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Reviews

Modern Trends in Monitoring and Analysis of Environmental Pollutants*

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Abstract

Both activities on quality improvement of the environment and a willingness to understand these processes are conditional on possessing reliable information that can be obtained from analytics and environmental monitoring. At present, analytics and environmental monitoring are among the most dynamically developing branches of chemical analysis.

The pursuit of getting the complex information on environmental quality leads to developing new methods and analytical techniques. Previous studies and own experience entitle to present the most important tendencies in the development of analytics and environmental monitoring. These trends can be classified into two basic groups:

- development of new methodical procedures,
- new achievements in construction of measuring instruments (instrumentation).

This paper presents the most important developments in both trends observed in chemical analysis.

Keywords: environmental pollution, analytics, monitoring, trends, methods, instrumentation

Introduction

According to a more and more common opinion, analytics and monitoring of environmental pollutants constitute the two pillars on which all of environmental science is based. Consequently, one can share the opinion of some specialists that there already exists a separate field of chemical analytics called *ecoanalytics.* However, we should be aware of the fact that neither analytics nor monitoring as such solve any problems concerning pollution or degradation of specific elements of the environment. They are only powerful tools which can provide information required for a reliable evaluation of the state of the environment and the changes taking place, as well as for making correct decisions for sozotechnical actions.

In general, the role and tasks of analytics and environmental monitoring can be summarized as in Fig. 1.

The above tasks can be accomplished through the application of a wide range of procedures, analytical techniques and instruments.

Monitoring should be considered as a specific branch of analytics where fully automated measuring devices are used. Requirements for this type of device are the following: **1. Methodical requirements:**

- high sensitivity of measurements,
- producing analytical information continuously in real time or with only negligible delay,

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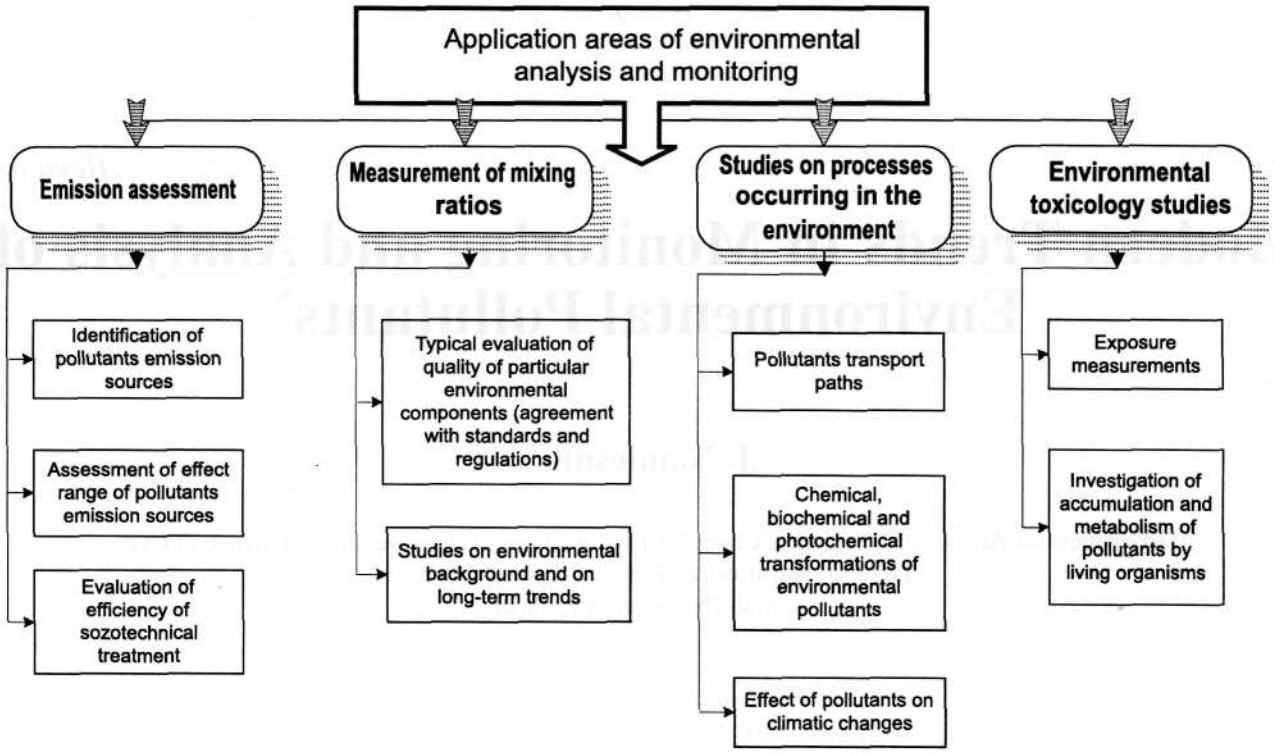

Fig. 1. Application areas of environmental analysis and monitoring.

- high resolution of results characterized by short re sponse time of the instruments,
- long time of autonomous operation.

2. Technical requirements:

- automatic zeroing and instrument calibration,
- protection against abrupt power failure,
- equipping instruments with:
  - independent power supply,
  - calibration module,
  - system for filling and refilling solution and reagents (electronic monitoring of liquid level),
  - system protecting flames from extinguishing (moni tors based on the use of FID and FPD detectors),
- possibility of automatic regeneration or exchange of filters.

The topic of this work is very wide-ranging and up to now only a few papers of this kind have been published. Please note the following:

- the first paper on basic developmental trends was pub lished in *"Chemia Analityczna"* in 1995 [1] and its shortened version [2];
- papers presenting some aspects of modern analytical chemistry [3] and its place in environmental manage ment [4];
- a treatise which is the widest known description of trends in monitoring and analysis of environmental pollution [5].

Classification of Trends in Monitoring Environmental Analytics

Environmental analytics and monitoring are the part of analytical chemistry which develops at the fastest rate. We can distinguish a spectrum of trends which can be classified into two basic groups:

1. methodological trends in environmental analytics and monitoring:

- dissemination of speciation analysis;
- use of total parameters to assess environmental pollu tion level;
- tendency to determine lower and lower analyte con centrations in samples of very complex matrix;
- search for methods applicable for determination of many analytes in the same sample during a single ana lytical process;
- introduction of solventless techniques to analytical practice;
- increase in significance of bioanalysis and biomonitor-ing;

2. trends in the area of instrumentation:

- new designs of sensors and detectors;
- introduction of coupled methods to analytical practice;
- computerization, automation and robotization of monitoring and measuring instruments;

Table 1. Varieties of speciation analytics

Lp.	Speciation analytics variety	Aim of speciation studies
1.	Physical speciation [9, 10]	Detection and determination of different physical forms of the same analyte
2.	Chemical speciation	Detection and determination of different chemical species containing a given element
	Screening speciation [11, 12]	Seeking for a specific analyte
	Distribution speciation	Determination of concentration of the same analyte in different parts of the material object
	Group speciation [13, 14]	Determination of total content of analytes belonging to a specific group
	Chiral speciation	Separation and determination of enantiomers
	Individual speciation [15]	Determination of all the species containing a given element

- use of expert systems;
- miniaturization of measuring systems (introduction of *"electronic nose"* and *"electronic tongue")* to analytical practice;
- design of passive devices and devices for conducting measurements *in situ,* including direct reading of analyte amount (concentration);
- development of remote control techniques for assess ment of environmental pollution;
- use of cine-camera techniques, photographic docu mentation and geographical information systems in as sessment quality.

I. Methodological Trends

1. Widespread use of speciation analytics

The question of what "speciation" means is often asked. The answer could be, as the IUPAC defines: "Speciation is the process-yielding evidence of the atomic or molecular form of an analyte". The term "speciation" can be used in its extended meaning [6]: binding forms of elements exactly definable or only operationally defined. Speciation analytics is the analytical activity of identifying and quantifying one or more chemical species or physical forms of an element present in a sample [7, 8].

A literature search allows one to distinguish some varieties of speciation analytics; the basic are presented in Table 1.

Chromatographic techniques, and especially the so-called hyphenated methods have become an ideal tool for speciation analytics due to their ability to separate even very complex mixtures into individual components [16, 17].

A more detailed description of different types of speciation analysis can be found in an article published in *"Trends in Analytical Chemistry"* [18].

2. Application of total parameters (summarical par ameters) to the evaluation of the degree of pollution in different parts of the environment

These parameters express the total content of a given element present in a sample in different chemical combinations and physical forms. Historically, the first total parameters used in analytics to determine the amount of organic matter in a sample being analyzed have been: Chemical Oxygen Demand *(COD)* and Biological Oxygen Demand *(BOD)* in liquid and solid samples, and Total Hydrocarbons *(TH)* in air samples. Recently, the best-known parameter which has found application in environmental analytics is Total Organic Carbon *(TOC).*

The importance of determining total organic carbon content *(TOC)* was already recognized in 1931. Since that time literature has brought many reports arguing for the necessity of determining TOC, DOC and POC.

The basic techniques for the determination of TOC in water have remained relatively unchanged for 25 years. Organic compounds are converted to CO_2 using combinations of techniques that may include: a chemical oxidizing agent, wet chemical oxidation (WCO method), ultraviolet irradiation (UV), high-temperature combustion, or high-temperature catalytic oxidation (HTCO method). CO_2 is then measured using nondispersive IR absorption, microcoulometry, conductometric techniques, or a flame ionization detector (after methanization of CO_2). Since many water samples contain inorganic forms of carbon (carbonate and bicarbonate ions), it is usually necessary to remove these species, typically using a gas stripping technique prior to measurement of TOC, or to directly measure total inorganic carbon (TIC) content of a sample as part of the TOC determination.

Present methods and techniques of determination of total parameters can be classified, taking into account the following:

1. Area of practical use
   - atmospheric air studies,
   - water and wastewater studies,
   - soil and sediment studies.
2. The parameter determined
   - total content of a given element in all pollutants pres ent in a sample,
   - content of a given element in a given group of pollu tants present in a sample.
3. Way of conducting chemical analysis
   - directly in a sample,
   - after analytes extraction (extract analysis).
4. Method of extraction of analytes from the sample studied.
5. Mineralization technique before final analysis
   - dry techniques based on catalytic oxidation at high temperature,

- wet oxidation at low temperature (with oxidant addition).

Taking into account the enormous number of chemical compounds that are potentially present in environmental samples, the determination of total parameters can constitute the first step of an analysis. In the next step, speciation analysis can be carried out by using suitable procedures to determine concentration levels of selected analytes or groups of analytes. Hence, the two analytical approaches are fully complementary.

3. Determination of increasingly lower concentrations (amounts) of analytes in samples with very complex matrices

Ecotoxicological considerations and the strive for an increasingly more accurate description of the state of the environment pose a great challenge to analytical chemists in terms of the necessity of determining still lower concentrations of various analytes in samples having complex and nonhomogeneous matrices. This task can be accomplished by one of two approaches:

- by using more sensitive and selective, or even speci fic detectors. This approach can be exemplified by the introduction of the photo-ionization detector (used in gas chromatography), which is more sensitive and more se lective than the flame-ionization detector (which has been commonly used in GC),
- by introducing to analytical procedures an addi tional step: isolation and/or enrichment of analytes prior to their final determination. This extra step facilitates removing the interference resulting from the components of a primary matrix (due to matrix simplification), but also, more importantly, it results in an increase in analyte concentration to a level above the detection limit of the method or the analytical instrument used. This approach makes possible routine determinations of analytes at the ppb level, or even determining analytes at concentration levels down to a fraction of ppq.

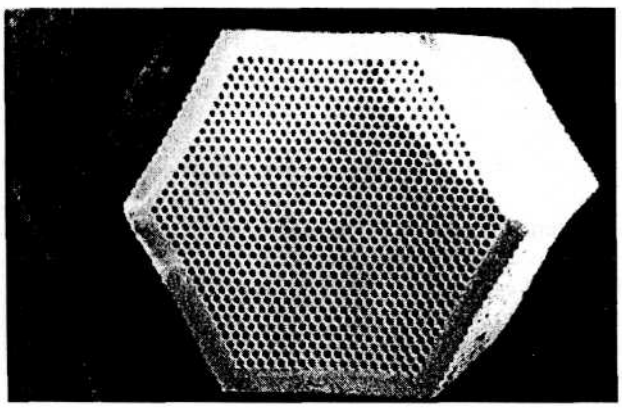

Fig. 2. Cross-section through a typical multicapillary column.

Table 2. Examples of biological material, analysed to get information on type and intensity of exposure to environmental pollution.

Biological material origin	Sample for analysis
Plants	Leaves (needles) Roots Fruit and seeds Branches and trunk (in the case of trees) Flowers
Animals	Osseous tissue Muscular tissue Eggs Fat Feather Hair Blood
Humans	Blood Urine Saliva Hair Cuticle cells Sperm Expiration air

4. Simultaneous determinations of many analytes using one sample and one analytical cycle

This trend in analytics and environmental monitoring is associated with the tendency to increase the information content of the results obtained by using a specific analytical procedure or instrument, and to streamline analytical procedures. An excellent example of this approach are high-efficiency capillary columns used in chromatography. The search for new columns with improved resolution continues in each fundamental type of chromatography (gas, liquid, supercritical fluid). In gas chromatography alone, the following new types of columns might be mentioned:

- Wall Coated Open Tubular - *WCOT,*
- Support Coated Open Tubular - *SCOT,*
- Porous Layer Open Tubular - *PLOT,*
- Graphite Layer Open Tubular - *GLOT,*
- Fused Silica Open Tubular - *FSOT,*
- Multicapillary (Polycapillary) Columns - *MC.*

It is unquestionable that the introduction of multicapillary columns started the revolution in the area of chromatographic separation techniques and was a new impulse to progress in fast chromatography. Short columns (even of less than 20 cm, and many up to 2400 microcolumns having an inner diameter of the order of 40 μm) are being applied. (Figure 2 presents a cross-section through a typical multicapillary column).

This permits us to shorten the time of analysis considerably when resolution is still preserved, since the height of the theoretical plate is very small.

Results from the plot representing van Deemter equation are in Figure 3. Using a multicapillary column a wide range of linear velocity of carrier gas with low values of HETP is obtained.

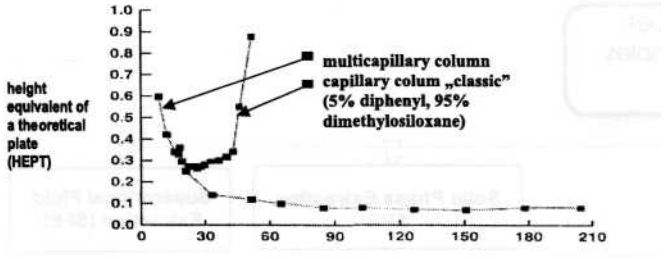

Fig. 3. Comparison of van Deemter plot for a multicapillary column and van Deemter plot for a capillary "classic" column.

The idea of using a bundle of small-diameter capillaries is quite old (1975) [21]. At its roots there was the goal of increasing the speed of separation by increasing the separation efficiency and thus introducing the possibility using shorter columns. The increase in efficiency can be achieved by a decrease in the inner diameter of the capillary while the reduced sample load should be compensated for by increasing the number of individual capillaries. Multicapillary columns offer a number of interesting features resulting from their production technology. In particular, the inhomogenities in the inner diameter of the individual columns has led to patenting [22] and commercialization of the multicapillary (polycapillary) columns [23].

It should be evident that in order to properly utilize the resolving power of chromatographic columns analytical procedures have to include a sample pretreatment step, as well as fractionation of sample components, prior to analysis.

5. Solventless techniques of sample preparation

Today special attention is paid in environmental analytics to such analytical procedures of sample preparation which ensure reduction of the amount of liquid solvents used or their complete elimination in the course of the analytical procedure, and also a decrease in the number of operations and processes utilized at the sample preparation stage.

In recent years, rapid development of the so-called solventless methods of sample preparation has taken place. The term "solventless method" refers to such a course of action which does not make necessary the use of liquid organic solvents. The classification of solventless methods of sample preparation is shown in Figure 4 [24].

In literature one can also find another scheme of classification of solventless (solvent-free) techniques of sample preparation for analysis [25].

Such a great rise in interest in this type of approach is the result of both ecotoxicological (dumping residual solvents, usually highly toxic, into the environment) and economic (necessity of using solvents of high purity, i.e. expensive and additional costs of recycling used solvents, e.g. through distillation, fractionation and purification) considerations. As can be concluded from Figure 4, four main classes of solventless methods may be distinguished:
- extraction of analytes from solid and liquid samples by means of a stream of gas;
- membrane extraction;
- solid phase extraction (SPE);
- supercritical fluid extraction (SFE).

The increasing popularity of these methods is not only due to their proecological character but also due to the fact that they provide the required sensitivity (up to ppt level). Furthermore, most of the. techniques can be automated and relatively easily connected with gas chromatograph.

6. Increase of application of bioanalytics and biomonitoring

The idea of using organisms, or communities of organisms, to register and evaluate certain characteristics of the environment is based on the ecological theorem of equilibrium between environmental factors and the requirements of the species, which can be traced back to the 16th century. At that time, certain forms of plant cover were already known to indicate the presence of ores in the ground while the composition of the vegetation was used to judge the fertility of the soil. With the beginning of the industrial era and the resulting increase in emissions, it became clear that organisms are not only capable of indicating the "natural" characteristics of a location, but also provide qualitative and quantitative information on changes in the environment brought about by man. As far back as 1866, Nylander drew conclusions on air pollution from the species composition of the lichens occurring naturally in Luxembourg. Since then, an immense amount of literature has been published on bacteria, fungi, plants, and animals, from both the aquatic and the terrestrial biotope, that provide information on the abiotic condition of their environment [26].

According to the literature data it is possible to classify organisms as follows:

1. Classification of organisms (or communities thereof) according to their "mode of reaction":

Accumulation indicators/monitors - Organisms that accumulate one or more elements and/or compounds from their environment.

Effect or impact indicators/monitors — Organisms that demonstrate specific or unspecific effects in response to exposure to a certain element or compound or a number of substances. Such effects may include changes in their morphological, histological or cellular structure, their metabolic-biochemical processes, their behaviour or their population structures.

2. Classification of organisms (or communities thereof) according to their "origin":

Active bioindicators/biomonitors - Organisms usually bred in laboratories that are examined for accumulation of elements or compounds and for specific or unspecific effects after exposure for a defined period in the area studied.

Passive bioindicators/biomonitors - Organisms that are taken from their natural biotope and analysed for accumulation of elements or compounds and for specific or unspecific effects.

In practice the following problems concerning bioanalytics and biomonitoring are discussed:

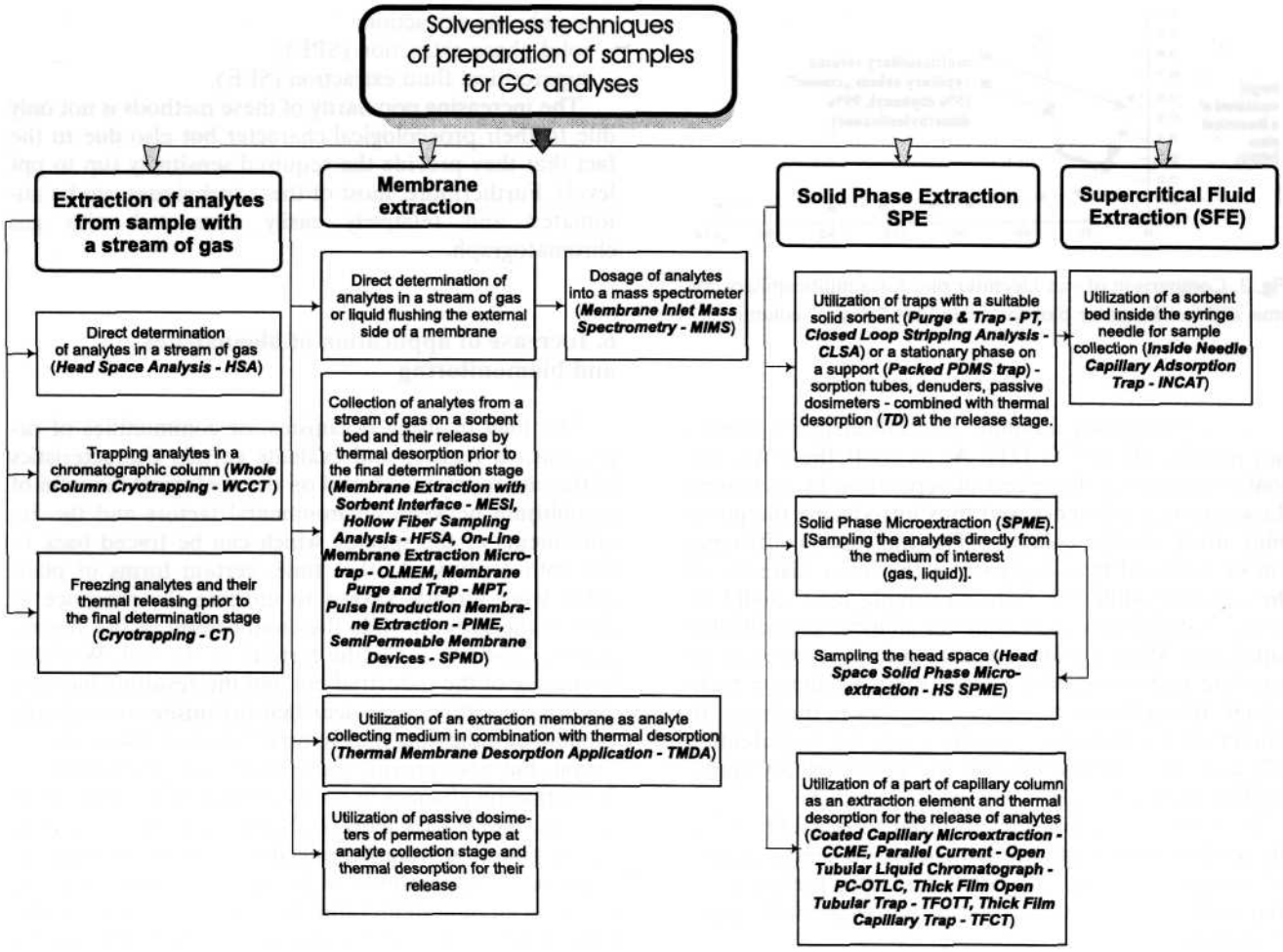

Fig. 4. General classification of solventless techniques.

1. The use of the results of chemical analysis of biota samples (so-called integrated samplers) to evaluate pol lution of the abiotic part of the environment (air, water, soil, sediment).

Biota analysis can be a source of information on effect of exposure to environmental pollutants and on changes inside a living organism, which can manifest themselves in different types of diseases.

The subject of interest of analysts can be biological material of plant, animal or human origin (Table 2).

2. Fauna and flora observation as a source of informa tion on the environmental state:

a) restrospective assessment
- analysis of diatoms,
- analysis of pollens,

b) Biological Early Warning System - BEWS.

The use of biological indicators to assess content of environmental pollutants and their effect on the environment are relatively wide. The criteria, which can be helpful when selecting living organisms as bioindicators, though proposed over 20 years ago, are still the same.

They are as follows:
- use of rather resident animals (to satisfy representativeness requirement with respect to the ecosystem studied);
- wide geographical occurence of species and their easy identification and sampling;
- possibility of collecting sufficient amount of material for studies;
- relatively high organism resistance to the pollutants studied (heavy metals, organic compounds);
- easy transfer and adaptation of organisms in new habi tats and easy transport to the laboratory;
- stability of population of a given species to ensure multiple sampling over a longer period (trends stu dies);
- reasonable correlation between pollution of a given en vironmental component (air, water, sediment, food);
- the same biomagnification factor (ratio of analyte con centration in an organism and in the environmental component studied) in different places (however, this requirement is not always satisfied due to a number of factors which can effect the pollutant accumulation process by a given organism);

c) prognostic assessment
- water booming,
- plant succession.

3. Immunoanalysis *(IMA)* and bioassays.

Many methods of trace components determination re-

quire the use of complex, laborious and time consuming techniques of sample preparation before final analysis.

For many years studies have been conducted on new methods which can be alternatives to those commonly applied, at least in the area of screening analysis.

Immunoanalysis is not a new approach since it has been used in clinical analysis for many years as a reliable, sensitive and selective method of determining low concentrations of organic compounds in blood, urine, tissue extracts, etc. [27].

History

1958 - the first paper dealing with an immunological test to detect pg amounts of human insulin in small-sized blood samples was published. For developing this technique R.S. Yalow was awarded a Nobel Prize in 1997 in the field of physiology and medicine. Later, that new technological revolution found a wide application in biochemistry, endocrinology and clinical analysis [28].

1971 - introduction of immunological techniques for environmental analytics [29].

1992 - introduction to laboratory practice of portable systems for *in situ* measurements with the use of immunological techniques [30]. Increasing popularity of immunological field tests mainly results from the fact that apparatus is easy to transport and requirements related to sample preparation are minimal [31].

1995 - development of the first commercially available immunochemical test (for pesticide detection) [32].

II. Instrumental Trends

1. New design of sensors and biosensors

Knowledge of the literature data leds to the conclusion that the most popular class of new sensors is biosensors. Due to their specificity, short response time, low cost, and portability, biosensors are becoming more popular in environmental analysis, especially of water samples [26].

A biological sensor (biosensor) is an analytical device, often miniaturised, in which a biologically active substance (biocatalyst, receptor), together with a suitable transducer is used for the detection of chemical substances in various samples. The biological component may either catalyse chemical reactions (enzymes, microorganisms) or specifically bind the analytes (antibodies or receptors). This component is responsible for selectivity, sensitivity, response time, and lifetime of the sensor. It is located on the surface of a transducer or close to the transducer. The role of the transducer is to change a biochemical or biophysical signal into an electrical signal proportional to the concentration (or amount) of the chemical or biochemical substance to which the biological element is sensitive. The signal is then amplified and converted into digital form by an electric circuit.

Figure 5 presents the principle of operation [33]. There is a special field of application for systems of chemical sensors: collecting of chemical signals from a plume (trace gases or smoke in air or water flow) [34]. The pollutant is carried by a plume in air or water flow,

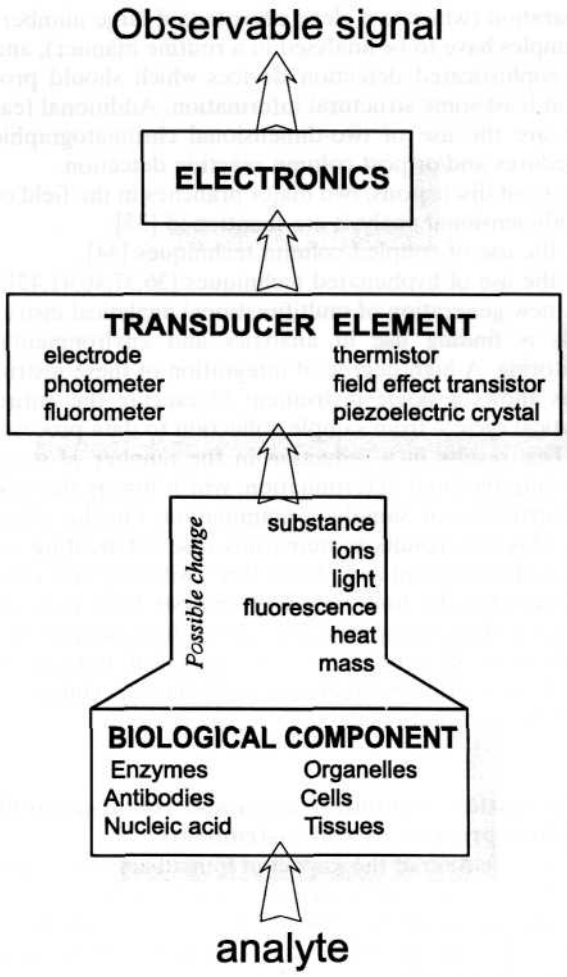

Fig. 5. Principle of operation of biosensor.

and its concentration fluctuates because of air or water turbulence. If we could see the shape of the plume or the fluctuating concentration of the pollutant we could place the inlet of the sampling tube inside the plume and control the suction timing synchronously with the fluctuation. Moreover, it is possible to trace the plume to its source and sample the pollutant most efficiently. Generally, the plume cannot be seen because an appropriate visual tracer is not available. Hence, knowing the plume shape and where and when to sample the pollutant is the dominating factor for efficient collection and reliable chemical analysis.

2. Introduction of multidimensional techniques into analytical practice.

In recent years, the use of multidimensional techniques has increasingly attracted attention as a means of solving many complex problems concerning detection, identification and quantification of microcontaminants at the trace and ultratrace level [35-43]. The complexity of the problems at hand generally requires the use of highly efficient separation techniques such as column liquid chromatography (LC) and/or capillary gas chromatography (GC), preferably combined on-line with sample

preparation (which is a clear advantage if large numbers of samples have to be analysed in a routine manner), and with sophisticated detection devices which should provide at least some structural information. Additional features are the use of two-dimensional chromatographic procedures and/or post column reaction detection.

In most discussions, two major branches in the field of multidimensional analysis are mentioned [35]:

- the use of coupled-column techniques [44],
- the use of hyphenated techniques [36,37,40,41,43].

A new generation of multifunctional analytical instruments is finding use in analytics and environmental monitoring. A high degree of integration of these instruments allows a single instrument to execute the entire analytical cycle - from sample collection to data processing. This results in a reduction in the number of steps preceding the final determination, which lowers the risk of analyte loss or sample contamination. On the other hand, this also results in numerous cases of treating an analytical instrument as a "black box", with negative consequences for the understanding analysts have of their operation. Such an approach leads to, for example, the introduction of samples into an analytical instrument without their prior pretreatment, with the expectation of obtaining a correct result.

3. Automation, computerisation and robotisation of analytical procedures and instruments.

The evaluation of the impact of human activity on the environment is one of the main goals of today's analytical chemistry. However, this evaluation can only be properly performed if the available data are highly precise and accurate. This can be achieved by:

- automation of procedures, techniques [45-48] and environmental laboratories [49].
- application of robots in the analytical laboratory [50-53].

4. Use of expert system [54-61].

Automated instruments have become essential components of modern laboratories. Unfortunately, however, unattended operation can result in delayed detection of instrument faults and improper sampling. In many cases when such faults occur, the instrument is unable to successfully analyse the current sample or the remaining samples in the batch. For example, an over-concentrated sample may contaminate the instrument and affect data collected from subsequent samples. Continuing to run an instrument after a fault has occurred can exacerbate the problem, create new problems and damage the instrument. For instance, continuing to inject samples into a gas chromatograph after the gas flow has been stopped will contaminate the injector and the column.

Ideally, the instrument should automatically assess the data and detect problems with sample preparation or instrument operation during or immediately after each sample is analysed. If a fault is detected, the instrument should stop processing and alert the operator. When no faults are detected, the instrument should pass the validated data to the automated data interpretation software and begin analysing the next sample in the batch. Potentially, some faults could be automatically corrected when detected. For example, if the assessment system determines that the most recently processed sample was too concentrated, the instrument could automatically process a series of blanks. More sophisticated error recovery may also be possible - an over-concentrated sample may be successfully reanalysed if the instrument will automatically direct an autosampler to inject a smaller sample volume, or to dilute the sample before reinjecting it. As laboratory automation capabilities improve, the range of faults that can be automatically repaired will increase. Although automated data assessment is certainly desirable it is difficult to implement. Currently, when the instrument malfunctions during analysis, or when the sample is not prepared properly, the chemist must detect the problem from the appearance of the data and use the data to diagnose the fault - a process that is often accomplished with trial-and-er-ror heuristics developed by experienced operators through years of problem solving. Automation of such heuristic, knowledge-intensive tasks can be accomplished using artificial intelligence (AI) techniques [62]. Artificial intelligence and, in particular, expert systems are playing an increasingly important role in providing a "built-in" intelligence in much modern analytical instrumentation. Some such instruments are even able to select the most suitable method available, schedule a work program, optimise the working conditions, and detect (in certain cases even repair) malfunctions. Expert systems (also known as "knowledge-based systems") attempt to model the human reasoning process. They permit a certain degree of computerisation of analytical expertise, thus providing a vehicle for maintaining and communicating this knowledge. A formal and complete definition of an expert system would be [60]: "the embodiment within a computer of knowledge-based component from an expert skill in such a way that the system can offer intelligent decisions about a processing function". Expert systems make judgements based on knowledge and selected arguments in an explainable and adaptable form. A rule-based approach permits dealing with some problems that could not be solved by conventional programming techniques. The introduction of the "rule-network" concept will be the basis for an expected sharp increase in the development and implementation of these knowledge-based systems.

Artificial neural networks (ANN's) are another tool for artificially encoding intelligence, typically in the realm of pattern recognition based on decision-making processes [62, 63]. The ANN technique takes its inspiration from our basic understanding of how biological brains work. The basic unit of all natural intelligence and processing is the neuron. Due to their manifold structure and their organisation in nets, biological neurons fullfil an unlimited number of tasks related to perception, recognition and learning. The human sensory system is able to recognise the environment much better than the most sophisticated machines and computers. Inspired by its capacities, lots of new methods have been developed using different architectures of neural networks. The use of natural principles seems to be suitable for a high fault tolerance treatment of complex non-linear, noisy, and waste data sets. Neural networks have proven to be

a powerful tool in numerous applications in the field of image processing and speech recognition, as well as problem solving and robotics.

The highest degree of development in the field of application of artificial intelligence (also in analytical chemistry) is the expert network [64-67], a hybrid of an expert system and an artificial neural network that has many advantages over the "traditional" expert system or neutral network AI techniques. Such expert network is able, for example, to automate the processes of validating routine GC data and diagnosing instrument malfunctions.

5. Miniaturisation of analytical instruments.

The search for faster and cheaper alternatives to laboratory-based analysis has been intense and throughout the 1980's chemical sensors were seen by many as the way forward [68]. This approach is attractive because measurements can be made quickly and easily. But sensors are designed to measure a specific analyte, do not always handle interference very well, and frequently contaminate quickly, so the potential originally envisaged for them has not been realised.

In recent years, researchers have looked for solutions which have the advantages of sensors but also the versatility and reliability of conventional instruments. At present the most promising technology for achieving this is carrying out chemical analysis on a very small scale by shrinking the standard laboratory techniques to fit on a "chemical chip". This process of miniaturisation has transformed electronics and computing and many see the potential for similar advances in chemical analysis. Miniaturisation is set to produce a generation of analytical instruments that will be similar, cheaper, more flexible and just as capable as the ones in use today, while vastly increasing speed. It has become one of the hot topics of analysis and with very good reason.

The lab-on-a chip concept is not new, and the idea of making miniature separation columns goes back to the late 1970's when S. Terry and co-workers at Stanford University demonstrated a working GC on a silicon wafer [69]. This pioneering device included a column, injector, valves and TDC and was able to separate a mixture of organics within ten seconds. Although the resolution obtained was relatively poor. The potential for improvement was clear and this paper has since become a landmark in the lab-on-a-chip world.

Even so, it was another decade before serious interest in microfabricated separation systems was revived, when A. Manz and co-workers at Ciba-Geigy laboratories (Switzerland) proposed the "miniaturised total analysis system" or μTAS as an alternative to chemical sensors for continuous monitoring [70]. To demonstrate how such systems could be built, Manz's group made capillary electrophoresis channels on glass chips and showed that separation of two fluorescent dyes could be achieved much more quickly than was possible using a standard system [71].

Capillary electrophoresis lends itself particularly well to microfabrication because no valves or pumps are needed to propel the sample through the column. With chromatography, on the other hand, the need for pumps and valves remains and this presents significant technical challenges. Although there are microfabricated pumps available, it is difficult to design a pump capable of generating the pressure needed to force a liquid through a very small channel. Producing a workable chromatograph on a chip will also require solutions to problems such as:

- making reproducable and stab', stationary phases for packed and open tubular columns,
- delivery of the pressure needed to pump fluids though the column at a constant flow rate,
- accurate and reproducable injection of sub-nanolitre volume,
- detection systems able to measure the very small quan tities of analytes,
- minimisation of dead volumes.

Work on miniaturised chromatography continues [72, 73].

In a recent development separation techniques have been successfully integrated into the concept of the so-called Total Chemical Analysis System - *TAS* [74-78]. The combination of all sample handling and measurement steps into a single package incorporating a high level of automation makes the TAS an ideal approach for continuous monitoring of different types of analytes. Total Chemical Analysis System μ -TAS) periodically transforms chemical information into electronic information. Sampling, sample transport, any necessary chemical reactions, separations and detection are all automatically performed. Much of sample pretreatment serves to eliminate most interfering chemical compounds; thus, the detector or sensor in a TAS does not need to be highly selective.

As an extension of this approach the concept of miniaturised Total Chemical Analysis System has been introduced [74, 75, 77, 78]. A miniaturised TAS would benefit from the fact that it could consist of several system elements, each designed to protect the subsequent element of the downstream system from components of the sample matrix. Compared with utilising a sensor alone, the use of such a TAS system should result in increased durability. At the same time, the performance required of any single component of the system could be less than that required of a sensor alone. Perhaps equally intriguing is the fact that to the user the system will seem very much like a stand-alone sensor, but its performance would be under the user's dynamic control. This would considerably improve the flexibility of a μ-TAS device, and should result in superior performance for chemical analysis relative to the stand-alone sensor approach. While such devices may not always be able to compete with benchtop scale laboratory equipment in terms of sensitivity and selectivity, integrated systems may prove superior in terms of speed of analysis and their cost of production.

The complete miniature modules aim at achieving the following goals [79]:

- total system size of the same order of magnitude as the transducer;
- enabling true on-chip referencing and multicomponent sensing by single-chip sensing-pad arrays;
- low complexity of the system;
- suitability for low-cost (mass) production;

- high ruggedness achieved by built-in-alignment of sen sor parts;
- standardized waveguides, sensing pads and schemes suitable for a wide variety of applications.

The development of the "electronic nose" [80-82] and the "electronic tongue" [83] was prompted by the desire to model, substitute and enhance human olfactory and tasting abilities. The design of these devices is based on biological principles of organisation of sensor systems - arrays of non-specific chemical sensors with subsequent image recognition by a neural network. Many modern achievements of neural computing are applied widely in sensor science for the "electronic nose" and "electronic tongue" systems. Thus, such systems can be considered as a specific branch of the development of artificial intelli gence and/or a field of the application of the "electronic brain".

The history of the "electronic nose" as an intelligent multisensor starts in 1982. The term itself became widely recognised around 1990. "Noses" usually provide a quantitative recognition of gas mixtures. The first mini-review on the applications of "electronic noses" was published recently [84].

The basic idea of the "electronic tongue" project has been the development of a new type of chemical sensors, poorly selective ones, displaying cross-sensitivity to multiple components in liquids, and their application as an array. The "electronic tongue" can be defined as an analytical instrument which includes an array of non-selective chemical sensors with partial specificity towards different solution components and an appropriate pattern recognition instrument capable of recognising quantitative and qualitative compositions of simple and complex solutions.

6. Design of devices for in-situ measurements.

Studies on emission reduction are frequently connected with *in-situ* measurements, e.g. in order to observe the changes in technological processes. It is desirable that instrumentation for such investigations should possess the following features [85]:

- mobility,
- the ability to determine simultaneously many compo nents,
- specificity in relation to particular chemical species with similar properties in composition to other compo nents of the matrix,
- the possibility of sampling in specified sites,
- usefulness of measuring analytes in a broad range of their concentrations,
- the possibility of obtaining data on sample composi tion; the following scientific equipment can be used:
  - satellites [86-88],
  - airplanes [89, 90],
  - helicopters [91],
  - cars,
- portable apparatus installed on special strechers [91] or transported by operating personal in specially designed handbags with mass from 5 to 20 kg [85, 91-93], or after placing them in portable housing [94],
- personal devices.

In such forms the following can be used: GC-MS sets with complete instrumentation for preparation of environmental samples (air, water, soil, sediments) for analysis [91, 92], equipment for capillary electrophoresis [93], analysers of toxic components of air based on FTIR technique [85], and relatively simple detectors with piezoelectric sensors [94].

7. Application of passive devices.

The use of passive samplers (dosimeters) is one of the modern approaches to the analysis of atmospheric air, indoor air and workplace atmosphere pollution. Recently such devices have become predominant in pollution monitoring. This is because they are simple in design and use, and are relatively cheap. They do not require any power supply and make possible simultaneous detection of vapours of many compounds.

Passive samplers are also often called diffusive samplers, having been defined as devices which are capable of taking samples of gas or vapour pollutants from the atmosphere, at a rate a controlled by a physical process such as diffusion through a static air layer or by permeation through a membrane, but which do not involve an active movement of air through the sampler. Compared with conventional pump samplers, passive samplers have the following advantages:

- neither power sources nor bulky and expensive pumps are required,
- more acceptable for wearing as personal dosimeters, and
- very simple to use.

Passive samplers, therefore, offer the most attractive alternative to the active sampling technique. Also, they have been widely used in the measurement of time-weighted average (TWA) exposure to airborne pollutants. The use of passive samplers to control workplace airborne health hazards can substantially reduce the cost of analyses. Modern passive devices correspond in size, weight and convenience to the well known radiation dosimeters. They are especially important to those health professionals (surgeons, dentists, nurses, and veterinarians) who use them for determining exposure to waste anaesthetics. Personal charcoal tube (CT) samplers which use battery-powered pumps require specially trained personnel in order to obtain valid results and do not fulfill the mobility and sterility requirements of operating rooms. These types of devices are often called active devices. Their main disadvantages and limitations of applicability are:

- relatively high unit cost;
- necessity of periodic replacement or repair of pumps (which usually have a relatively short service per iod/lifetime);
- sampling time limited by the batteries' lifetime;
- workers' reluctance towards wearing active units through the whole working day, due to their bulk, weight, and the noise generated by the pump.

Theoretical aspects of diffusive sampling, as well as

Table 3. Classification of passive dosimeters used in environmental studies.

No	Classifying parameter	Dosimeter type	Additional explanations
1.	Dosimeter use area	Area dosimeter	Used to sample analytes to determine medium quality (surface waters, atmospheric air, indoor air, workplace air);
		Personal dosimeter	Used to sample analytes to assess personal exposure.
2.	Type of analytical information	Dosimeter for long term sampling	Used to sample analytes to determine average analyte concentration in a long time (week, month);
		Dosimeter for short term sampling	Used to sample analytes to determine average weighted concentration during 8-hour workday.
3.	Phenomenon used to transport analytes to trapping medium in dosimeter	Diffusive dosimeter	Layer of stagnant air or porous membrane constitute diffusion barrier.
		Permeation dosimeter	Thin film made of semipermeable material is diffusion barrier.
4.	Dosimeter design	Tube dosimeter Badge dosimeter	Dosimeter design influences considerably possibility of automation stage of determination of analytes trapped in dosimeter during exposition.
5.	Type of trapping medium (trap packing)	Dosimeter with sorbent packing Dosimeter with absorption solution; Dosimeter with strip or filter impregnated with proper reagent.	
6.	Way of getting analytical information (concentration/ /amount of analyte)	Direct reading dosimeter	Such dosimeter give semiquantitative analytical information. Due to maintenance simplicity such dosimeters can find wide application;
		Indirect reading dosimeter	Concentration/amount of analytes is determined from change of: – mass, – colour; – electrolytic conductivity of medium inside dosimeter. Measurement is made in laboratory (after dosimeter exposition);
		Sorption dosimeter	Analytes are trapped in dosimeter as a result of adsorption, absorption or chemisorption. After exposition analytes are liberated in laboratory and quantitatively determined.

the state-of-the-art techniques involved, have been comprehensively reviewed [95, 96].

According to one approach, passive samplers can be classified into the different types presented in Table 3.

The field of practical application of passive samplers is continually expanding. During the last ten years new types of passive dosimeters have been designed to sample different types of contaminants from water. First extended review papers describing this aspect of application of passive samplers have been recently prepared [97, 98].

8. Expanding of spot tests.

In environmental analytics as well as in medical (hospital and out-patient) diagnostics there is a great need for fast methods of getting analytical information on material objects. That kind of information is one of the basic decision-making elements. Therefore, more and more papers are published concerning quick tests having the following characteristics:

- easy to use,
- not laborious,
- easily available,
- low unit cost,
- possibility of self measurement (by patients),
- possibility of use for different goals (drinking water, vegetables, fruit).

There is still a lot of ambiguity in the area of nomenclature related to quick tests. Different terms are used for the same things which can be a source of mistakes or misunderstandings.

Most often the terms "quick test" and "rapid test" describe a few types of tests characterised by the following common features:

- rapid measurements of parameter of interest (concen tration of analyte, pH, etc.),
- availability of a complete reagent set containing ma terials, vessels, possibly auxiliary equipment necessary to carry out analysis. These sets are called "kits",
- possibility of carrying out analysis outside the labora tory or field analysis.

Taking into account the principle of operation we can distinguish the three types of tests which found application in laboratory practice:

- *dry tests.* In this case the test is generally based on adsorptive material saturated with reagent mixture which ensures all the conditions necessary to detect and deter mine a compound or ion of interest. Such material is called testing field material, which can be in the form of bands of different length for single use or in a long rolled band whose pieces can be torn off for actual use. The testing field material can be fixed to supporting material, most often made out of white plastics (PS, PUC, polyes ter) giving a test strip. The dry test can be in a form appli cable to automatic reflectance reading unit, i.e. in the form of a slide in Kodak tests. Some tests can be in the form of plates with the testing field shielded with a plastic cover or tubes packed with a support-coated reagent.
- *semi-dry tests.* A semi-dry test is a test to which at least one liquid reagent is added. Such a design results most often from chemical reasons, though it happens that technological requirements are the cause. It should be added that outside construction of semi-dry tests the reagent area is in a housing which has some additional functions (mechanical protection, filter, transport pack age, etc).
- *wet tests.*

A comprehensive description of over 140 dry-tests used in medicine, biology and chemistry has been recently published [99].

Test methods have been developed for many analytes: metal ions, anions, dissolved oxygen and chlorine, hydrogen peroxide, ammonia, pesticides, nitrite, nitrate, PAH's, petroleum products (in water and solutions), as well as for sulphur dioxide, hydrogen sulphide, ozone and many other gases (e.g. in air). Short reviews on these test methods can be found in literature [100-102].

9. Remote sensing **techniques.**

The traditional use of the central laboratory for measurement of pollutants is too expensive and time consuming. Also, samples often undergo changes during their collection, handling, transportation and other delays, ultimately leading to unreliable results.

In situ measurements, in which the target pollutant is determined in its own environment, are preferable since they afford the option of rapid warning and proper feedback, while avoiding the errors, delays and costs connected with the collection of individual samples for subsequent laboratory-based analysis. New real-time analytical methods, capable of monitoring variations of priority pollutants in both time and location, are thus highly desirable.

The term "remote sensing" takes on a number of different meanings depending on the discipline involved. At present, the term is used most often for imaging objects near the Earth's surface by means of observation from airborne or satellite platforms. This section will concentrate (by a rather subjective selection of examples) on remote "chemical" sensing.

Lidar (light detection and ranging) is a pulsed laser system used like a radar system where the time of return of reflected light is measured and used to determine the distance to the cloud of reflecting material or solid reflecting target.

The literature on the subject contains some information on another remote measuring technique called *Sodar* (Sound detection and ranging) [103]. This acoustic sounder *(SODAR),* popularly called "acoustic radar", functions as an active sonar or a pulsed radar system. Highly directional short bursts of sound energy in the audio frequency range 1500 Hz to 10,000 Hz are emitted into the atmosphere. These waves get scattered along their propagation path by fluctuations in temperature, wind speed, and humidity, and are received either by the same antenna (monostatic or backscattering mode) or by another antenna (bistatic or forward scattering mode). The information carried by the waves is processed, stored and displayed on the facsimile chart. Useful qualitative and quantitative information about ground-based thermal activity, nocturnal inversions, and symmetric and asymmetric waves can be seen on the facsimile chart. Quantitative information about wind velocity and the wind zone (in the portion of air in which scattering occurs) at various heights in the atmospheric boundary layer can be computed on the basis of amplitude and frequency measurements of the received scattered signal.

10. Visualisation of exposure.

Conventional measurement techniques, such as sampling followed by analysis and direct-reading instruments, when used in isolation cannot record all the information needed for an occupational hygienist (for example) to make an accurate assessment of the situation. However, an exposure visualisation system [104-106] can help to resolve this problem. This technique combines the measurement of personal exposure with the simultaneous use of a video camera to record the work activity; the real-time exposure level being displayed as a bar graph on the video image. The key activities associated with high exposure can be readily identified from the video, which focuses attention on those areas where control or hygiene measures may be best applied in order to reduce exposure.

11. Application of GIS.

The continuous development of geographic information system (GIS) technology is increasing the demand for integrated environmental simulation models, more efficient data models, and expert systems. Advances in methodologies of data generation and access in the field of environmental monitoring including remote sensing, global positioning systems (GPS) and the Internet have been described in papers recently published [107, 108].

Final Remarks

We should realize that the discussion presented in this paper is to a large extent very subjective in terms of assigning significance to particular groups of analytical techniques and procedures. This is due to two reasons:

- a growing variety of analytical instruments and pro cedures used in analysis of environmental samples;
- different levels of confidence analysts have towards particular types of analytical methods.

Discussions and exchange of information among a wide range of specialists are necessary. The author hopes that the presented material will contribute to such a discussion.

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