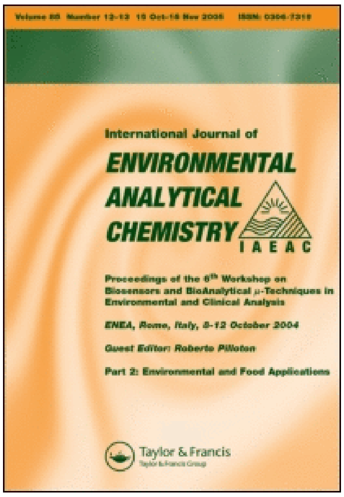

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Trends in Surface Water Analysis. Conclusions of the Workshop

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TRENDS IN SURFACE WATER ANALYSIS. CONCLUSIONS OF THE WORKSHOP

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The analysis of surface water for the determination of toxic elements and organic compounds is nowadays required in the frame of some EC Directives for the monitoring of the quality of the environment. The need for a good quality control of surface water analysis has led the Measurements and Testing Programme (BCR) to organize series of interlaboratory exercises over the last ten years. The projects included the preparation of certified reference materials for the improvement and quality assurance of these determinations. However, the control of the quality of critical analytical steps such as e.g. sample collection and storage has not been considered in classical interlaboratory studies. It was deemed necessary to critically examine the present state of the art of surface water analysis, to investigate where limitations exist and to discuss the trends that can be expected in a near future. The workshop on Trends in Surface Water Analysis held in Lisbon allowed to make recommendations based on round-table discussions. The participants in these discussions are listed in the Annex.

SAMPLING TECHNIQUES

It is of common sense that sampling strategies depend on the objectives of the analysis, the chemical nature of the target compounds and the type of water e.g. drinking water, surface water etc. Sampling techniques are more simpler for water containing low contents of suspended solids, e.g. drinking water.

As a general comment, two needs were identified which have broad implications:

- need for validation of sampling methodologies;
- need to involve the analysts in the sampling programme.

Inorganic analysis

For inorganic constituents, filtration is considered to be a critical point in sampling-related procedures. Some laboratories apply a filtration step for samples with a maximum amount of suspended matter of e.g. 100 mg/l; others filter systematically the samples. The use of filtering cartridges is a good procedure as it minimises risks of contamination, but the particulate fraction cannot be collected using this method. It is clear that the use of filtration is not systematic and depends on the aim of the study and the type of water. The lack of guidelines on sampling and filtration often hampers a good comparability of the analytical data obtained. The establishment of such guidelines including sampling strategy and procedures (collection and filtration, if required) was recommended.

The development of sampling devices for the collection of several samples at the same time and place (e.g. 4 identical sub-samples) is a trend which should be followed-up. The organisation of programmes for the evaluation of existing sampling devices (interlaboratory studies) and training was recommended.

Organic analysis

The selection of sampling procedures is often guided by information on the compound's persistence and their physical properties, the regulatory needs and the assessment of ecological impacts. At the moment the main demand for data is on the occurrence of specific compounds in "whole" water samples, i.e. the dissolved analyte together with compounds associated with suspended solids and colloid phase. The extent of the partition of the target compounds between the three components has important implication not only on the sampling strategy, but also on the sampling method, extraction and the clean-up steps. It was considered that research is needed to elucidate how the character of the sample affects the sampling strategy, the pre-treatment(s), e.g. filtration, and the implications for sample extraction, particularly when using solid-phase extraction.

Research related to the factors affecting sampling strategy should be undertaken particularly when sampling heterogeneous systems, i.e. those showing temporal and spatial variability. The use of a filtration procedure was discussed. Regulations require the analysis of the whole samples. However, physical properties of the contaminants should be considered which are related to their octanol/water coefficient (K_{ow}). For the study of fluxes, both the dissolved phase and the contaminants bound to suspended matter are of interest. For low K_{ow} values, the contaminants are mainly present in the dissolved phase; in this case filtration is recommended. For medium K_{ow} values, the compounds are partly bound to suspended matter, then the analysis of both the dissolved and particulate fractions is the best compromise. Finally, for high K_{ow} values, the compounds are mainly bound to the suspended matter; suspended matter can therefore be collected by centrifugation and analysed which will be sufficient for the contamination assessment. The strategy for the selection of filtration or non-filtration procedures is, however, hampered by the lack of information on the K_{ow} values for organic contaminants. Systematic studies are necessary to investigate the validity of this approach.

In some research areas, e.g. oceanographic studies, a need was identified to optimise the ratio of the volume of sample and the final volume of extract needed for the injection into the analytical equipment to achieve the desired sensitivity. Problems were noticed about the importance of interfering compounds in solvents after high sample concentration.

The development of on-line or "in-situ" methods incorporating sampling was also found necessary. Other trends could be the use of sensor devices adapted to the determination of particular compounds. These systems have to be developed and validated for a defined type of water as the response may vary from one matrix to another.

Biomonitoring may also be applied to supplement chemical data, e.g. bioaccumulation of lipophilic compounds in mussels. It was generally recognised that biomonitoring is not comparable with "time integrated sampling" simply because the uptake by organisms depends on many environmental factors and not only from the concentration of the compounds in the water.

STORAGE

Inorganic analysis

Currently used sample stabilization and storage techniques are acidification and storage at 4°C. Freezing leads to risks of irreversible precipitation of some elements/complexes.

Owing to the large number of procedures carried out in water analysis, several recommendations can be made:

- Guidelines on preservation/conservation procedures based on existing updated information should be produced; valuable information can be obtained from the procedures used for the storage of CRMs. The guidelines should include information on the type of containers and cleaning procedures (assessment of risks of losses by e.g. adsorption and contamination), preservatives to be added (under specified situations/parameters) and maximum storage time prior to the final determination;

- establishment of validation procedures for non-standard/routine situations;
- development of automated devices for integrated sampling and preservation;

One of the trends discussed in storage procedures was actually to avoid sampling and storage by developing miniaturized, automated procedures for on-line field measurements.

Organic analysis

For several families of organic contaminants no, or only scarce, information is available on the stability of the compounds in water and possible ways of their stabilization. For some families analytical knowledge is nearly entirely inexistant, e.g. surfactant/detergents (except CAS), water soluble polymers, hormones, brominated compounds, humic and fulvic acids. Knowledge is mainly limited to pesticides, phtalates, PCBs, PAHs etc.

Acidification of the water sample is a commonly used stabilisation procedure. Storage is generally done in clean glass bottles, rinsed prior to sampling. Transport is performed at low temperature. Acidification, however, destroys the colloidal phase; therefore, particular precautions are necessary when this phase is to be analysed.

Different ways of stabilising compounds were discussed. The trapping of organic compounds on adsorbants, e.g. C18 silica columns, is a procedure which is in rapid development for the concentration/stabilisation of unstable compounds. The selective trapping is possible with some substrates following some precautions, e.g.:

- for surface water a preliminary filtration or a cleaning pre–column has to be used to avoid clogging of the Solid Phase Extraction (SPE) column: disks are more user-friendly than columns (easier to dry and to transport);

- after trapping, the adsorbant has to be dried to stop chemical and microbiological activity;

- the validation of SPE should include the determination of the loading capacity of the column or disk;

- a careful control of possible contaminants from SPE substrates has to be performed;

it has been too often noticed that SPE systems are contaminated with organic compounds (e.g. pesticides, PCBs etc.)

Stabilization by freeze-drying is an attractive development but this procedure is difficult to apply in routine work as transportable freeze-drying systems hardly exist. This procedure is more adapted to the preparation of reference materials. Deep-freezing is not a recommended method as it may induce precipitation after defreezing.

For many compounds and families of compounds fundamental research on the stability/stabilization procedures is necessary for a proper validation of the analytical techniques. In addition, research is still necessary and should be promoted for the development of more selective SPE phases to be used in on-line determinations of organic compounds in water. The ideal situation to avoid risks of errors would be to determine the compounds in the field so that no transport, storage and stabilisation is necessary.

SAMPLE PRE-TREATMENT

Inorganic analysis

Further efforts are necessary to validate each step of the pre-treatment process, on-line pre-treatment techniques or in situ monitoring. Two main recommendations were given:

- Preparation of broad guidelines (not standards) on methodologies for sample treatment that are specific to particular matrices, e.g. open ocean, coastal, estuarine, river, drinking and waste waters.
- Further development of on-line pre-treatment procedures, e.g. on-line filtration and on-line digestion.

Organic analysis

Solid Phase Extraction (SPE): Research on the development of new selective phases for polar compounds and on desorption procedures should be promoted. Several optimization procedures exist and have been published on how to select a proper solid phase extraction (SPE) adsorbent. Selective extraction/separation of polar compounds should be developed further, especially specific phases to separate reliably the real dissolved fraction of polar compounds to be determined from the inorganic substances. A promising feature is the development of metal loaded columns able to chelate the polar compounds. SPE can easily be integrated in an automated system. The opinion was that for almost every analyte a suitable SPE material could be produced, e.g. chiral, immunological etc.

Supercritical Fluid Extraction (SFE): SFE using CO_2 as supercritical fluid was not considered to be a suitable extraction/clean-up system for water analysis for several reasons:

- the liquid matrix is not adapted to contacts with supercritical fluids;
- polar compounds are badly extracted by CO_2 with or without modifier;
- sample volumes handled in SFE systems are too limited in size.

Isotachophoresis (ITP): ITP is a promising technique for the sample treatment in the determination of charged compounds. Research is still necessary to investigate its full potential as compared to (non-satisfactory) ion-exchange columns. This procedure should be developed as a new clean-up system; it allows the addition of electrical properties of compounds to classical polarity/adsorption properties into the separation of polar compounds.

Automation: All new methods should be developed and optimized in view of their automation, i.e. fully automated methods or automation of individual steps. Automation should lead to more reproducibility with a higher through-put. Liquid-liquid systems such as flow injection devices should be investigated to automatise extraction and clean-up.

FINAL DETECTION

Inorganic analysis

Short-term and long-term trends in final detection techniques for inorganic determinations were identified, related to (i) within-laboratory methods and (ii) development of field measurements techniques.

Within-laboratory methods: A major trend in final detection techniques is the actual coupling of existing detectors with on-line pre-treatment procedures. In this field, flow injection procedures are most promising, enabling possible digestion and/or pre-concentration to be performed on-line with detection. Studies of matrix effects in ETAAS for the analysis of e.g. turbid waters, samples rich-in-organic matters etc should be undertaken. The development of new types of instrumentation should also be continued.

Finally, research should be strengthened for the validation and development of multi-element detectors (e.g. ICPMS, TRXRF, EDXRF).

Field-measurement techniques: The development of sensor technologies was considered to be very promising, e.g. flow-through sensors, biosensors. For the time being, laboratories developing sensors are rather focusing on electronics, clinical applications (i.e. determinations at high levels of concentrations) and are far from applications related to e.g. water analysis. It is, however, clear that sensor technologies could be developed for the determinations of a wide range of elements/compounds in different types of waters. These devices present the advantages to be cheap, easily transportable and reliable (possibility of internal calibration systems).

Another trend which has been identified was the necessary development of integrated, miniaturised, devices for field-measurements, i.e. including sample clean-up, digestion, pre-concentration and calibration facilities. In this aspect, electrochemical techniques would be a promising detection technique. The electrochemically-based devices are cheap and do not necessitate a high power; moreover, they can be applied to the analysis of different types of water for a wide range of elements and be successfully carried out in the field. There is a potential in the development of new electrodes enabling low detection limits to be reached. Further research is also necessary to investigate the limitations of these techniques (studies of matrix effects and ways to solve them).

Biomonitoring using living organisms and chemometric techniques were also considered as promising trends. In particular, there is a need of developing methodologies for the determination of "bioavailable" contaminants, i.e. elemental fractions which are linked to biological effects.

Organic analysis

Detection techniques important for organic analysis include LC with UV, FLUO, MS detectors, GC with ECD, FID, AAS, AED, FTIR, MS detection, CZE in different configurations, HRTLC. These techniques are in different stages of development, although for the more established methods still improvements can or need to be made. It was emphasized that method development or optimization should be approached in an open-minded manner. An example was given for GC-FTIR: a laboratory did not use an instrument because of background problems and "lack of sensitivity". For the particular application the problems could be overcome by bringing the instrument into the proper condition (reduction of leakages) and making use of modern large volume injection techniques. Too often the potentials of a technique or procedure are not used due to wrong pre-conceived notions or incomplete preparation. Training and education were mentioned as necessary tools to improve this situation.

With regard to the development of new methods and techniques, immuno-sensors constitute a field where rapid evolution takes place, although not all participants were satisfied with the present developments. Immuno-sensors and other rapid screening techniques provide at present insight in the concentration range which can be expected. This information may be sufficient for several objectives. The low costs of measurement may be attractive but there are risks that the procedures be used in an inappropriate manner. Nevertheless, their development desserves support.

Chemometrics was identified as an important area. It was emphasized that close collaboration between the "rather theoretical" chemometricians and experienced analytical chemists was essential in order to obtain products which are relevant for practical work. A role for chemometrics was seen in quantification when resolution is low, calibration procedures (e.g. number of calibration points taking the objective of measurement into account), and the development of optimization strategies for complex analytical procedures. The advent of new LC-GC-MS techniques was given as example for the latter: in such cases a large number of degrees of freedom is present, chemometrics may provide guidance to arrive at a good procedure in an efficient manner. Chemometrics may also contribute to the development of efficient screening techniques, e.g. some laboratories active in residue-analysis need to apply time-consuming two dimensional separation techniques in order to check whether a particular compound is present or not. In most cases (100:1) no residues are found. Chemometrics may aid in developing strategies in which rapid techniques can be used as a first check, which may be followed by a more detailed investigation triggered by a certain statistical evaluation. Finally, chemometrics may contribute in method development, specifically to find a match between the required performance characteristics of the method and the degree of sophistication thereof.

A need was identified for certified calibrants and calibrant solutions. Information on proper calibration procedures needs to be disseminated.

Sources of error in detection were discussed. The possible occurrence of interferences from non-detected substances was emphasized and studies should be undertaken to improve the analytical performances (e.g. checks with FID (GC-MS) or UV-DAD (LC-MS) prior to selective detection with MS). Also, here, education and training are needed. Mass spectrometry is an important technique in analytical chemistry. Experience from interlaboratory studies shows that most laboratories using mass spectrometry techniques perform rather poorly (e.g. MS versus ECD for PCBs, MS versus HPLC for PAHs). It was recommended to support research resulting in improved quantification with MS techniques.

APPENDIX

Participants at the Workshop round-table

On organic analysis

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E. Maier	M & T Programme, Brussels (N)
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P. Pestana	Instituto Hidrografico, Lisbon (P)
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P. Sztajnbok	Compagnie Générale des Eaux, Maisons-Lafitte (F)
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On inorganic analysis

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