



## **SEWING**

*IST-2000-28084*

*System for European Water monitorING*

### *Deliverable 18 ver.2: Realisation of prototypes*

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Deliverable N°: 18 ver2 . Realisation of prototypes

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#### Short Description:

Deliverable 18: Realisation of prototypes (Version for public dissemination)

Deliverable No. 18 is based on the development and measuring experiences done with the two first prototypes developed during the project, which are already described in Deliverables n.16 (design and partitioning of the system) and n.17 (functional prototypes of particular chips).

The work summarized in this Deliverable is the description of the final prototype, which summarizes the research results of the effort done by all partners, which is aimed to demonstrate the feasibility of the measurements with both Back Side Contact (BSC) and Front Side Contact (FSC) Chemfet sensors.

The final prototype is based on a standard SYSTEA product, the Micromac-1000 MP, specifically modified:

- to integrate up to n.7 Chemfet sensors + reference electrode + temperature sensor integrated in a dedicated linear flow-cell
- to manage the dedicated A/D acquisition boards developed and tested under the project to manage and read the signals from Chemfets and temperature sensor
- to manage the automatic measurement sequences under the specific procedures used by LFA based units and the computation software developed by SEWING partners.

The final prototype takes advantage of most of the features already available in the Systea's standard product, which is used as base of the final prototype, like cyclic storage of measured data, interactive programming cycles capability, system interactive configuration and remote serial communication capability.

The document describes system layout and all the specific new functions developed for the research final prototype, both hardware and software, which were studied within the project SEWING.

They are flexible and can be used in different final forms. So for presentation as prototype they can be inserted in this analytical device, where hydraulic and controlling parts are standard.

In the Dissemination of the results, Exploitation Plan (Deliverable 21) the industrialized product will be prospected; this final system will be designed and developed using all elements prepared under SEWING and the scientific results provided by the different prototypes developed and tested during the project, in order to have a cheaper and competitive new product to be developed after the end of the project to be launched on the environmental market.

Partners owning: SYSTEA - Systems Technology Advance Srl

Partners contributed: Politechnika Warszawska

Made available to: Mr. Antonios Barbas, Project Officer.

## 1. - FINAL PROTOTYPE OVERVIEW.

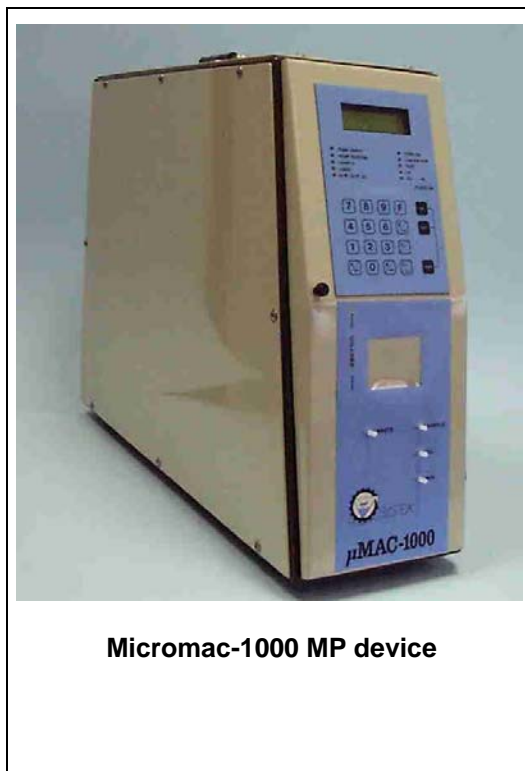
The final prototype will be based on the standard SYSTEAM **Micromac-1000 MP** portable and on-line analyser, shown in the picture; this analyzer is able as standard to manage sequentially and automatically up to four colorimetric analytical methods.

The final prototype is divided into five main sections:

- Hydraulics, mounted on the front side of the internal slid
- Sensors mounted in dedicated flow cell, placed on the right side of the internal slid
- Electronics and actuators, mounted on the right side of the internal slid
- Internal reagents compartment, accessible from the upper side of the unit
- Display and keyboard and printer, mounted on the front panel which can be opened to access the hydraulics and the electronics.

The external compartment is IP-55 proof and the unit is designed to be used as a portable and on-line field system, easily powered by an external 12 Vdc power supply.

The unit is equipped with a standard RS-232 serial port to manage the analyzer using a local or a remote device, like a PC or a data-logger.



**Micromac-1000 MP device**

The LFA (Loop Flow Analysis) technology is able to manage automatically a complete measuring sequence using the patented Loop Flow Reactor (LFR) analytical technology. The LFA unit contains as main parts the sensors, the conditioning part electronics and the main processing subsystem.

The standard Micromac-1000 MP unit is modified to integrate:

- To integrate up to n.7 Chemfet sensors + Ag/AgCl reference electrode + temperature sensor integrated in a dedicated linear flow-cell or two linear flow-cells connected in series (one for BSC and one for FSC sensors)
- to manage the specific A/D acquisition boards developed under the project to manage and read the signals from Chemfets and temperature sensor
- to manage the automatic measurement sequences under the specific procedures used by LFA based units and the new computation software developed by SEWING partners.

The following main chemical compounds will be measured using Chemfets:

- nitrate ion ( $\text{NO}_3^-$ )
- ammonia ion ( $\text{NH}_4^+$ ).

The following ions will be also measured, with additional Chemfets to minimize the interferences on the main measurements:

- $\text{K}^+$ , as main interferent of ammonia measurement
- $\text{Na}^+$ , as secondary interferent of ammonia measurement.

The hardware and software resources available will allow the prototype to manage other additional sensors like:

- $\text{Ca}^{2+}$ , as secondary interferent of ammonia measurement
- $\text{Cl}^-$ , as main interferent of nitrate ion
- pH sensor.

The typical applications of the new final prototype will be:

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

The final prototype is fully configurable and open to operator's modification of the analytical sequence which manages the reactor; using the local keyboard and LCD display, as any other standard SYSTEA's LFA analyser; for example it is possible:

- to bias the reference electrode and CHEMFETs drain terminals with predefined voltages
- to modify all the interval times of the analytical sequence
- to program the opening and closure of any valve included in the analytical reactor
- to turn on or off the peristaltic pump in both versus, at two different speed (low and high)
- to modify the quantity of solutions which can be injected in the loop reactor
- to perform automatically a double standard addition method to perform the calibration of each Chemfet sensor during each measurement.

The final prototype uses n.4 injection valves, in order to give the way to:

- add the proper ISA solution to the unknown sample
- to use three separated stock solutions for standard addition on each sensor, according to the computation algorithms developed by PW and UPC partners.

The analyzer is designed to manage two different A/D acquisition boards:

- commercial A/D and D/A boards already used in the first two prototypes developed during the research project (LFA test unit and probe demonstrator), which will be managed by a specific software procedure developed with PW partners in order to measure the drain current response of voltage driven Chemfets.
- the voltage sensing board developed by VTT partner, which will be managed by new dedicated software module developed by UPC partner, using a second parallel board connected directly through the PC-104 bus to the main CPU unit

The firmware which will manage the analyzer is developed to be compatible with the other two prototypes developed under the project:

- LFA test unit
- probe demonstrator

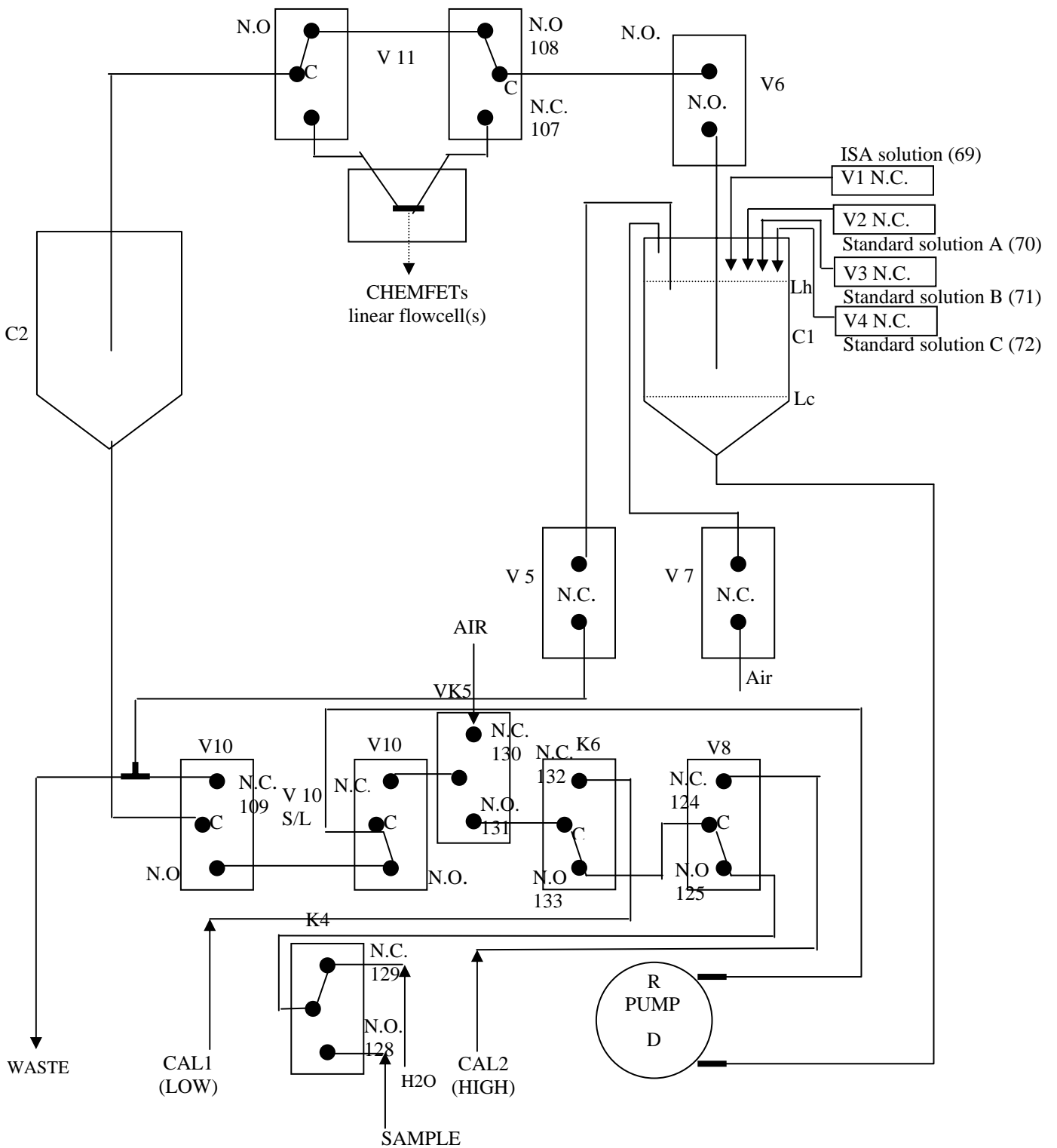
in order to allow an easier future updated based on the last results achieved with the final prototype; please refer to Deliverables n.16 (design and partitioning of the system) and n.17 (functional prototypes of particular chips) for the technical description of these first two prototypes.

The final prototype will be the base for the design of the future industrialized product, which will be the spin-off result of the project.

The preliminary design of the industrialized product is prospected in the Dissemination of the results, Exploitation Plan (Deliverable 21), considering all the necessary aspects to improve a cheaper and competitive product to be successfully launched on the environmental water market, to be used as a portable or on-line monitoring system.

## 2. - THE HYDRAULIC LAYOUT.

In the figure below the hydraulic circuit of the Loop Flow Reactor is shown; the total volume of the LFR is about **8.25 ml.**



### 3. - LFA CIRCUIT DESCRIPTION.

The LFA reactor includes several devices (mechanical, hydraulics, Chemfets mounted in the flow-cell) sequentially interconnected to form a ring defined **Loop Flow Reactor**, in short **LFR**.

The LFR hydraulic schematic diagram of the final prototype is shown in the previous drawing.

The two valves **V10 S/L** when switched to **N.C.** allows to open LFR to pump sample, washing and maintenance solution or an external standard solution ,when in **N.O.**, LFR is closed in LOOP, to allows mixing, reaction and so on.

Cylinder **C1** allows the injection in the LFR of:

- The ISA stock solution (using **V1** fast valve), to perform sample pH adjustment before each measurement
- Three different stock calibrants (using **V2**, **V3** and **V4** fast valves), to perform “know addition” method on the unknown sample, according to the computational algorithms developed in the project.

More, the cylinder C1 contributes to create a strong turbulence inside the circuit, in order to speed up the mixing phase.

Valve **V6**, when activated, interrupts the LFR hydraulic connection and contributes to the vacuum production inside **C1**.

Pump **P** is a single tube peristaltic pump that can be activated in bi-directional direction

Valve **V4** makes the selection of Sample and pure water for washing, while:

- Valve **V8** selects CAL1 external solution
- Valve **V3** selects CAL2 external solution.

CAL1 and CAL2 solutions can be used to routinely test the performance of the system and they can be normally chosen as a mixture of the main pollutants ( $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) one a decade over the other; more, these inlets can be used to provide external calibrant solutions for the pH sensor (pH=4 and pH=7).

Valve **V7** is used to introduce air in the loop, while valve **V5** is used to produce an overflow level in C1 cylinder before the vacuum production phase.

The cylinder **C2** is normally filled with air and contributes to the vacuum production in **C1**, containing temporarily the volume of liquid pumped out from **C1** by the pump **P**.

The two valves **V11** are used to by-pass the flow-cell during sampling, preparation and washing phases, minimising the contact time between sample and the sensors, in order to achieve a longer life time of sensors membranes.

Additional injection valves (up to 3) can be easily integrated in the analytical circuit, in order to allow injection of standard solutions for additional Chemfets (like  $\text{Ca}^{2+}$  and  $\text{Cl}^-$ ).

## 4. - DESCRIPTION OF ELECTRONICS.

### 4.1 Standard electronics

Power supply board

RFIO Board

CPU+RF I/O Boards



**right side internal electronic compartment**

The electronic of final prototype is composed by the following boards already used in the standard product Micromac-1000 MP:

- **CPU board**, based on a PC-104 architecture, which manages the analyser with a programmable step-by step program, which can be modified by the User according to Systea's specifications
- **I/O board**, which manages all the LFR actuation and signal acquisition, using the auxiliary RFIO board
- **RFIO board**, the auxiliary input/output board
- **Power supply board**, which gives to the other boards the necessary DC power supplies
- **Chemfets signals electronic conditioning and acquisition subsystem**, specifically developed under this research project.

### 4.2 Chemfets signals electronic conditioning and acquisition subsystem

As already described in Deliverable n.16 (design and partitioning of the system), the conditioning subsystem has several functions. It sets proper bias point for the CHEMFET sensors located in the flow cell. It measures the source voltages of the CHEMFETs. Source voltage variations indicate variations in the ion concentrations in water under measurement. The conditioning subsystem also monitors the temperature of the CHEMFET sensors, which are sensitive to the temperature variations. This sensitivity can be compensated if the temperature is known.

The final prototype will be able to integrate two different conditioning subsystems:

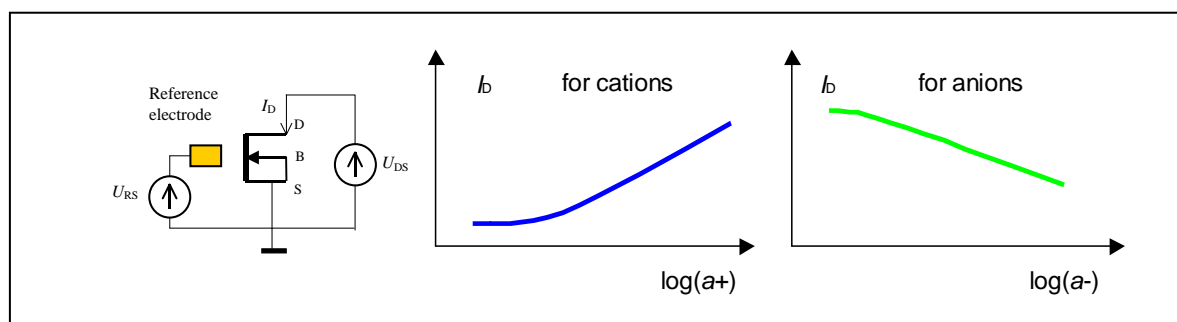
- commercial A/D and D/A boards already used in the first two prototypes developed during the research project (LFA test unit and probe demonstrator), which will be managed by a specific software procedure developed with PW partners in order to measure the drain current response of voltage driven Chemfets.
- the voltage sensing board developed by VTT partner, which will be managed by new dedicated software module developed by UPC partner, using a second parallel board connected through the PC-104 bus to the main CPU unit

In the final prototype a measurement technique is provided that is based on the following commercial standard A/D and D/A modules used by SYSTEA to develop the first two research prototypes (LFA test unit and probe demonstrator):

- n.1 Ex9017 board, with n.8 differential analogue inputs, 24 bit sigma-delta ADC
- n.2 Ex9022 boards, with n.4 programmable 4-20 mA analogue outputs each, 12 bit resolution

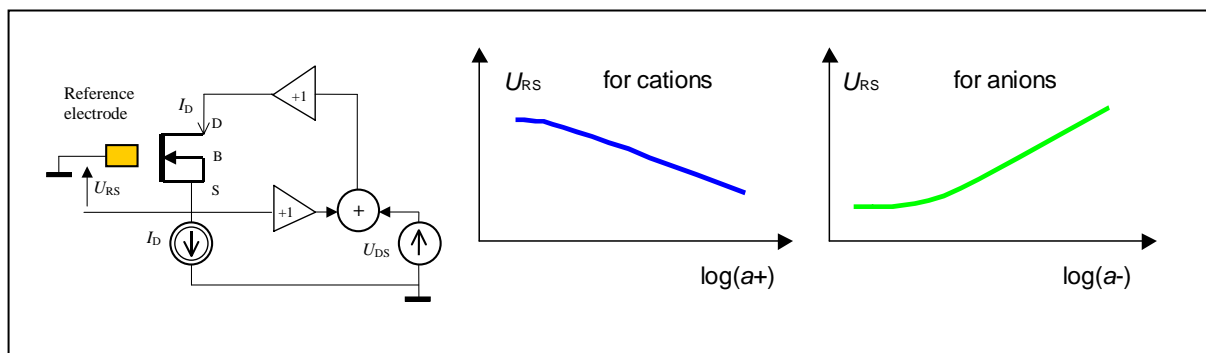
The two units, manufactured by TopsCCC company, are managed by the standard PC-104 CPU using a built-in RS-485 port.

In measurement mode the drain current  $I_D$  is dependent on the ionic activities in the solution and measured with 16-bit resolution using preset voltage ranges (see sec. 5.2 for a model). Thus the signal from the  $i$ -the sensor, denoted generally with  $U_i$ , is proportional to its  $I_D$  current. The coefficient of proportionality is immaterial for the software, but has to be kept constant for each sensor after the adjustment of  $U_{RS}$  has been performed (that is during measurement phase). Dependence of the drain current on the ion activities is sketched in the figure below.



The reference electrode to source biasing ( $U_{RS}$ ) is to be adjusted at stand-by probe mode algorithmically (i.e. by software) so that the drain current (flowing also through  $U_{DS}$  source) has the value close to what was determined to be best for sensing (0.1mA for BSC sensors). D/A conversion is performed with 12 bit resolution (-10...+10 V). The iterative adjustment of  $U_{RS}$  is to be made by a new function specifically developed in internal firmware.

The originally planned constant drain current measurement setup, as implemented in the VTT board, is sketched in the figure below (it has been already extensively described in Deliverable n.16). Its main advantage over the first setup is smaller influence of electric/thermal properties of the FET structure of CHEMFET sensor upon the measurements. However, it is more complex due to necessary feedback circuitry (opamps). The appropriate software interface for the VTT board will be available from UPC (in a form of a C callable library function), in order to replace the firmware library function that controls the circuitry shown in the figure above.



Because directions of  $I_D$  and  $U_{RS}$  changes, due to change of main ion activities, are opposite for the two setups -- the software which controls the measurement equipment has to do appropriate sign conversion. It is assumed here, that the constant drain current setup controlling software provides direct value of  $U_{RS}$ , i.e. the signal  $U=U_{RS}$ .

For the drain current sensing setup the signal  $U = -R \cdot I_D$ , where  $R$  is a positive constant. It would be desirable to select value of  $R$  such that dependence of  $U$  on  $\log(a)$  would be similar for the two measurement setups. An example of  $R$  calculation procedure is given in the sec. 5.2.

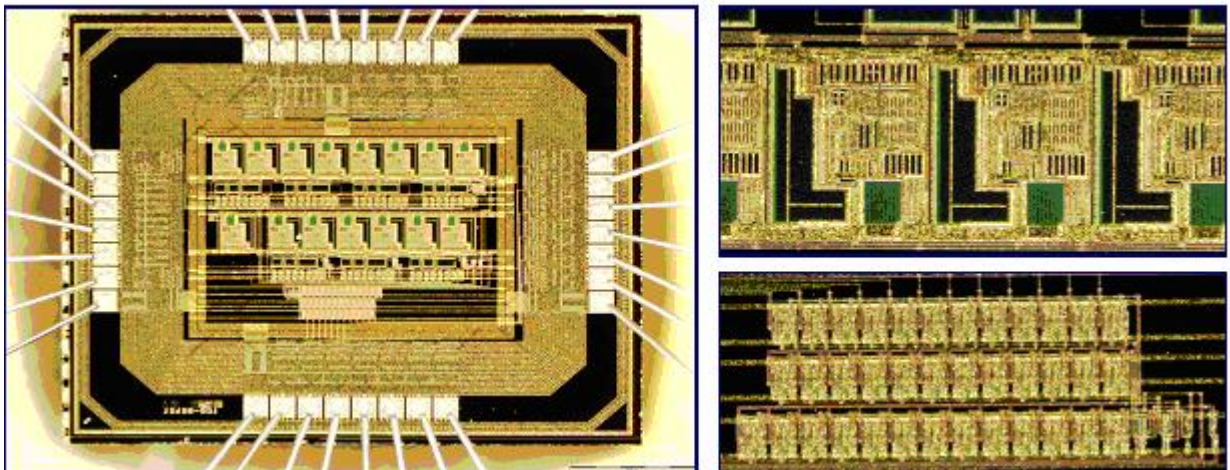
### 4.3 Alternative solution for signals electronic conditioning and acquisition subsystem

In the case of strong demand and necessity of production of some tens thousands of Microsystems an ASIC solution should be taken into account in the future industrialized product. All the electronics described above can in such a case be put into one chip. The key point is the design of Sigma-Delta Converter as a Optimal Solution for Processing Part of the System and the CMOS temperature sensor PTAT (Proportional To Ambient Temperature) which can be implemented in standard ASIC (Application Specific Integrated Circuit) CMOS technology.

The main advantages of this solution are:

- A Simple Construction of the AD Converter
- A Possibility of the Setting Order of The AD Converter
- Small Size
- Low Power Dissipation
- Interference Resistant
- PTAT is implemented together with all the circuit in standard CMOS technology

The prototype of this solution is shown below:



## 5. - SIGNALS PROCESSING ALGORITHM.

### 5.1. General description

To simplify hydraulics (and decrease cost off the future industrialized product) it was decided to skip separate calibration of sensors: instead a special modification of a double standard addition method was proposed to calibrate and measure in one procedure.

Furthermore, the procedure developed by PW (see description further on) is able to achieve better resolution at low concentrations of some ions (see description below). The measurement processing software specifications were also formulated (see next par.5.3 – New C++ data processing interface), so that it will be possible, if a need arises, to handle different main measured compounds, interfering ions and number of sensors, when the final prototype design reaches industrialization stage.

A clear interface between the analyzer's firmware (that controls operations of the analyzer and specifically modified to manage the new functions) and the data processing software has been defined.

The proposed Data Fusion software will be adapted to the agreed specifications and is expected to be one of possible data processing means that will be available in the probe. Other software, such as IsfetSS (UPC) or dynamic Inverse Problem solution (TUL) methods can be used as well – if they will be provided as one C callable function with predefined prototype – in a form of a library module.

The basis of dynamic Inverse Problem solution is the improving of accuracy of measurements by employing the function specification algorithm. This algorithm can be easily implemented as a digital filter. The averaging of measured values increases the delay between the occurrence of the ion change and its detection. On the other hand, the introduction of additional sensors increases the computational effort and consequently the estimation time. Therefore, for the on-line estimation of ion concentration, the function specification algorithm combining both averaging techniques to reduce the measurements error influence is suggested. The digital filter approach renders possible the design of an ion concentration monitoring unit, containing a digital filter implementing the function specification algorithm and some additional logic circuitry, which can be integrated within a single IC ASIC (see point 4.3). This solution is ready to implement on the end user demand.

There was established a four step measurement plan. At each step signals from up to 7 CHEMFETs and 1 temperature sensor are collected for the following contents of the reactor of the LFA:

1. The reactor contains a sample of the water under test with Ionic Strength Adjuster (ISA) added
2. Standard solution A is added to the reactor
3. Standard solution B is added to the reactor
4. Standard solution C is added to the reactor

Selection of such a special measurement plan in place of a more standard 3-step procedure (i.e. a double standard addition, with solutions A and C) allows potentially for a better resolution at low level activities of some ions. In our case the ammonia sensors are known to have relatively small selectivity towards interfering potassium ions. Since we measure also activity of the potassium with a relatively selective sensor – the proposed plan allows for calculation of selectivity coefficient for NH<sub>4</sub> sensor towards K ions and nonlinear representation of ammonia sensor response. Responses of all other 5 sensors are approximated linearly which seems reasonable taking into account ion activity range for targeted operating conditions of the probe and also cost of more complete characterization of all CHEMFET sensors.

The contents of the three solutions is given in the table below.

Solution\Ion	H <sup>+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>
A	low	low	low	Low	low	low
B	0 or low	0 or low	0 or low	0 or low	0 or low	high
C	high	high	high	high	high	0 or low

The effect of injecting standard solution depends on the ratio of the injection volume relative to the sample volume. For simplicity of table description we can assume the ratio to have some fixed (and small) value for all three injections (steps: 2, 3, 4). The meaning of table entries:

- Low** a value of the given ion activity in the solution that creates a level of activity for the particular ion in the reactor which is close to the minimum value for a sensor. For  $\text{NH}_4$  the minimum value should be selected at the “knee” of sensor response for the high level of the potassium interfering ion. For other sensor the minimum value should be selected at the left end of the linear part of sensor response.
- High** a value of activity in the solution that creates a level of activity for the particular ion in the reactor which is close to the maximum value for a sensor. Ratio of maximum to minimum activities of the additions should not be smaller than 10.

The concentration of each solution (in moles) and the expected injected volume ratio (volume of each solution / real loop flow reactor volume) are presented here below:

Solution	Volume ratio	Concentration
ISA solution	0,1	$\text{CH}_3\text{COOLi}$ 0.5 M
A	0,122	$\text{NH}_4\text{NO}_3$ $10^{-3}$ M $\text{Na}_2\text{SO}_4$ $5 \cdot 10^{-4}$ M $\text{K}_2\text{SO}_4$ $5 \cdot 10^{-4}$ M
B	0,136	$\text{KCl}$ $10^{-2}$ M
C	0,15	$\text{NH}_4\text{NO}_3$ $10^{-2}$ M $\text{Na}_2\text{SO}_4$ $5 \cdot 10^{-3}$ M

Note: the injected volumes are always injected in the fixed volume of the Loop Flow Reactor.

## 5.2. PW processing algorithm

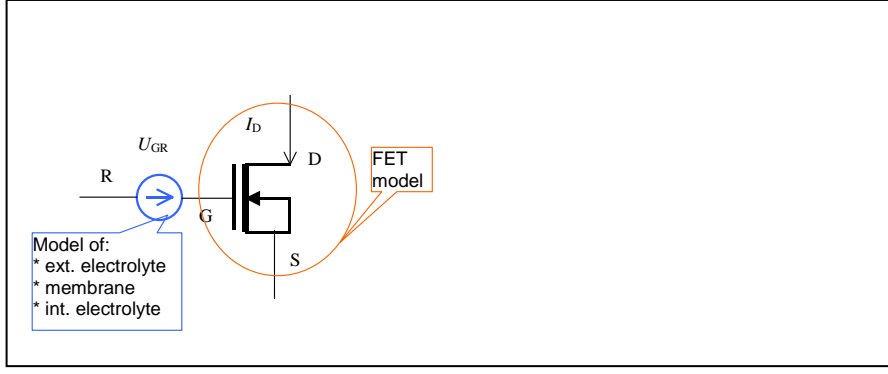
For the drain current sensing setup it can be assumed, that the internal FET of the CHEMFET sensor (see Fig. A1) operates in the linear region and that the Nikolsky-Eisenmann (NE) model can be used to describe sensor operation (selection of the chemical model is not important here). The NE model expresses  $U_{GR}$  as a sum of an ionic activity dependent component  $U_N$  and some “chemistry-independent” offset voltage  $U_{N0}$ :

$$U_{GR} = U_N + U_{N0} \quad (5.2.1)$$

$$U_N = N \frac{V_T}{z_0} \ln \left( a_0 + \sum_{j=1}^{m-1} K_j a_j^{z_0/z_j} \right) \quad (5.2.2)$$

$z_0, z_1, \dots, z_{m-1}$  denote electro-valencies of ions with molar activities  $a_0, a_1, \dots, a_{m-1}$  (all electro-valencies are of the same sign).  $K_j$  are selectivity coefficients of the  $j$ -th ion w.r.t the main ion (indexed with 0 in the formula).

$V_T = kT/q$  is the thermal voltage (approx. 25mV at room temperature).  $N$  is a non-ideality coefficient introduced here to better fit actual sensor behaviour by the model.



For the assumed linear region of FET operation the drain current can be expressed as follows:

$$I_D = \beta \cdot \left( (U_{GS} - V_{th}) \cdot U_{DS} - 0.5 \cdot U_{DS}^2 \right) \quad (5.2.3)$$

where  $\beta$  and  $V_{th}$  are FET parameters. Since  $U_{GS} = U_{RS} + U_{GR} = U_{RS} + U_N + U_{N0}$ , therefore

$$I_D = I_{D0} + g \cdot \underbrace{N \frac{V_T}{z_0} \ln \left( a_0 + \sum_{j=1}^{m-1} K_j a_j^{z_0/z_j} \right)}_{U_N}, \quad \text{where} \quad (5.2.4)$$

$$I_{D0} = g \cdot \left( U_{RS} + U_{N0} - V_{th} - \frac{U_{DS}}{2} \right), \quad g = \beta \cdot U_{DS} \quad (5.2.5)$$

Value of  $g$  can be readily calculated if the operating point of the FET is iteratively adjusted, as proposed in section 2. To see it let us note that for fixed ion activities and  $U_{DS}$  voltage – the drain current is linearly dependent on  $U_{RS}$ , and so:

$$\frac{\partial I_D}{\partial U_{RS}} = g \quad (5.2.6)$$

can be determined in the course of iterative adjustment of  $U_{RS}$  (to get a desired drain current value).

Since in the constant drain current measurement setup with the same operating point the output sensor voltage  $U \equiv U_{RS} = U_{GS} - U_{N0} - U_N$ , i.e.

$$\frac{\partial U}{\partial U_N} = -1 \quad (5.2.7)$$

For the drain current sensing measurement setup the output sensor voltage has been defined as:  $U \equiv -R \cdot I_D$ . Hence

$$\frac{\partial U}{\partial U_N} = -R \cdot g \quad (5.2.8)$$

Therefore one should select

$$R = 1/g \quad (5.2.9)$$

to equal sensitivity of the output sensor voltages to changes of the ion activities for the two measurement setups.

### 5.3. New C data processing interface.

Currently the following two functions are planned for communication between the standard Systea's firmware and the measurement data processing software (e.g. Data Fusion based).

**int** /\* the function returns 0 on correct initialisation \*/

```
iCalc_init(  
    char *conf_file_name, /* configuration file name */  
    char *log_file_name, /* if not NULL – passes name of the log file */  
    unsigned long log_file_max_size, /* >=0 – maximum length of the log file */  
    struct iCalc_mcnf *mpars /* measurement configuration parameters */  
);
```

where

```
struct iCalc_mcnf{  
    short int nr_of_ions;; /* nr of ions to be considered, currently 6 */  
    struct ion *ions; /* vector with descriptions of ions of interest */  
    short int nr_of_sensors; /* nr of sensors, currently 6 */  
    struct sensor *sensors; /* vector with descriptions of sensors */  
    short int nr_of_bottles; /* nr of bottles with standard addition liquids, currently 3 */;  
    float *bottles; /* row-wise stored 2-D array (nr_of_bottles by nr_of_ions) with  
    ionic activities in each bottle */  
    short int nr_of_steps; /* nr of steps in the measurement procedure, currently 4 */  
    float *ticks; /* row-wise stored 2-D array (nr_of_steps by nr_of_bottles) of  
    injections, each entry contains nr of drops (ticks) from each bottle  
    to be injected at each step */  
    float sample_vol; /* volume of the sample [liters] */  
    float loop_vol; /* volume of the loop [liters] */  
    float tick_vol; /* volume of the tick (smallest drop) that can be injected [liters] */  
    float ISA_relcontent; /* relative content of ISA in sample and in std liquids */  
};  
#define      NAMLEN      6      /* defined in iCalc.h */  
struct ion{  
    char iname[NAMLEN]; /* ion name, e.g. "NH4+"; no trailing \0 assumed */  
    short int valency; /* ion valency, eg. +1 for NH4 ion */  
    float pmin, pmax; /* log10 of lower and upper bounds for ion molar activities (mol/l)  
    in the sample */  
}  
struct sensor{  
    short int main_ion; /* index of the main sensor ion in the ions vector; indices start from 0 */  
    float UDS, ID; /* operating point of the sensor */  
    float U0min, U0max; /* min. and max. value for the sensor offset voltage in the NE model */  
    float Nmin, Nmax; /* min., max. values for the sensor response slope non-ideality factor N */  
    float Kmin, Kmax; /* min. and max. value for the log10(sensor selectivity factor) w.r.t. all the  
    considered interfering ions */  
    unsigned int ident; /* a unique number that corresponds to ASCII identifier of  
    each particular sensor item, e.g. "SE-06_NH4-pHEMA-PCV-DOS_0008-09" */  
}
```

The function **iCalc\_init** reads configuration data from a file that is specified with the first parameter. Format of this file will be specified separately. All important activities of the data processing software can be logged to a file if a valid file path is specified with the 2<sup>nd</sup> parameter and the 3<sup>rd</sup> parameter is greater than 0.

Upon correct processing of the configuration file the function returns 0, otherwise an error code (and the reason for the error written to the log file). If the 4<sup>th</sup> parameter is not NULL, than the structure pointed at by the pointer will receive respective numbers of ions, sensors, steps of measurement procedure and standard addition bottles.

The second function is prototyped as follows:

```
int /* the function returns 0 upon correct performance or an error code */
iCalc_perform(/* performs ion activity estimation */
    struct iCalc_mcnf *mpars, /* measurement configuration parameters */
    void *apars, /* ion estimation algorithm parameters */
    float *Measurements, /* row-wise stored 2-D array nr_of_steps by
        (nr_of_sensors+1), that holds measurements (temperature and U of each sensor) */
    float *Activities, /* a vector of nr_of_ions estimates of ion activities */
    short int *sensor_status, /* vector of (nr_of_sensors+1) elements.
        On function call:
            sensor_status[k] ==0 means the k-th column of the measurement table
            contains valid measurement
            sensor_status[k]== -1 means that data of the k-th column should be discarded
            (presumably because of sensor malfunction)
        On function return:
            sensor_status[k] ==0 means the k-th column of the measurement table
            was successfully used for calculation of the ionic activities
            sensor_status[k]== -1 means that the k-th column was not used for calculations
            (as requested on function call)
            sensor_status[k]==1 means that the k-th column contains data from
            a faulty sensor */
    short int ion_status /* vector of nr_of_ions elements.
        On function return:
            ion_status[k]==0 means that the k-th ion was calculated successfully
            ion_status[k]==-1 means that the k-th ion could not be calculated (e.g. no data
            from a sensor)
            ion_status[k]==1 means that lower bound of declared ion concentration (pmin) has
            been reached
            ion_status[k]==2 means that upper bound of declared ion concentration (pmax) has
            been reached */
);
```

The function calculates estimates of ion activities in the solution for given measurement data. Algorithm specific parameters are read from a separate configuration file; an opaque data structure is dynamically allocated and the pointer to it is returned via the second parameter of the following function:

```
int /* the function returns 0 on correct initialisation */
iCalc_apars_init(/* ion estimation algorithm parameter initialisation function */
    char *conf_file_name, /* ion estimation algorithm configuration file name */
    struct iCalc_mcnf *mpars, /* measurement configuration parameters */
    void **apars /* it is used to pass to the caller ion estimation algorithm parameters
        that are read from the configuration file to an algorithm specific
        data structure. The data structure is created with the first call to
        iCalc_ainit(). Subsequent calls to iCalc_apars_init() with previously
        set pointer can change the data structure. To free the dynamically
        allocated data structure call iCalc_apars_free() */
);
```

Dynamically allocated parameters can be freed, when not needed, via the call to the following function:

```
int /* the function returns 0 on success */
iCalc_apars_free( /* deallocates data structure, allocated with iCalc_apars_init() call */
    void *aparams /* pointer to the dynamically allocated ion estimation algorithm
        specific parameter data structure */
);
```

For software developers there is also a function:

```
int iCalc_log(const char fmt,...) /* writes formatted text messages to the log file;
    returns the number of bytes printed, or a negative number for error condition */
```

which can be used to print messages to the log file. Calling arguments – as for the standard C function printf.

## 6. - FINAL PROTOTYPE DESIGN.

### 6.1 Physical dimensions and space requirement

A picture of the final prototype is shown below; the physical dimensions are the following:

55 x 35 x 11 (d x h x w) cm

Including the reagents it weights about 15 Kg.



### 6.2 Front door

Keyboard, display and status led

Door opening screw

Hydraulics Inlet/Outlet



### 6.3 Solutions compartment




Side view

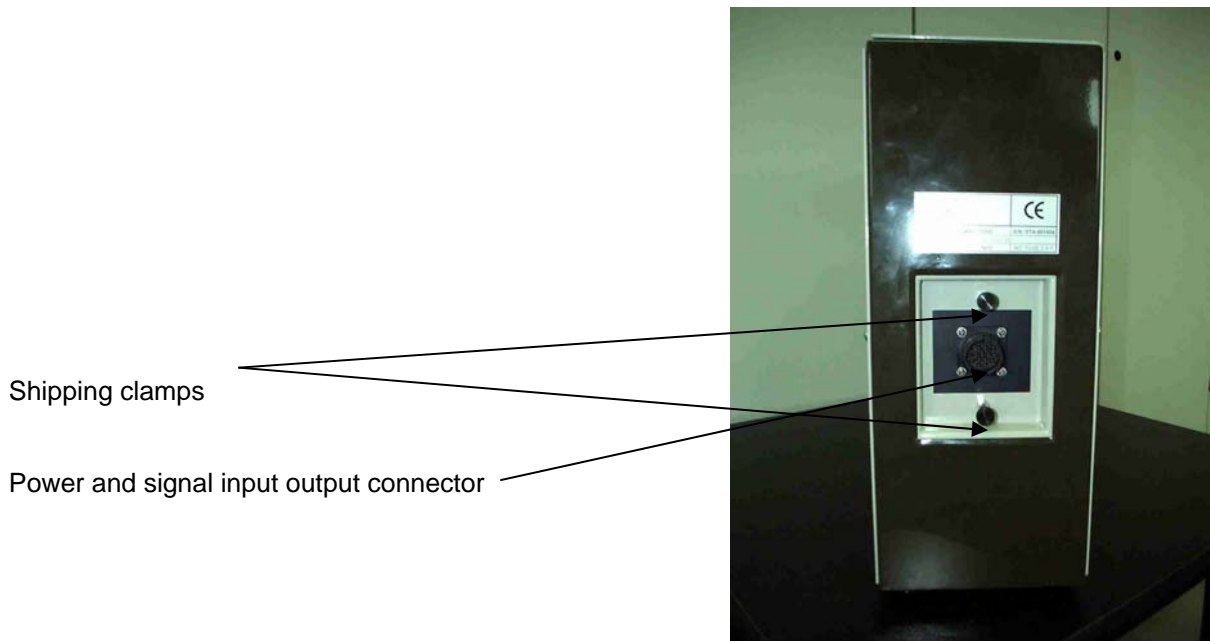


Solutions straws (top view)

## 6.4 Hydraulic interconnections

 <p>The image shows the front panel of the μMAC-1000 system. On the left side, there is a vertical label 'μMAC-1000'. In the center, there is a white rectangular area. Below this area, there are five labeled ports: '- WASTE', '- SAMPLE', '- DIL', and '- AUX'. At the bottom, there is a logo for 'SYSTEVA' and the text 'μMAC-1000'.</p>	<p>The hydraulics lines can be connected using silicone tube 2 x 4 mm as follows:</p> <ul style="list-style-type: none"><li>- Sample line to: SAMPLE</li><li>- Waste line to: WASTE</li><li>- Diluent line to: DIL</li><li>- AUX: not used</li><li>- Calibrant line 1 to: CAL 1</li><li>- Calibrant line 2 to: CAL 2</li></ul>
--	--

## 6.5 Back Side



### 6.6 Opening front door



Reagents valves V1, V2, V3 ...V7  
Reagent injection tubes, teflon

Valve V6

Reaction Cylinder C1

Reaction Cylinder C2  
Valves V11 V/DIL

Valves V6, V7 ;V8 V9

Valves V10 S/L

Peristaltic Pump

### 6.7 Opening right side

Reagents valves

Linear flow-cell

Reagents compartment

Peristaltic pump

Pump motor

Electronics

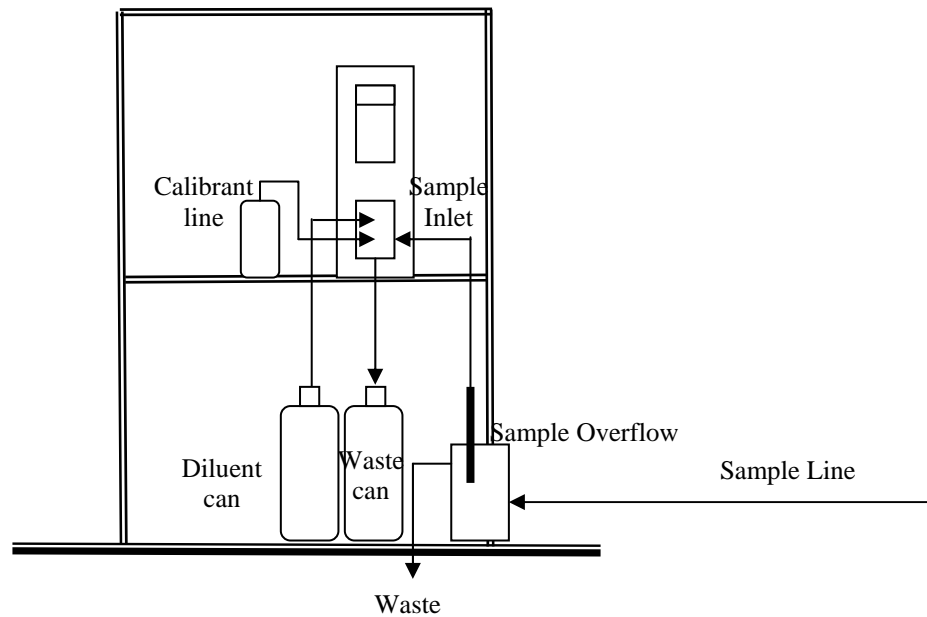


## 6.8 Positioning of the measuring unit

The final prototype is designed as a portable and on-line analyzer; it can be positioned over any horizontal table or support; normally the analyzer has to be positioned over the inlet and waste point (see layout).

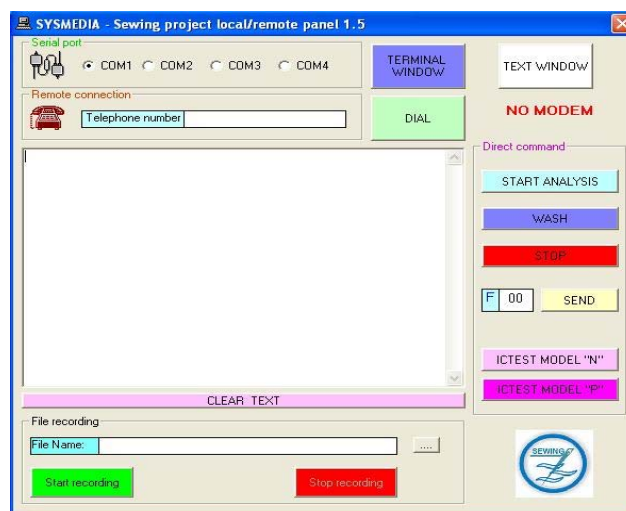
Sampling point have to be pressure free; max distance from the analyzer 2 mt.

A typical installation layout in a water monitoring station is the following:



## 6.9 Local/remote control panel software

In order to allow an easier handling of the measurements performed with the final prototype, a program running on the PC under Windows ® operating system was designed and developed, to allow the remote handling of the measurements using a serial port or a GSM device connected to the same serial port.



This program allows the start the measurement cycle or a wash cycle, to run off-line the calculation algorithm integrated inside the firmware of the device, to see the measurement results on the window of the screen.

## 7. - TECHNICAL SPECIFICATIONS.

### 7.1 General characteristics

- Portable and on-line analyzer, IP-55 water proof
- Operating temperature range: from +10 to +40 °C, with storage temperature from -10 to +60 °C

### 7.2 Measuring requirements

- Multiparametric measurements capability: up to 7 parameters measured at the same time
- Fast measurement capability: a complete measurement cycle is performed in less than 15 minutes
- Measuring unattended autonomy: at least one month
- Automatic sample conditioning with ISA buffer solution; automatic cleaning using distilled water
- Double standard addition method measurement capability, with automatic compensation for temperature, unknown compounds matrix effect and long term drifts using specific algorithm for sensor data processing and extraction
- Automatic built-in calibration procedure during the measurement
- Capability to perform fast change of solutions and CHEMFET electrodes and easy maintenance.

### 7.3 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.

### 7.4 Power supply and dimension requirements

- Low power supply: 12 Vdc, max 10 W during measurement, with sleeping mode capability
- Compact external dimensions: 55 x 35 x 11 (d x h x w) cm

### 7.5 Chemical compounds detected and measuring ranges

Table 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 <sub>3</sub> <sup>-</sup> )	6-6000	25 / 50	50
Ammonium (NH <sub>4</sub> <sup>+</sup> )	1.8-1800	0.05-2	0.5
pH	2-12 pH	6-9 pH	6.5-9.5 pH

One of the main aim of the final part of the project is to lower of a decade the minimum ranges of NO<sub>3</sub><sup>-</sup> (down to 0.6 mg/l) and NH<sub>4</sub><sup>+</sup> (down to 0.2 mg/l), in order to better fit with EC emission limits.

In order to have a better response on the NH<sub>4</sub><sup>+</sup> parameter, primary interference compound potassium (K<sup>+</sup>) and secondary interference compound sodium (Na<sup>+</sup>) are measured in the analyzer and used by the algorithm to have a better signal definition.

The same algorithm will allow the interference correction on NO<sub>3</sub> measurement for Cl<sup>-</sup> ion (primary interferent) and on NH<sub>4</sub><sup>+</sup> measurement for Ca<sup>2+</sup> ion (secondary interferent) as soon as these Chemfet sensors will be available.

## **8. - REFERENCES.**

LFA Test Unit User Manual (2003). Sewing Project Documentation. Version 1.0

Filipkowski A., et al. (2004) An innovative automated flow measuring probe for the measurement of chemical parameters in water based on CHEMFET sensors. AutoMONET conference, Vienna, Austria 2004.

Deliverable n.16 (design and partitioning of the system). Sewing Project Documentation.

Deliverable n.17 (functional prototypes of particular chips). Sewing Project Documentation.

SYSTEa Micromac-1000 Instrument Maintenance manual, ver.1.0

Memo on working meeting in SYSTEa and its outcomes, by Leszek J. Opalski (PW). Report of meeting done in Systea, Anagni (Italy) on 22-07-2004. Sewing Project Documentation.