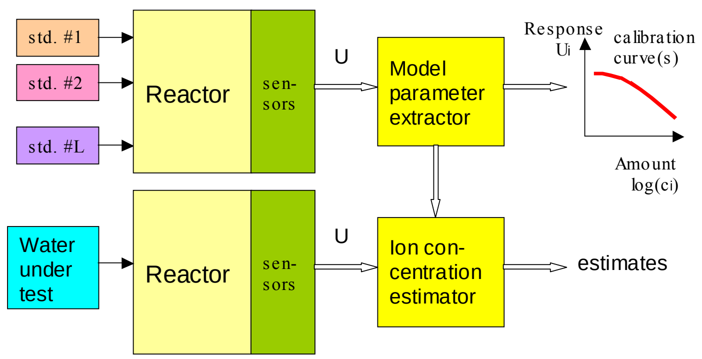

Fig. 24

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

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

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

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

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

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

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. 25.

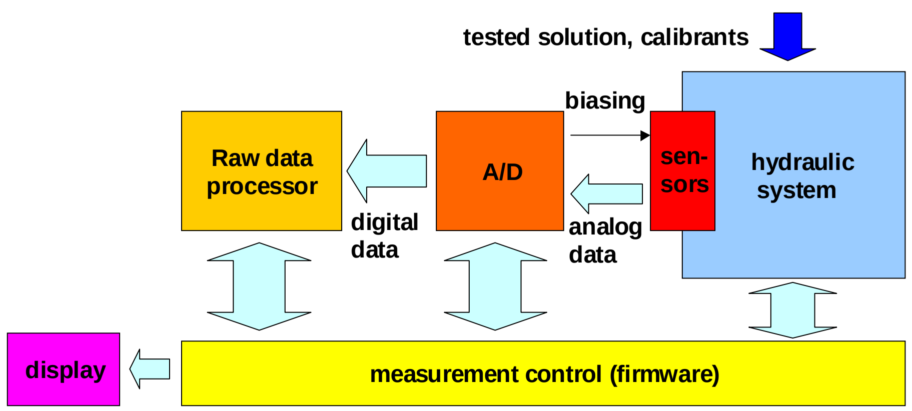

Fig. 25

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.

4.4. 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 build 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 26.
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 27, also built by SYSTEA.

Figure 26 Figure 27

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 28. Fig 29 shows the inside of the prototype.

Figure 28 Figure 29

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. 30 and 31.

Figure 30

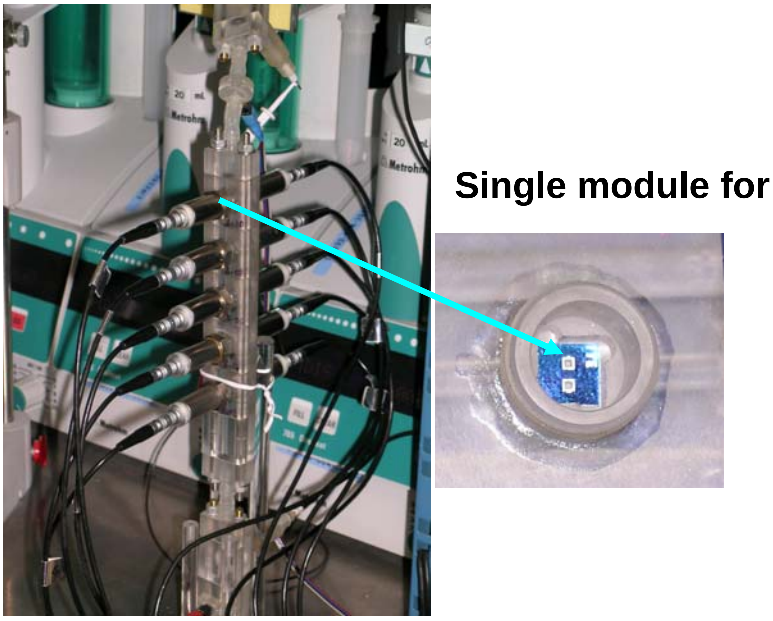

Figure 31

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 Systea 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 ΣΔ a/d converter, realised by TUL.

The first two realisations are shown in fig 32, while the last in fig 33.

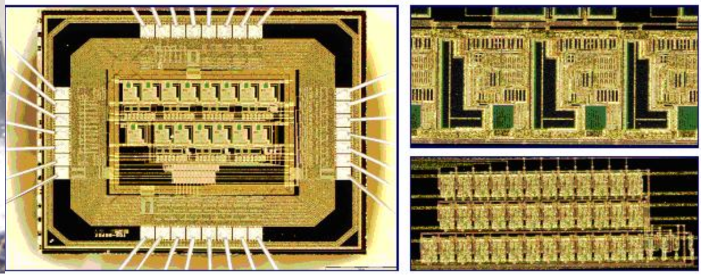

Figure 32 Figure 33

4.5. 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:

<u>LFA test unit</u>

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

<u>Final prototype</u>

- 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 34, 35 and 36 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).

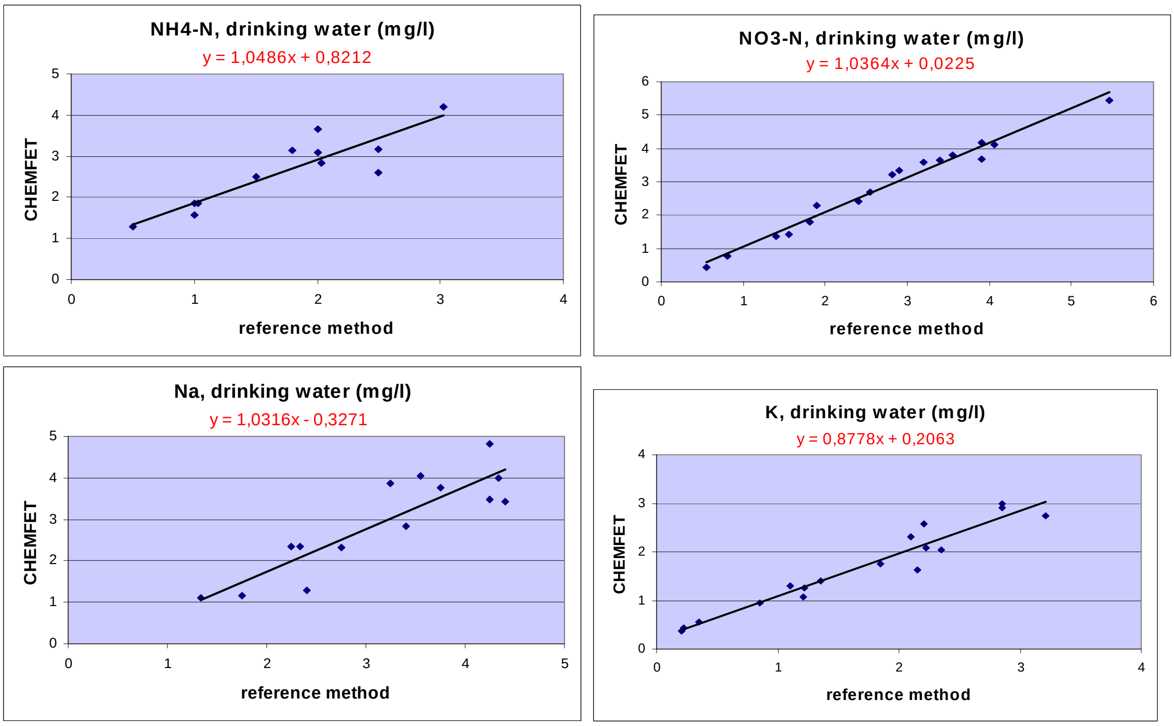

Figure 34

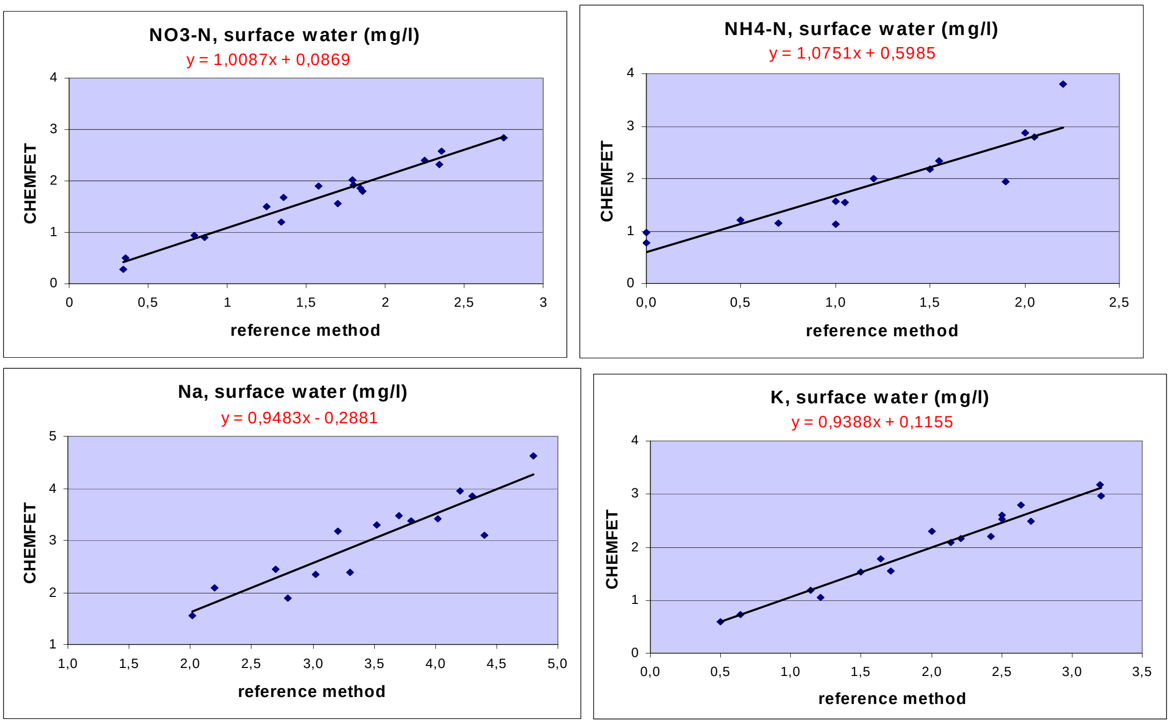

Figure 35

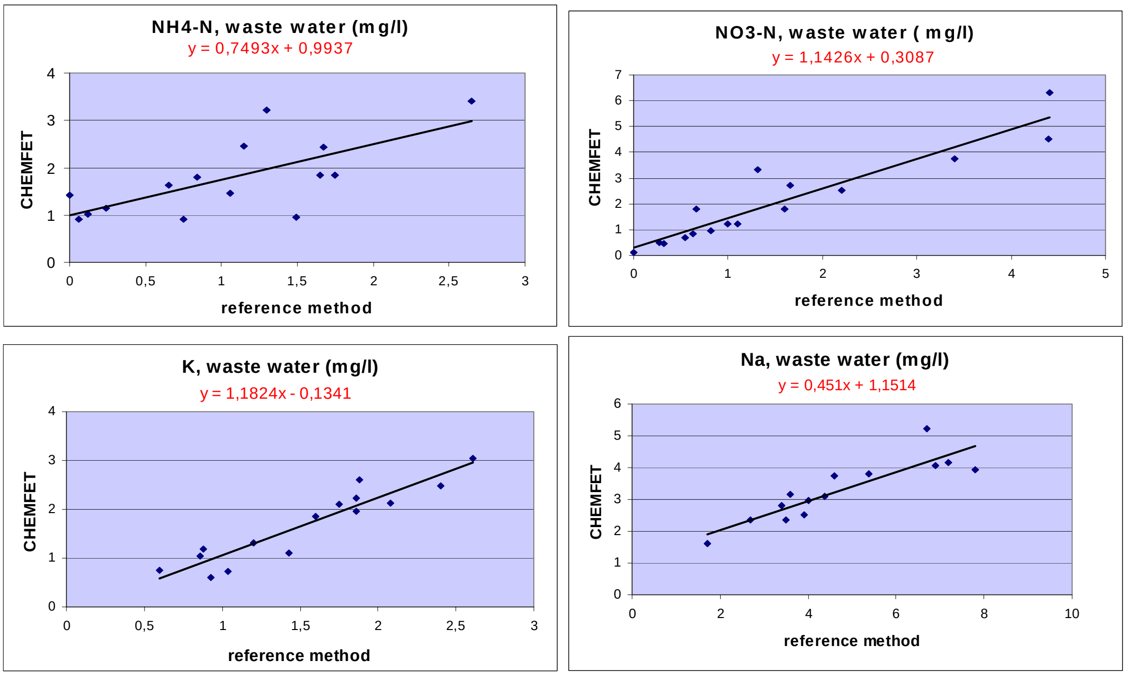

Figure 36

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.

5. Deliverables and other outputs

During the realisation of the project SEWING 24 deliverables were done. Here is the list of deliverables with short comments.

1. Reports, summaries

- During the whole duration of the project co-ordinator took care about reporting and dissemination. This deliverable was not submitted as a separate document, with agreement of P.O.

2. Plan of work

- Duties were attached to particular partners, as it was planned at he beginning of the project..
3. Fixing technical data for the system
- Studies concerning ranges of pollution to be monitored according to European standards were performed.
4. Project Presentation
- Text for the Commission, describing the project SEWING was presented.
5. Dissemination & Use Plan
- Preliminary vision of project usefulness was elaborated. Available on SEWING WEB page.
6. Preparation of polymer materials for optimal ionophore membranes
- One of the most essential works: finding materials for realisation of ISFETs selective for chosen ions.
7. Realisation of CHEMFETs selective for different pollutants
- Depositing membranes and obtaining first approach of CHEMFETs.
8. Measurements of sensors
- Verification of these sensors through measurements in specially prepared measuring system.
9. Encapsulated and optimised sensors for use in microsystems
- After measurements upgraded sensors were done.
10. Physical models of CHEMFETs
- Mathematical models, to be used later in software for the system.
11. Behavioural models of CHEMFETs
- The same as deliverable 10, but concerning models identified through measurements.
12. Optimisation and parameter extraction software
- First approach to use the model parameters in software.
13. Computer simulation of analogue interface
- First approach to design interface between sensors and DSP circuits.
14. Software for digital & analogue data processing
- First approach to Data Fusion and Data Acquisition software.
15. Simulation of the overall system
- Use of advanced simulation programmes for the whole system.
16. Design and partitioning of the system
- Theoretical approach to combining all elements into one system.
17. Functional prototypes of particular chips
- Final hardware realisation of particular parts of the system.
18. Realisation of prototypes
- Realisation of prototypes of particular parts of the system and of the whole system.
19. Measurements of prototypes
- Verification of prototype through measurement.
20. Evaluation of the whole system through measurements
- Stating usefulness of the whole system.
21. Dissemination of the results, exploitation plan
- Work conducted continuously during the whole project to disseminate partial and final results. The document listed all publications and summarised plans for industrialisation.
22. Technology Implementation Plan
- Preparation of document according to FP rules.
23. Assessment and evaluation of partial results
- Internal assessment of the project results.
24. Final report
- Final document for the Commission.

Only the Deliverable 1 was not prepared as a separate document. The remaining 23 deliverables were all resented to P.O., some of them in 2 or 3 versions, if further progress in the item was interesting for up-grading. New versions of deliverables 14, 15 and 21 were done according to request of Reviewers during the 3rd Annual Review.
Dissemination of results was continuously realised during the whole duration of the project through contributions on conferences, publishing articles, organising stands on professional conferences, participating in thematic EU Commission meetings, giving materials on CORDIS pages and organising the SEWING WEB page. Contacts with other institutions, being interested in the results of SEWING were also done.
All contributions are available on SEWING WEB page http://www.sewing.mixdes.org. During 40 months of SEWING realisation 42 international and national conferences were attended by partners and 67 contributions were presented. Conferences EUROSENSORS, MIXDES and AutMoNet were attended regularly.
During AutMoNet 2002, AutMoNet 2004 and Eurosensors 2004 conferences an exhibiting booth was organized to promote to the international scientific community and to any potential commercial partner the results of the project, with the support of a commercial flyer describing the aim of the project and prototype devices.
In the home page of Systea's SME partner a link to the project's home page was inserted; Systea's main scientific Customers and commercial partners were regularly updated about the developments done in the research project.
Two local Polish conferences had contributions about SEWING. All were published and information about the project was inserted in the texts.
Six papers were published in international journals, presenting partial results of SEWING project. Other interesting ways of disseminations: two notes in bulletins edited by FP5, information on CORDIS page (No 60437) and a lecture (in Polish) on the academic WEB page ATVN.
On seven seminars or meetings organised by the Commission or other FP5 or FP6 projects contributions about SEWING were presented. Cluster and concertation meetings were the most important. On a Polish-Italian seminar near Warsaw, on governmental level, SEWING was presented to potential end-users.
The SEWING WEB page with the address http://www.sewing.mixdes.org consists of two parts. One open for public with the following topics: home, what is SEWING, research partners, project presentation, conferences, papers, selected deliverables and final results. Reports and minutes of meetings are under a password, available to all partners. Many contacts with potential end-users were done thanks to that WEB page. 22500 persons visited this page. This page is permanently updated.

6. Project management and co-ordination aspects.
It was a hard job to manage and co-ordinate the work of 9 partners from 7 countries, which had to bring to a successful end combining all partial results in one, working system. This was done through the following activities:

- permanent e-mail contacts, often telephone contacts,
- 6 milestone meetings:
  Opening milestone meeting - 7-8 September 2001, Warsaw
  1st milestone meeting - 20 May 2002, Vienna
  2nd milestone meeting – 3 September 2002, Brussels
  3rd milestone meeting – 28 June 2003, Lodz
  4rd milestone meeting – 28 June 2004 Vienna
  extra milestone meeting – 16-18 September 2004 Anagni,
- Many working visits, during which common work was done,

- exchange of papers, publications,
- Regular supplying all partners with documentation sent to P.O and received from P.O.,
- Exchange of information about conferences and meetings interesting for realisation of SEWING project.

All these managerial activities had as the aim smooth realisation of particular parts of the system in such a way, as to have all parts of the system working together. These parts were discussed in details in section 4.

As mentioned previously, to have better probability of success, some elements of the system were elaborated in more than one version. It occurred a good solution. During the extra milestone meeting in Anagni it was realised that not all versions of particular parts of the system are ready for implementation in the prototype. So the final decision was taken, which will be used, and several working visits afterwards brought the prototype to working version and made possible to make a successful presentation during the Annual Review in Brussels on November 29, 2004.

Versions not used in the prototype are on the laboratory level of implementation and are ready for use in future industrialised versions of the system SEWING, according to end-user demand.

7. Outlook

Generally speaking all partners were engaged in the realisation of the project SEWING. The following benefits can be listed, which individual partners got from this project:

- Good recognition of the chemical pollution monitoring problem,
- Obtaining R&D results, in the form of working prototypes of particular parts of the system, papers, doctor dissertations etc.
- Involvement in international co-operation and international team work.
- Possibilities of future works on industrialisation of the project with perspective of financial income.

In particular the last point is important. Now some partners decided to make follow-up activities in the respect of SEWING industrialisation.

In the prototype built in SYSTEA, the SEWING industrial partner, the selected versions of particular solutions of parts of the system were used. The choice has been made on the basis of availability of final solutions and on the simplicity and flexibility of the whole system.

There are versions ready for eventually using them in industrial versions of SEWING, depending of the customer's demand. This idea concerns mainly the following parts:

the Front-Side-Contacts sensors, including the Ca sensor,
the voltage based interface circuit and ASIC solution of it,
more sophisticated solutions of Digital Signal Processing of information got from sensors,
more sophisticated data transmission from the sensor to the main computer.

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. Sensors 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.
SYSTEA, 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.

8. Conclusions
To conclude, the main objectives presented in the Annex 1 to the Contract were met. The vision of the system was rather ambitious and loaded with quite a large risk. So, some deviations from the previously assumed properties of the system occurred. These were:

- The final prototype is not as small as expected. The micro-probe version was constructed, but it occurred difficult to make experiments on it in a flexible way. The idea of smaller instrument is still alive and will be used in industrialisation phase.
- The prototype is not as cheap as expected. It occurred that CHEMFET sensors, to work properly, need to be calibrated and standard addition method should be used, so the hydraulic system is quite sophisticated and raised the cost.
- Only 4 ions are finally monitored, the fifth is in development phase. Preparation of selective membranes occurred quite difficult. Further research in this area is expected.

Even with these limitations the prototype occurred very useful and was positively evaluated by Reviewers. Now the following activities should be done.

¤ Industrial fabrication of CHEMFET sensors based on the SEWING know-how is needed. To do this a SME should be found or created and equipment for fabrication passed to it.
¤ R&D activity in the field of new sensors is necessary, and according to it up-dated algorithms for modelling and data fusion.
¤ More user-friendly housing for the whole system should be done. Up-dated data transmitting and data visualisation would be necessary.

To achieve these objectives, funds are necessary. The market production will bring profit in the future, to start its realisation there are some initial costs. This is why a proposal of a STREP is planned, which will give financial possibility of elaborating new micro-technology used in industrial version of the system SEWING.