III. CONCLUSIONS

1. Present situation and needs

1. 1. General remarks regarding all categories of water

The functioning of several existing types of monitoring equipment poses a problem. It results not only in a lack of reliability of the equipment itself but also in problems of fouling. This state of matters is likely to affect the development of the market.
There is need for a validation of sensors and analysers functioning under field conditions. For this, specific methodologies (procedures, test benches) are to be developed bringing together realistic conditions of evaluation and reproducibility of these conditions over a period of time.
The development of new equipment suffers from a problem relating to the cost of final stages which correspond to proportions of 1/10/100 respectively for research, development and industrialisation. These costs are all the more difficult to support when the market is limited and the development is carried out on national scales.
Toxicity monitoring poses specific problems particulary with respect to the interpretation of results.
The measurement step itself in not the only aspect to be considered, as sampling and the presentation of results are just as important. In each case it is necessary to start by answering a few questions. Why is there a need to measure? Where are the measurements to be obtained? What are the quantities to be measured? What time resolution is required? It is not necessary to measure all the relevant quantities in real time, but a selection must be made taking into consideration the time constant of the process or the phenomenon studied.
A wide gap exists between field research results of sensor technology and effective implementation by the end user. Several innovative prototypes have been developed on a laboratory scale to deal with traditionally measured quantities, however, only a small number of them reach the market.

This can result from :

- Inadequate communication between research workers and users. The use of a common vocabulary could be a starting point.
- A lack of confidence of the users in the effective functioning of samplers ans analysers.
- A gap between the required sensitivity and the level effectively achieved.

One should not strive to develop identical equipment for "small" and "big" users (size of the installation, technical levels).

It is necessary to rank the monitoring according to their status: those which are designed and developed, those which are validated and finally those which are commonly used in the field.

1. 2. Specific remarks applying to different categories of water

One may consider in general and to simplify matters two major types of water, taking into account similarities in needs and/or type of apparatus used:
Water that is (relatively) clean natural water, potable water, water for industrial use, certain types of water in industrial processes (e.g. cooling water).
Water that is highly polluted: urban or industrial wastewater, sewage sludge.
The identification and ranking of needs can be take place at the level of each of these two main categories:

Table 1 : Characterisation of clean water : The present situation concerning a certain number of species of major interest

Species	Laboratory analysis*	Field (**)	Remarks
Cl_2	+++	+++	Miniature sensors are needed for field measurements
O_3	Not applicable	+++	Air monitors currently markeded may be used although they are expensive
BrO_3^-	++	0	Difficult to measure in the lab though currently feasible
ClO_3^-	++	0	
NO_3^-	+++	++	uv-abs. measurements require very clean waters
HPO_4^{2}	+++	++	Titrator colorimetric units ; require absence of particles
NH_4^+	+++	+	Low level analysors (in-situ) do not work properly
Cr^{III}/CR^{VI}	++	0	Speciation will be essential in the near future, still needs laboratory development and instrument Maybe it will not be needed " in-situ "
VOC_S	+++	+	Electrical sensor arrays look promising ; it's possible to use SERS to monitoring individual chemical species, and not VOCS as a whole. Immunoassays are certainly possible, but still needed the proper antibodies. Promising by IMS.
Drug metabolities	+++	0	Immunosensors are possible, with targeted antibodies
Pesticides	+ (+)	+	" Strip " immunoassays for field analyses are available, with precision similar to that reached in the lab for certain pesticides ; immunosensors are promising
Desinfection by products (DBP_S)	+	(0)	They need still to be defined (organochlorides, chlorophenols, BrO3- etc.)
CO_2 Hardness	+++	++	May be necessary in certain areas where water is preconditionned ; already being measured in those areas

(*) Keys :
+++ : well developped
++ : need some " tuning "
+ : still in its infancy
0 : not available yet

(**) refers to both sensors and miniaturized total analysers systems

1. 3. Characterisation of waste water

Table 2 : The present situation concerning a certain number of species of major interest in urban waste water

Parameters	laboratory analysis*	Field (**)	Remarks
pH	+++	++	Need of ruggedness, autocleaning, auto-calibration
rH	+++	++	Need of automatic cleaning, prevention of electrode contamination
O2		+++	Need automatic cleaning and automatic calibration
H2S	++	+	In sewers, very harmful
TSS at inlet	0	+	Indirect measurement via turbidity, need automatic cleaning of detritus, grease
TSS at discharge	0	+	Need of cheap sensors with auto-cleaning, without maintenance
Settlability of sludge	+	+	Equipment derived from lab, too complex & costly
Siccity of sludge	+	0	Field test, not on-line instrument, IR or EM radiation absorb. Possible
Sludge blanket level	no applic.	++	Optical absorb. or U.S. reflection, need auto-cleaning and sensitively
NH4+	+++	++	Not yet in-situ (off line), too costly, too much maintenance
NO43-	+++	++	Not yet in-situ (off line, too costly, too much maintenance
Total nitrogen	++	+	Not really available, too complex, too costly
PO43-	+++	+	Only by colorimetry for analysers, too costly, much maintenance
Total phosphorus	0	+	Nedd to convert P to PO4 first, not really available on-line, not effective
COD	++	+	Derived from lab, national standard, not CEN not really available on-line, too costly
BOD	++	0	Analysers far from standard (5 days)
TOC	+++	+++	Too costly, too much maintenance
Biodegrada-bility	++	0	Concept to be clarified and standardised
Toxicity	++	++	Many test, very costly, high maintenance, difficult to interpret

Keys :

+++	:	well developed
++	:	need some " tuning "
+	:	still in infancy
0	:	not yet available
*	:	refers to automatic analyser system
**	:	refers to both sensors and miniaturised total analysers systems

The round table experts developed a double classification of priorities: at the level of fields of application and at the level of parameters to be monitored. They arrived at the following situation where " * " indicates priority for real-time monitoring.

Areas :

- environmental quality :
  - evolution/modelling
  - monitoring physical, chemical and biological processes (*)
- treatment process :
  - feed water alarm (*)
  - process control (*)
- distribution system and transport (control of quality degradation) :
  - drinking water (*)
  - industrial water (*)

The following parameters were considered as being important with respect to the above mentionned areas, where the " + " indicates the priority for improving methods or developing new techniques :

Parameters :

- Physical :
  - turbidity (+)
  - conductivity
  - temperature
  - pH
  - redox
  - particle number concentration (+)
- Global :
  - toxicity (+) (note : toxicity with respect to drinking water refer to : continous monitoring system of global water quality with respect to human health.
  - TOC (+)
  - BDOC (+)
  - humic acids
  - VOC (as a global parameter)
  - taste and odour
- Organic :
  - DBP's (+)
  - pesticides (+)
  - PAH's
  - pharmaceutical residues
  - vinylchloride
  - acrylamide
  - VOC (es specific compounds)
  - surfactants

- Inorganic :
  - sulphate
  - chloride
  - phosphate (+)
  - nitrate (+)
  - ammonium (+)
  - hardness
  - alkalinity
  - aluminium
  - heavy metals
  - speciation (i.e. Cr, As, Se) (+)
  - chlorine (free redidual) (+)
  - nitrite
  - lithium
  - ozone (+)
  - bromate (+)
  - lead
- Microbiological :
  - coliforms (fast method) (+)
  - giardia and cryptosporidium (sampling)

The COD is not standardised at the European level and there is a lack of relation between COD and alternative parameters such as total organic carbon (TOC).

COD, total suspended matter (as such, and not as evaluated by traditional measurement of turbidity), total nitrogen and total phosphorous are not accessible to continuous monitoring.

New concepts of measurement are necessary to determine COD, BOD and TOC - the techniques and methodologies developed must be correctly defined.

One does not have suitable concepts and parameters for the measurement of biodegradability in anaerobic media.

It is desirable to carry out intensive monitoring in industrial process circuits to control and prevent discharges.

2. Strategy for the application of advanced measurement technologies : improvement of existing techniques or development of alternative techniques?

After presenting a few of the advanced measurement techniques and highlighting their potential (refer to chapters III and IV), it is necessary to identify potential applications for meeting the needs expressed previously. This problem was evaluated differently for global parameters (description of behaviour) and for well defined and identified chemical species.

2. 1. Measurement of global parameters

General issues highlighted

- Complexity of global parameters / no " traceability audit trail "
- Appropriate selection of global parameters to fulfil user needs / due to complexity, rational choice of parameters difficult
- Fouling of devices (different for optical and electrochemical techniques)
- Need to relate multiple global parameter data to yield increased information - validated approach to global parameters selection using chemometrics
- Remote diagnostic / reporting state of " sensor health "

Specific issues of global parameters

- pH, Redox, conductivity : fouling
- Suspended particulate matter : Unclear relationship between turbidity and suspended particulate matter, standard turbidity methods do not fully exploit the technique
- Total Organic Load : requires clear definition BOD, COD etc only give an indication of TOC lack of suitable on-line methods
- Toxicity : must relate measurement result to specific needs, e.g. for waste or drinking water, alarm systems on-line measurements, low cost, sub-classes toxicity
- Odours : need to relate measurement to process control regulation / difficult to standardise
- Global parameters to be measured otherwise : BOD, COD, TOC
- Other Global parameters desired :
  - Total heavy metals
  - Nutrients
  - Halogenated compounds
  - Total hydrocarbons
  - Pathogens and microbiological contaminants on-line (time dependency of global parameters useful, e.g. BOD)

2. 2. Measurement of individual chemical species

6.2.1. A first point that was discussed concerned the choice between multiple component analysis and highly specific analysis. The strengthening of regulations will induce the need for a greater specificity. These two approaches are not mutually exclusive as shown in the three examples below :

Spectrometric analytical methods such as atomic absorption, plasma optical emission spectrometry or coupling of plasma torch and mass spectrometers can be installed on-line (subject to miniaturisation and adaptation of the technology).

Use of immunological techniques allows the rapid detection of specific families of pollutants (e.g.: PAH, PCB...) but not of individual species.

Chemometrics can be used for increasing specific information extracted from multiple measurements having a more global character (multiple component analysis).

In all the cases, fouling may be a crippling problem. There is then an urgent need for co-ordinated research regarding the prevention or solution of problems related to fouling for all different types of online monitoring and measurements.

6.2.2. A pre-separation integrated in the measurement system can improve the selectivity of the measurement and by this means its significance for the nature of sample. Pre-separation, however, can disturb the precision of the measurements. The possibilities for pre-separation are dependent on the nature of the water to be analysed and on the time of frequency at which the measurements have to be carried out : on line, discontinuous, instantaneous etc. In all cases, the most critical operations in the complete analytical method - i.e. sampling, pre-concentration, pre-separation - must be subjected to validation, which requires the development of corresponding procedures.

It is difficult to carry out measurements that strictly continuous and instantaneous but this is generally not necessary (except in the case of drinking water, concerning bromate and organochlorides)

The choice depends on the intended application and particularly on the dynamics of the process monitored.

6.2.3. With respect to validation, no notable work seems to exist. The validation procedures and criteria must be established for each case, depending on the working principle of the monitoring apparatus. Validation needs are expressed both at field and laboratory levels.

6.2.4. It is necessary to carry out pilot projects on a demonstration basis to convince end users of the advantages new techniques (sensors, miniaturized analysers) have for on-line monitoring. Resources are needed for conducting such long-term projects. Actions are underway for measuring dissolved oxygen. There are needs regarding other chemical species.

6.2.5. Highly specific techniques have been introduced, thet may be solution for the demand in-situ and/or on-line of field analyses of individual chemical species:

- miniturized ion mobility spectrometers (IMS), coupled to compact separation systems
- surface enhanced Raman scattering (SERS)
- laser diode atomic absorption spectrometer (LD-AAS)
- optical sensors (optodes).

Other techniques were also mentionned in the Workshop :

- electrochemical sensors and biosensors
- microbiological sensors
- biosensors.

2. 3. Application of data processing techniques

Because of their generic character, multivariate techniques may be applied to all measurement results with a special interest for the characterisation of water behavior (properties having a global character).

6.3.1. The situation is characterised by a large variety in the form of measurement data to be processed:

- specific sensors and sensor array (less specific), redundant sensors
- continous or discrete data ?
- constant sampling period ?
- heterogeneous data
- noise
- time series
- data without time reference
- data with superposed effects
- information given by the operators (qualitative ou semi-quantitative)
- minimal sensors and soft sensors

6.3.2. The techniques to be used are determined by the measurement objective and information to be obtained. Here are some of these:

- to monitor the process
- to detect changes in the process
- to follow the process evolution
- better understand the process
- to analyse sensor functioning

6.3.3. Depending on each case, responding to these objectives will face difficulties:

- global treatment is impossible
- local treatment is possible
- data continuity during the time
- data storage

6.3.4. For solving these problems, research efforts and in particular the transfer of knowledge and skills (applied mathematicmetrics) are necessary in the following fields:

- tools for data validation
- signal and image processing
- standardization of protocols
- system modeling
- design of sensor networks
- sensor modeling
- estimation of missing data
- maintenance and calibration of sensors
- release correct information to the operators

3. Towards an overall synthesis and immediate recommendations

The seminar allowed the updating of a list of needs in the field of monitoring the water quality that presently cannot be satisfied or only poorly satisfied and provided the state of the art (summary) regarding currently available means. These needs have been identified and ranked.
Several advanced measurement technologies of physico-chemical, chemical, biochemical, biological nature have been developed at the laboratory level and seem to have interesting potential :

- Several technologies were well covered and illustrated during the workshop:
  - Optics
  - Microbiology
  - Electrochemistry for VOC measurement in gas phase

- Because of lack of time, other technologies which were just as interesting could not be studied:
  - Electrochemical techniques in general (aqueous phase)
  - Separation techniques
  - Micro-electronics
  - Materials
  - Miniaturized analytical systems

4. Recommendations

4. 1. First recommendation

As a result of the above, it was agreed to pursue the objectifs identified during this workshop.

For this, it is proposed to carry out a study, a number of research topics, which should :

- provide additional details of needs (parameters to be measured, limits of detection necessary, degree of acceptable uncertainly etc.)
- have the objective of being more exhaustive, detailed and justified by quantitative and reference elements

This study must extend the scope and examination of possible contributions of advanced measurement technologies (notably those which were not examined in detail during the present workshop), basing itself on:

- all available scientific and technical literature
- research work conducted under specific European Union programmes (SMT, ENVIRONMENT AND CLIMATE, ESPRIT, BRITE EURAM, EC MAST) with the perspective of valorization of their results.

Finally, the study must include the following points :

- Analysis of limitations to transfer to real application, using selected examples on the basis of information given above.
- Recommendations for removal of limitations:
  - technological aspects
  - regulatory aspects
  - institutional aspects

4. 2. Second recommendation

The problem of validating on-line and in-situ monitoring systems for the quality of water appears to be a key element in the dissemination of new techniques. Faced with the lack of suitable validation methodologies and protocols, it is proposed to prepare a collective research project oriented towards the most delicate type of monitoring technique.
The title of this project could be: "Validation in real conditions of new water quality monitoring systems with biological respose and related physico-chemical measurements".

4. 3. Third recommendation

It is proposed the the definition of future research programmes should consider on a priority basis all the problems limiting the effective application of new measurement and monitoring technologies arising from research.
Priority must be given to more general problems (notably the fouling of measurement devices) and to research on generic solutions (instrumentation, data processing...) likely to be applied in all the fields related to the monitoring of water quality.

4. 4. Fourth recommendation

Participants of the Workshop expressed their wish to pursue their contacts in a formal or informal manner, favouring a pluridisciplinary approach and dialogue between researchers and users in Europe.