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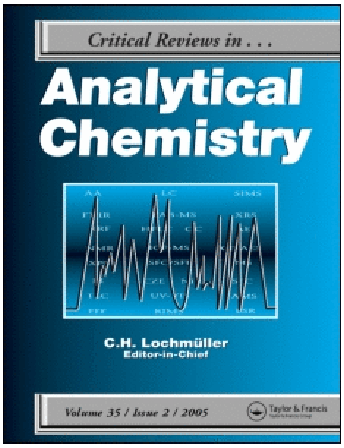

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Trends in Environmental Analytics and Monitoring

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ABSTRACT: On the basis of vast literature research, it can be concluded that analytics and, particularly, environmental monitoring, are those areas of analytical chemistry that are expending most rapidly. Monitoring is a branch of analytics which employs fully automated measuring devices that have a very long time of unattended operation and are capable of providing information about the investigated object in a continuous manner in real-time, or with only a slight time delay. It constitutes the two pillars on which the entire environmental science is based.

The tasks of analytics and environmental monitoring are discussed in this article. An examination of literature data leads to the conclusion that there is a number of trends in the area of application of various methods, techniques, and instrumentation to analytics and environmental monitoring. In general these trends fall into two different categories.:

- Development and practical application of new procedures,
- Novel designs of measuring devices and analytical instruments.

Trends of both categories are discussed below in a more detailed manner.

KEY WORDS: environmemtal analytics, monitoring, speciation, total parameters, biomonitoring, hyphenated techniques, remote sensing techniques, expert systems, miniaturization, passive dosimeters, *in situ* measurements, direct reading instruments.

I. INTRODUCTION

Literature on analytical chemistry uses the term **analytics** more and more frequently. This new term emphasizes the interdisciplinary character of methods of obtaining information about material systems, i.e., the methods exceeding the strict definition of **analytical chemistry**. Analytics, so far practiced mostly as analytical chemistry, and to a large extent identified with the work of chemists, has developed recently becoming a scientific discipline in its own right, whose role far exceeds chemistry and covers almost all branches of science and technology. Hence, analytics has become an interdisciplinary science. This interdisciplinary nature is revealed through a variety of phenomena utilized at the measurement stage. Analytics is a scientific discipline that embraces:

- Various areas of chemistry (particularly physical chemistry and biochemistry)
- Physics
- Computer science
- Electronics, automation and robotics
- Instrumentation
- Chemometrics

Analytics can be subdivided in terms of:

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- Kind of instrumentation (including its level of sophistication) used for acquiring analytical information about the investigated object
- Area of practical application of analytics that would consider type of the sample as well as the kind of analytes and their respective concentration levels

Classification of the main branches of analytics is shown in Figure 1.

Monitoring should be considered as a specific branch of analytics where fully automated measuring devices are used. These devices might possess some specific features:

- High sensitivity of measurements
- Delivery of analytical information about the investigated object in a continuous manner in real time or with only slight time delay
- High resolution of results characterized by a short response time
- Long period of unsupervised operation

Next, monitoring poses several requirements concerning:

- Instrument zeroing and calibration
- Protecting the instrument functioning against power surges
- Providing the instrument with an independent power supply
- Automatic filling up with solution and reagents (electrochemical monitors)
- Installation of devices preventing flame extinguishing (in certain detectors, e.g., FID and FPD)
- Exchange and regeneration of spent filters

II. APPLICATION OF ANALYTICS TO THE EVALUATION OF THE STATE OF ENVIRONMENT

On the basis of extensive literature research, it can be concluded that analytics and, particularly, environmental monitoring, are those areas of analytical chemistry that are expanding most rapidly. The first review on trends in environmental analytics was published in 1995.[1] The last decade should be considered a period of rapid development of this branch of analytics. New trends and interesting methodological and instrumental solutions have been proposed. It is the main reason why a new articlefocused on the same subject can be useful.

According to a more and more common opinion, analytics and monitoring of environmental pollutants constitute the two pillars on which the entire environmental science is based. Consequently, one can share the opinion of some specialists that there exists already a separate field of chemical analytics named **eco-analytics**. 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 that can provide information required for a reliable evaluation of the state of 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 follows:

- Standard quality assessment of individual elements of the environment (conformity to standards and regulations),
- Identification of sources of pollution and determination of emission as well as estimation of the extent of their influence on the environment
- Evaluation of phenomena and processes taking place in the atmosphere, in the water, and in the soil (transport and deposition of pollutants; chemical, biochemical, and photochemical conversions that pollutants undergo in individual elements of the environment)
- Elucidation of the ways of transfer of pollutants. Examination of the effect of pollutants on climatic changes

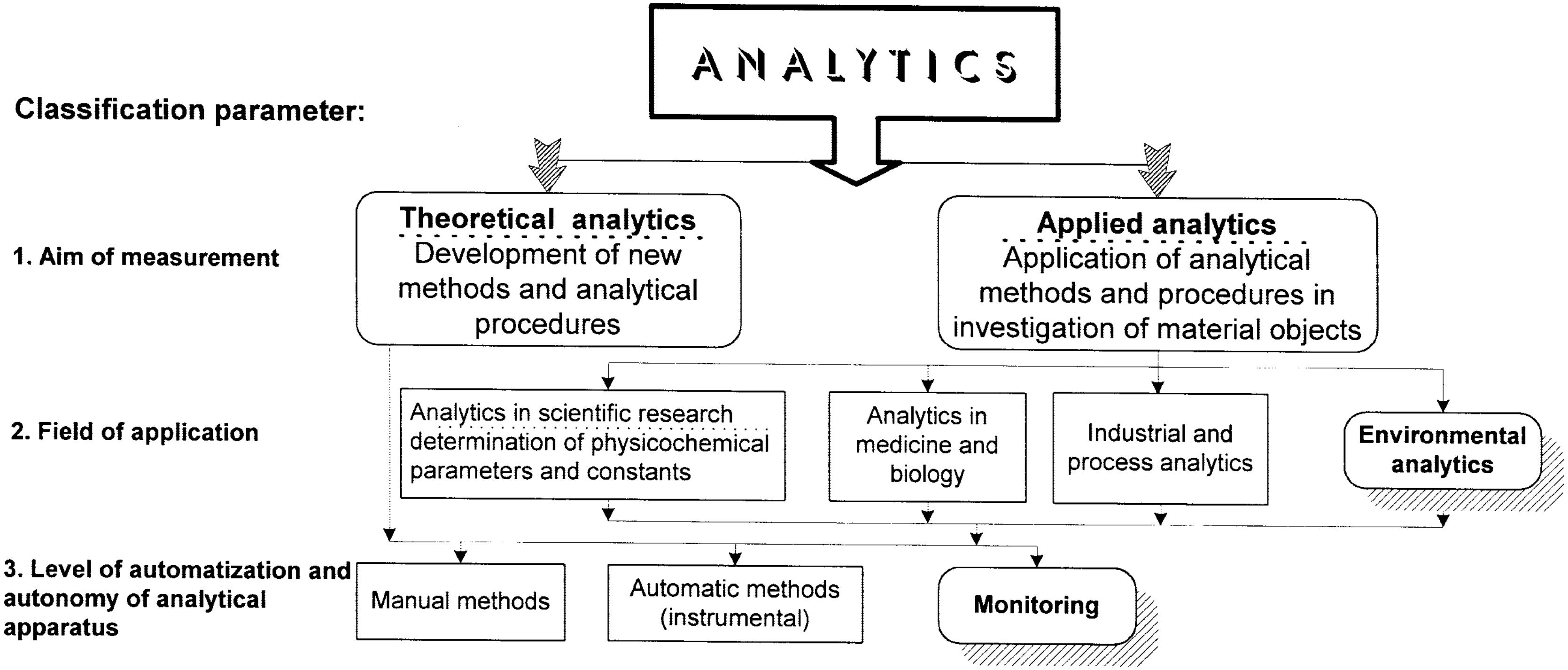

FIGURE 1. Classification of the main branches of analytics.

- Determination of the effect of pollutants on the environment and on human health (monitoring combined with, e.g., epidemiological or ecotoxicological studies)
- Investigation of the background and trends

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

Classification of analytical methods used in environmental studies is presented in Figure 2.

III. TRENDS IN ANALYTICS AND ENVIRONMENTAL MONITORING

A thorough examination of scientific literature leads to the conclusion that there is a number of trends in the area of application of various methods, techniques, and instrumentation to analytics and environmental monitoring. In general, these trends fall into two different categories:

- Development and practical application of new procedures,
- Novel design of measuring devices and analytical instruments used for:
  - Collection and pretreatment of environmental samples
  - Isolation and/or enrichment of analytes prior to their final determination
  - Calibration of measuring devices being used
  - Separation, detection, identification and quantitative determination of analytes
  - Statistical evaluation of the analytical data obtained.

Based on the common opinion, expressed not only by analytical chemists, it would be easy to conclude that trends in analytics and monitoring are generally related to the tendency to determine an increasing number of

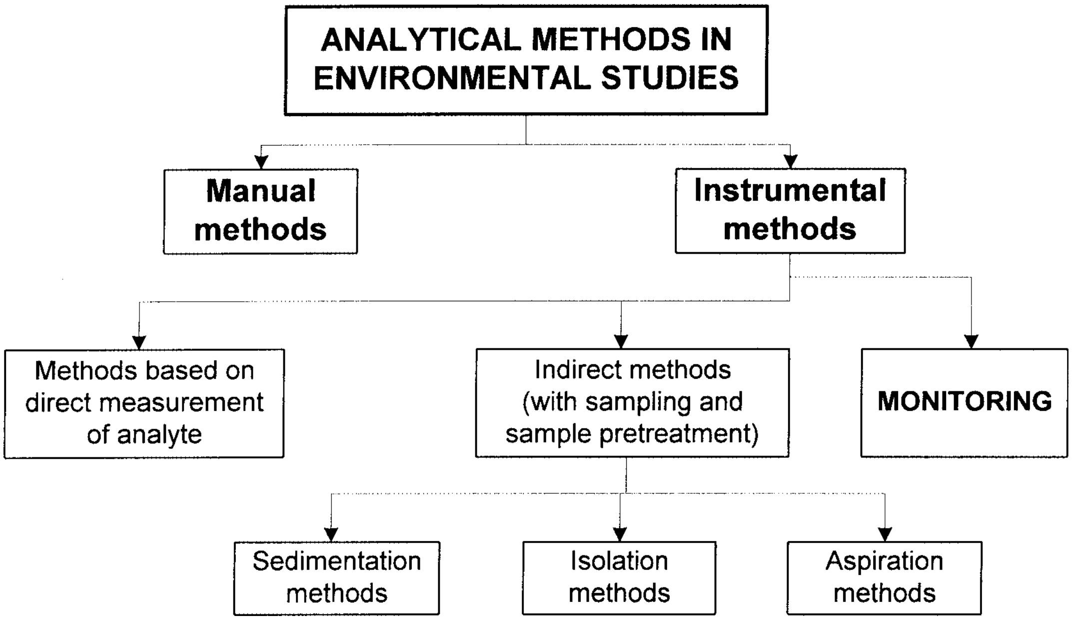

FIGURE 2. Classification of the main types of analytical methods used in environmental studies.

analytes at still lower concentration levels.[2] Naturally, this opinion is correct, although for a professional it is decidedly too limited. Deeper analysis supported by literature leads to a conclusion that there are still more trends in analytics and environmental monitoring.[3]

The fundamental procedural and instrumental trends in analytics and environmental monitoring aree discussed below.

A. Procedural 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:[4] 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.[5,6]

As an example, the chemical species that have been considered important for mercury in biological and environmental samples are listed in Table 1.[7]

Generally speciation analytics plays a very important role in:[8]

- Studies of geochemical cycles of elements and chemical compounds
- Determination of toxicity and ecotoxicity of selected compounds
- Quality control of food products
- Research on the impact of technological installations on the environment
- Examination of occupational exposure
- Control of medicines and pharmaceutical products
- Clinical analysis

In the past, most chemical analyses sought to determine the total content of specific elements. For species analysis, therefore, the classic analytical process must be revised in its entirety. Speciation requires new analytical strategies for the determination of bonding and a new philosophy of quality management in determination.[9] A combination of separation techniques and selective detection systems is typically required for this kind of analysis. Unfortunately, the use of such techniques frequently leads to alterations in the original sample composition due to disturbances in the chemical equilibria, as well as losses and/or contamination during the aforementioned processes. However, sampling itself, as well as sample processing, handling, and storage all

TABLE 1
Major Mercury Species in Environmental and Biological Samples

Elemental mercury		Hg^0
Inorganic mercury species	Mercuric ion	Hg^{+2}
	Mercurous ion	Hg^+
	Mercury sulphide	HgS
Organic mercury species	Methyl mercury	CH_3Hg^+
	Ethyl mercury	$C_2H_5Hg^+$
	Phenyl mercury	$C_6H_5Hg^+$
	Dimethyl mercury	$(CH_3)_2Hg$

influence the original species pattern, resulting in the loss of original species information. In this case, no analytical procedure, no matter how sophisticated, will be successful in reflecting the initial situation. Samples cannot be stabilized by preservatives. Some techniques of sample preparation (ashing, mineralization, combustion) preclude speciation analysis. Care must be taken to ensure that bioactivity in samples does not affect speciation.

Attempts at environment or health protection can yield only dubious results, if any, if they are based on suspicious data. Therefore, a rigid quality control program is required for speciation analysis.[9] Species alterations have to be avoided or minimized. Information on the degree of possible changes of species must be elucidated.

A literature search allows one to distinguish some types of speciation analytics:

- **Physical speciation**[10,11]—takes place when different forms of the same chemical species have to be determined in a sample. Examples include adsorbed forms, dissolved forms, complexed forms, etc.
- **Chemical speciation**—it is possible to distinguish four types of chemical speciation analytics:
  - **Screening speciation**[12,13]—leads to the detection and determination of one definite analyte, for example due to its especially high environmental toxicity
  - **Group speciation**[9,14]—in this case, analysis leads to the determination of the concentration level of a specific group of compounds, or elements existing in different compounds at a specific oxidation level, and their physical forms. (For example, determination of all species of chromium having the same oxidation number—Cr III or Cr VI.There are significant differences between the forms of chromium as far as their toxicity with regards to living organisms is concerned. Cr VI is from 100 to 1000 times more toxic than Cr III, which in small quantities is indispensable for an organism to develop and function properly.)
  - **Distribution speciation**—takes place when the same chemical species need to be determined in different compartments of the material object under investigation (for example, determination of heavy metals in different parts of the plant)
  - **Individual speciation**[15]—it is the most difficult type of speciation analytics and involves the broadest range of analytical work. Its task is to separate, detect, determine and identify all species of an element in a sample

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]

2. Application of Total Parameters (Summarical Parameters) 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. There are two major reasons for determining the organic carbon content in waters:[18]

- TOC value makes possible an evaluation of the level of pollution and the extent of biological degradation of surface waters and waste waters
- It is very useful for evaluating the results of water treatment.

Traditional methods of measuring the total content of organic compounds such as COD and BOD have a number of drawbacks. The determination of BOD involves measuring the amount of dissolved oxygen that is consumed in the process of oxidation of organic pollutants present in sample for a certain period of time. The reproducibility of the determination is questionable, and its sensitivity is not high enough to detect small changes. Determination of the COD requires expensive and toxic reagents, and the measurement includes inorganic compounds that may give inaccurate results as far as impurities with strong refractory properties and resistance to biological degradation are concerned.

The measurement of TOC content in water is widely used to assess the level of contamination by organic compounds in a variety of water samples ranging from ultra-high purity waters in power generation, pharmaceutics, and the electronics industry, to industrial and municipal wastewaters. Typical TOC concentrations can range from less than 1 μg of carbon per liter (less than 1 ppb), for high-purity water, to more than 1000 mg of carbon per liter (greater than 1000 ppm) for some wastewaters.

The measurement of TOC in high-purity waters is of particular importance. The presence of even ppb levels of organic compounds in the high-purity waters used in the electronics industry can cause problems in the manufacturing process. These problems include uneven deposition and oxide growth, defects in the photoresist layer due to poor adhesion, and altered electrical properties such as lower breakdown voltages and high leakage currents. In the power industry, organic compounds in water contribute to corrosion, while trace organic contaminations, particularly endotoxins, are a major concern in high-purity waters used in the pharmaceutical industry.

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). Because 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.

A full classification of nomenclature of total parameters used to evaluate the degree of water and waste water pollution is shown in Table 2. The table uses parameters associated with the determination of carbon content as an example.[19]

A similar classification of total parameters can also be done for other elements present in an analyzed sample.

Taking into account the enormous number of chemical compounds that can be potentially present in environmental samples, the determination of total parameters can constitute the first step of an analysis. In the next

TABLE 2
Nomenclature of Total Parameters of the Degree of Water Pollution, with Carbon as an Example[20]

Criterion	Names of parameters		
Type of chemical combination	Total Organic Carbon (TOC)	Total Inorganic Carbon $\left(CO_{2-}^{2}, HCO_{3-}, CO_{2\,\mathrm{solv}}\right)$ (TIC)	Total Carbon (TC) TC = TOC + TIC
Form of occurrence of chemical compounds	Dissolved Organic Carbon (DOC)	Suspended Organic Carbon (SOC)	Total Organic Carbon TOC = DOC + SOC
Volatility of organic compounds	Volatile Organic Carbon (VOC)	Non-Volatile Organic Carbon (NVOC)	Dissolved Organic Carbon DOC = VOC + NVOC
Method of isolation of organic compounds from water			
Solvent extraction	Extractable Organic Carbon (EOC)	Non-Extractable Organic Carbon (NEOC)	Dissolved Organic Carbon DOC = EOC + NEOC
Adsorption on a sorbent	Adsorbable Organic Carbon (AOC)	Non-Adsorbable Organic Carbon (NAOC)	Dissolved Organic Carbon DOC = AOC + NAOC
Extraction with a stream \ of gas	Purgeable Organic Carbon (POC	Non-Purgeable Organic Carbon (NPOC))	Dissolved Organic Carbon DOC = POC + NPOC

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 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. The task can be accomplished by one of the two approaches:

- By using more sensitive and selective, or even specific detectors. This approach can be exemplified by the introduction of the photoionization detector (used in gas chromatography), which is more sensitive and more selective than the flame-ionization detector that has been commonly used in GC
- By introducing to analytical procedures an additional 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.

Sample pretreatment may serve the following goals:[20]

- To raise the concentration of analyte(s) up to a level that can be measured by the selected analytical method
- To transfer the analytes to a (organic) solvent or to a stream of gas that can be handled more easily by the analytical instrument
- To improve the detectability or analytical performance of the analyte

The first two goals can be reached by extraction procedures, in which the analytes are transferred from their natural matrix to a solvent (gas, liquid, supercritical fluid) and the third is taken care of by chemical derivatization like, e.g., methylation of organic acids prior to GC analysis.

The tendency to analyze still lower concentrations in samples of very complex and often nonhomogenous matrix can be related to determination of materials purity. Purity is usually expressed by the number of decimal places; a material designated 5 N has a purity 99.999%. Until now, the purest material obtained by man is germanium (Ge) having purity better than 11 N, which means that the total content of all contaminants is lower than 0.01 ppb.

At the present, special attention is paid in environmental analytics to such analytical procedures of sample preparation that ensure:

- Reduction or complete elimination of the use of liquid solvents in the analytical procedure
- 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 took place. The term “solventless method” refers to such a course of action that does not make necessary the use of liquid solvents.[21-23] 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 of used solvents, e.g., through distillation and purification) considerations. The main classes of solventless methods are the following:[22,24]

- Extraction of analytes from various matrices by means of a stream of gas
- Membrane extraction
- Solid phase extraction coupled with thermal desorption
- Supercritical fluid extraction

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:

- Biocolumns
- **W**all **C**oated **O**pen **T**ubular—WCOT
- **S**upport **C**oated **O**pen **T**ubular—SCOT

- **P**orous **L**ayer **O**pen **T**ubular—PLOT
- **F**used **S**ilica **O**pen **T**ubular—FSOT
- **M**ulticapillary **C**olumns—MC
- **M**icroengineered **O**pen **T**ubuler—MOT (with rectangular cross section[25])

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 proper.

5. Bioanalytics and Biomonitoring

Modern analytical techniques allow the acquisition of reliable results that provide the information necessary for proper evaluation of the degree of pollution in different parts of the environment, such as air, water, or soil. However, the use of such techniques is often time and labor consuming, expensive, and it requires highly qualified personnel. Furthermore, many of these techniques can only be used in the laboratory. There is a growing need in everyday analytical practice for rapid and more specific methods, which would allow field measurements (*in situ*) in the on-line mode. Such a need is met by the analytical techniques utilizing biological material, e.g., living organisms or living matter (biota), as an integral element of the process of gaining analytical information. Such methods, due to the biological principle of operation, are often specific, which makes it possible to avoid the sample preparation step. In addition, the biological principle of operation makes them suitable for applications related to human health and safety. Devices using biological elements can be made portable, which makes them less expensive when compared with stationary devices. For these reasons, biological methods enjoy an ever-growing popularity both in monitoring and in analysis of environmental pollution. This tendency is sufficiently evident to be considered one of the significant trends of modern analysis.

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 the 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]

Almost as great as the variety of organisms said to have bioindicative properties is the variety of definitions of the technical terms in use. The rapid development of this field of biological science, especially in the last few years, has resulted in an extremely ambiguous use of the nomenclature. Many terms are not yet unequivocally and uniformly defined, or properly distinguishable from each other; usage differs from one country to another, and also within the international literature. Let's consider, for example, the meaning of the term "bioindicator" and how it can be distinguished from the term "biomonitor".

- **Bioindicators**—Organisms or communities of organisms whose content of certain elements or compounds and/or whose morphological, histological or cellular structure,

metabolic-biochemical processes, behavior or population structure(s), including changes in these parameters, supply information on the quality of the environment or the nature of environmental changes.
- **Biomonitors**—Organisms or communities of organisms whose content of certain elements or compounds and/or whose morphological, histological, or cellular structure, metabolic-biochemical processes, behavior or population structure(s), including changes in these parameters, supply information on the quantitative aspects of the quality of the environment or changes in the environment.

Thus, both boindicators and biomonitors may be considered as organisms or communities of organisms that react to changes in environmental conditions with a change in their "signs of activity". These changes may manifest themselves:

- In element concentrations or levels of certain compounds
- In morphological structures from the cellular to the organological or habitus level
- In the course of intracellular and intercellular biochemical processes
- In the pattern of innate or acquired behavior
- In the structure or dynamics of the population, or community, of organisms

The difference between bioindicators and biomonitors lies in the information they supply. While bioindicators only provide information on the quality of the environment or its changes, the "reactions" of biomonitors make it possible to determine the quantity of the environmental pollutants or its changes.

Considerable differences in definitions have also emerged depending on the field of research (e.g., microbiology, mycology, botany, zoology, physiology, morphology) in which the "systems" with bioindicative properties originated. On the basis of present knowledge of ability of organisms to indicate pollution, especially in the case of bioindication of metals, the definition may contribute to reaching agreement on standard nomenclature at the interdisciplinary and international level.

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

a. 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 behavior, or their population structures.

b. 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 analyzed for accumulation of elements or compounds and for specific or unspecific effects.

When studying accumulation processes, it would seem useful to distinguish between the different means by which organisms take up elements/compounds. Various mechanisms contribute to the overall accumulation (bioaccumulation), which mainly depends on the species-related interactions between the indicators/monitors and their biotic and abiotic environment.

- **Biomagnification** is the term used for absorption of the substances from nutrients via the epithelia of the intestines. It is therefore limited to heterotrophic organisms and is the most significant contamination pathway for many land animals, except in the case of metals that form highly volatile compounds (e.g., Hg, As) and are taken up through the respiratory organs (trachea, lungs).
- **Bioconcentration** means the direct uptake of the substances in question from the surrounding media, i.e., the physical environment, through tissues or organs (including the respiratory organs). Besides plants that can only take up substances in this way (mainly through roots or leaves), bioconcentration plays a major role in substance takeup of aquatic animals. The same may also be said of soil invertebrates with a low degree of sclerotization when they come into contact with water in the soil.

Bioindication and biomonitoring can be carried out at various levels of organismic life (macromolecule, organelle, cell, tissue, organ, organism, population or biocenosis). Since at the higher organizational levels in biological systems bioindication/biomonitoring becomes more complex and the detectable reactions (both accumulation and biological effects) become less and less specific, there has been a definite trend toward the use of lower degrees of organization, in particular in recent years. The "boom" in biomarkers and biosensors can be partly explained by the possibility they offer of conducting more substance-specific biomonitoring, but their drawback is that the information they provide has less relevance for the ecosystem.

A general classification of biological methods used in the field of environmental analysis and monitoring is shown in Figure 3. There are two basic groups of application of these methods:

The first group of biological methods is associated with the term *biomonitoring*. This term is usually understood very broadly, which leads to numerous misunderstandings. Biomonitoring is a part of monitoring understood as a process in which the analytical instruments ensure the aquisition of the appropriate information on a continuous basis, in real time or with a slight time lag.

On the basis of available literature, three analytical approaches associated with biomonitoring can be distinguished. One of the approaches uses samples of living matter (biota) in classical analysis to assess the state of non-living matter, i.e., air, water and soil. Biota has the ability to accumulate various environmental pollutants; thus its samples are typical examples of integrated samples that are the subject of investigations aiming at collecting the appropriate analytical information about the state or quality of non-living parts of the environment.[27–33]

The second approach, called *bioindication*, is associated with the use of living organisms (plants and animals) for determining the state of the environment (and the degree of its pollution) based on observations of their state *in situ*. The organisms used for this purpose are called bioindicators. The most commonly used bioindicators include mosses and lichens, as well as tree leaves and needles.[34–42] Often, bioindicators allow to determine the state and the degree of pollution of the environment over a large area. In this case, we are dealing with the so-called **B**iological **E**arly **W**arning **S**ystem (**BEWS**).

The third approach is based on the use of biological sensors (*biosensors*) in classical monitoring.[43,44] This approach is closely re-

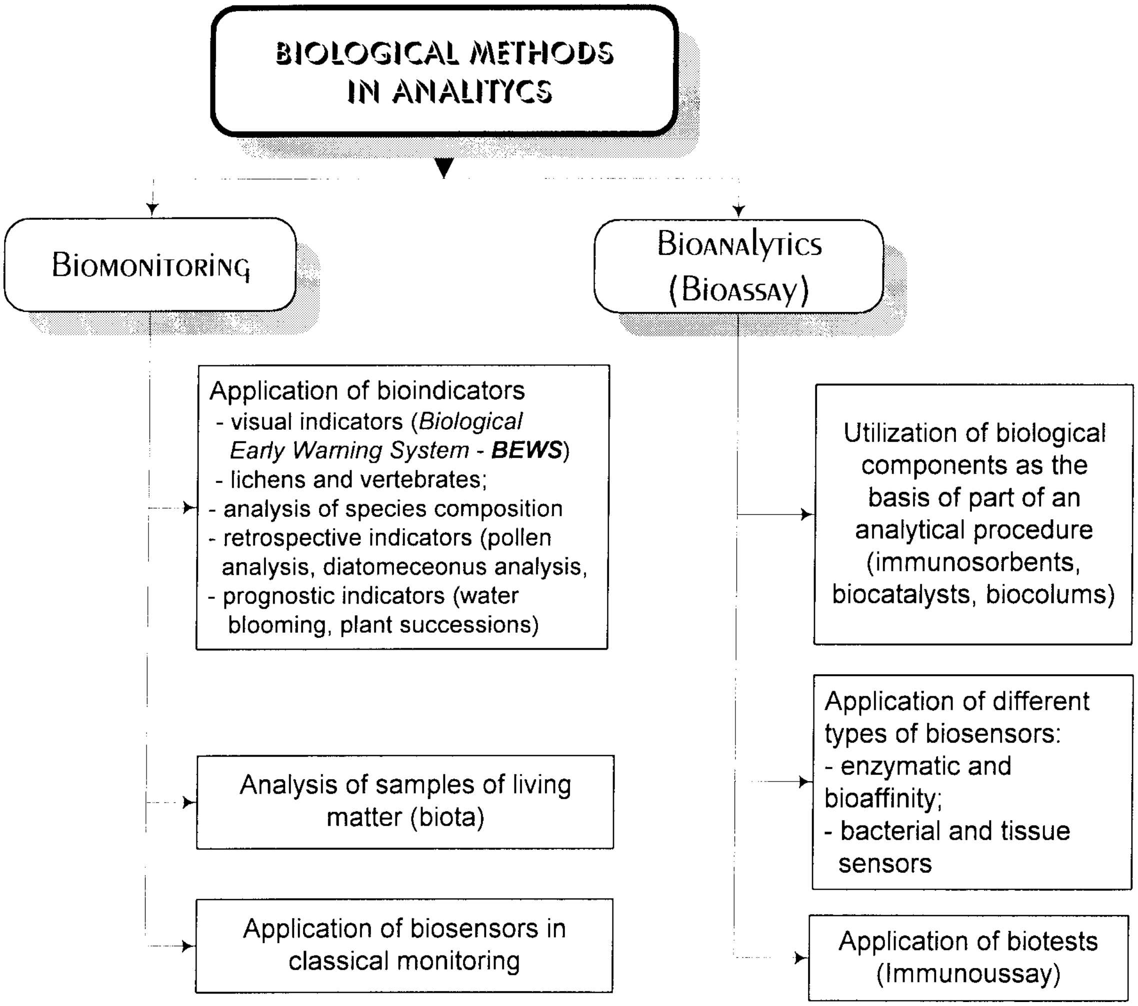

FIGURE 3. Classification of biological methods utilized in environmental analytics and monitoring.

lated to the second group of biological methods and will be discussed later.

The second group of methods, called *bioassay*, makes use of biologically active substances as receptors of specific pollutants. Further classification is based upon whether a biological element is used in a single step (other than detection) of a given analytical method, whether it is used for detection and quantitative determination, or whether it forms the basis of a complete analytical procedure.[45]

Analytical columns utilizing a biologically active substance to separate specific mixture components (*biocolumns*) are an example of the first application. Another example of such applications are immunosorbents.[46,47] The use of biological material at the stage of analyte detection is an example of the second application. Currently, biosensors represent a large and diverse group of analytical instruments, finding a variety of practical applications. In turn, the use of biological components as the basis of a complete analytical procedure, called a biotest, is widely used in immunoassay. A typical example of such a biotest is ELISA.[48–50]

During the last decade, the following new bioindication techniques have been introduced:

- **biomarkers:** measurable biological parameters at the suborganismic (genetic, enzymatic, physiological, morphological) level, the structural or functional changes of which indicate environmental influences in general, and the action of pollutants in particular, in qualitative and sometimes also in quantitative terms. Examples: enzyme or substrate induction of cytochrome P-450 and other Phase I enzymes by various halogenated hydrocarbons; the rate of occurrence of different forms of industrial melanism as a marker for air pollution; tanning of the human skin caused by UV radiation; changes in the morphological, histological or ultrastructure of organisms or monitor organs (e.g. liver, thymus, testicles) following exposure to pollutants.[51–57]

- **biosensors:** measuring equipment that produces a signal in proportion to the concentration of a defined group of substances through a suitable combination of a selective biological system, e.g. enzyme, antibody, membrane, organelle, cell or tissue, and a physical transmission device (e.g., potentiometric or amperometric electrode, optical or optoelectronic receiver). Examples: “Toxiguard bacterial toximeter”.[58–60]
- **bioassay:** (biotest): a routine toxicologico-pharmacological procedure for testing the effects of agents (environmental chemicals, pharmaceuticals) on organisms, usually in the laboratory but occasionally in the field, under standardized conditions (with respect to biotic and abiotic factors). In the broader sense, this definition covers cell and tissue cultures when used for testing purposes, enzyme tests, and tests using micro-organisms, plants, and animals for either single-species or multi-species procedures in model ecological systems (e.g. microcosms and mesocosms). In the narrower sense the term only covers single-species and model system tests, while the other procedures may be called suborganismic tests. Bioassays use certain biomarkers or, less often, specific biosensors and can be used in bioindication and biomonitoring.[61–64]

Suitable specimen banks play a very important role in biomonitoring. For example, the Environmental Specimen Bank (ESB) has been successfully established[65] as a permanent environmental surveillance tool in Germany. The few comparative studies which have been carried out show that, in general, the most efficient biomonitors of atmospheric pollution are either mosses or lichens. Soil pollution may be best monitored by earthworms or by coniferous trees. Some of the problems occurring with plants and animals as biomonitors are highlighted in Table 3.[66]

IV. INSTRUMENTAL TRENDS

Developments in analytical chemistry have kept pace with developments in electronics and instrumentation. The availability of electronic measuring devices has transformed analytical chemistry from an art to a modern science. Instrumental trends are closely related to the procedural trends discussed previously. The most important instrumental trends in the field of environmental analytics and monitoring include:

A. New Design of Sensors and Detectors

The literature contains a lot of information concerning construction and practical application of new or modified types of sensors and detectors. It seems the following devices should be mentioned here:

- Piezoelectric sensors[67,68]
- Optical waveguide sensors[69]
- Chemiluminescence detector[70,71]
- Photo-ionization detector[72]
- Sensors with hot-wire electrodes[73]
- Solid state gas sensors[74]
- Semiconductor laser-based gas monitors[75]

TABLE 3
Comparison of Advantages and Disadvantages of Using Plants and Animals as Biomonitors of Atmospheric Deposition

Advantages	Disadvantages
Plants	
1. Available for sampling at all times (some)	1. Seasonal growth effects must be taken into account
2. Sampling relatively cheap	2. Growth may be affected by a wide range of environmental variables
3. Possible to easily relate tissue concentration to deposition (mosses & lichens)	3. Effects of pollutant on growth make interpretation difficult
4. No licensing needed for common species, and little special training necessary	4. Differential discrimination of pollutants may influence uptake patterns
	5. Population may contain a mixture of resistant and non-resistant genotypes
	6. Risk of contamination from substrate (some)
Animals	
1. Can link body concentrations to effects via toxicological tests	1. Organisms may range over more than one habitat
2. Indirect nondestructive measures possible; blood samples, roadkill, eggshells	2. Receptor organism may need trapping
	3. Populations may fluctuate considerably from year to year (some)
	4. Population may contain a mixture of resistant and non-resistant genotypes
	5. Biomagnification through food chain may increase the variability of the pollutant
	6. Accumulation may differ between organs and even within organs
	7. Determining the correlation between the pollutant in the body and the deposition may be difficult
	8. Organisms may be relatively isolated from direct effects of changes in deposition, resulting in a possible time lag
	9. Work may require high levels of training and licensing to work with animals
	10. Public opinion may prevent work on some organisms.

- Photoacoustic gas sensors[76]
- Sensors based on the field effect principle[20,77]
- Ultrasonic sensors[78]
- Biosensors[79]
- Electrochemical sensors and detectors including:
  - Electrochemiluminescence detector[80]
  - Amperometric sensor[81]
  - Conductometric detector[82]
  - Electrochemical sensors based on bilayer membranes (BLM's)[83]
  - Ion-selective electrodes,[84–92] including disposable screen-printing electrodes[84–86,88,93]

The knowledge of the literature data leads to the conclusion that the most popular class of new sensors are biosensors. Due to their specificity, short response time, low cost, and portability, biosensors are becoming more popular in environmental analysis, especially of water samples.[23]

A biological sensor (biosensor) is an analytical device, often miniaturized, 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 catalyze 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 a digital form by an electric circuit.

Biosensors are usually classified according to the type of biological receptor used. The most commonly utilized biosensors include enzymatic biosensors and affinity biosensors. Such systems utilize enzymes or antibodies immobilized on a support in close contact with a transducer. They can detect substrates of enzymatic reactions, inhibitors, or antigens bound to an antibody.

A transducer is an essential element of a biosensor. The most common transducers used in biosensor design are

- Electrochemical transducers (change in voltage or current)
- Optical transducers (change in fluorescence, absorbance or intensity of reflected light)
- Acoustic transducers (change in frequency due to change in mass of substance on the surface of the device)
- Thermometric transducers (change in temperature)

The dominating group of sensors, both in research and practical applications, are amperometric sensors, thanks to their simplicity and universality. This technique employs a three-electrode system: a working electrode to which potential is applied, a reference electrode, and an auxiliary electrode through which the current flows. Every substance that undergoes electrochemical oxidation or reduction at the applied potential is detected at the working electrode. Three types of electroactive substances can be monitored: substrates of biological reactions (e.g., O_2, nicotinamide adenine dinucleotide—NADH), products of biological reactions (e.g., hydrogen peroxide for the reactions of oxidase, benzoquinone for the oxidation of phenol), and electrochemical mediators enabling direct transfer of electrons from an enzyme to the surface of the working electrode (e.g., hexacyanoferrate, ferrocene, methylene blue).

Potentiometric transducers have also found widespread application as biosensors. Some ion-selective electrodes are based on this principle. Interferences can be substantially reduced by using selective membranes.

Optical transducers are, after amperometric and potentiometric transducers, the third most common group of devices. Recent developments in fiber optics have significantly broadened their applicability. Biosensors of this type make use of a variety of optical techniques, from simple absorption of light by a reagent layer following binding of a substrate, to such techniques as emission spectroscopy, atomic absorption, and Raman scattering.

Depending on the way a biological substance reacts to the analyte, two groups of biosensors are distinguished:

- Catalytic biosensors based on biocatalysts (e.g., enzymes or micro-organisms recognising, binding and chemically converting substances)
- Affinity biosensors using molecular receptors (e.g., antibodies, nucleic acids, lec-

tins or hormone receptors binding molecules irreversibly and not exhibiting catalytic activity).

Enzymes, plant micro-organisms and animal cells, intracellular organelles or slices of animal tissues can all be used as biocatalysts. Catalytic biosensors allow identification of the analyte, based on or followed by its binding. Subsequently, they catalyze chemical conversion of the analyte with the simultaneous release of products, which are detected by the transducer and recorded. Enzymes (natural protein biocatalysts) interacting specifically with a given substrate or a group of substrates were the first biocatalysts used in biosensors and still are the most common biological component in catalytic biosensors.

One can distinguish two kinds of enzymatic sensors:

- A pollutant is a natural substrate of an enzymatic reaction; the enzyme catalyzes its transformation and remains unchanged in the reaction. Examples include H_2O_2 decomposed by catalase and phenols oxidized by tyrosinase
- A pollutant is an inhibitor of an enzymatic mechanism via binding to or reacting with one of components at the active site. This binding may be a result of a structural analogy to the substrate, or of a specific chemical affinity. In this case the enzyme is blocked almost irreversibly. Examples of such pollutants include organophosphorus compounds and carbamates, which inhibit the activity of cholinesterase, and cyanides, which inhibit metalloenzymes such as cytochrome oxidase and tyrosinase due to their affinity to metal ions.

Popular biosensors also include devices based on bioaffinity.

Biosensors have already found application in the following areas:

- Determination of a given analyte in a complex mixture
- Process control
- Evaluation of toxicity of chemical compounds
- Detection of mutagens
- Monitoring of individual parts of the environment

Two tendencies exist in the design of biosensors utilized for environmental monitoring and should be pointed out:

- Enzymatic and bioaffinity biosensors, characterized by high specificity and sensitivity, and used for the detection of specific pollutants in environmental samples under investigation
- Bacterial and tissular biosensors characterized by high sensitivity to a wide range of substances and used for monitoring of unexpected (abrupt) changes in the state of the environment (also in an on-line mode), e.g., due to ecological catastrophes.

A developing area in sensor research is the use of a number of detectors (an array) to give simultaneous information about a complex mixture.[67,68,92,94–96] Because these types of devices are often designed for field usage, sophisticated separation is not possible, nor is the use of detection methods based on high vacuum. It is hoped, therefore, that information obtained from the array, will compensate for deficiencies in exact chemical analysis. In this regard, multiplicity of response is a way of maximizing the available information.

The development of the "electronic nose"[95–97] and the "electronic tongue"[94] 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 organization of sensor systems—arrays of nonspecific 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 intelligence and/or a field of the application of the "electronic brain". Table 4 compares the characteristics of human sensing systems and the artificial version of senses of smell, hearing, sight, and touch.[96]

The history of chemical sensors can be divided into four periods (Table 5).[94] The first three of them have been devoted to selective detectors and the last one to multisensor arrays.

The history of the "electronic nose" as an intelligent multisensor starts in 1982. The term itself become widely recognized around 1990. "Noses" usually provide a quantitative recognition of gas mixtures. The first mini-review on the applications of "electronic noses" has been published recently.[98]

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 recognizing quantitative and qualitative compositions of simple and complex solutions.

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 the detection, identification and quantification of microcontaminants at the trace and ultratrace level.[99–107] 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 analyzed 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 postcolumn reaction detection.

In most discussions, two major branches in the field of multidimensional analysis are mentioned:[99]

- The use of coupled-column techniques[108]
- The use of hyphenated techniques[100,101,104,105,107]

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 permits to lower the risk of analyte losses 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 analyticians 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 expectaion of obtaining a correct result. LC and GC are predominantly used as separation techniques in environmental analysis, playing only a minor role in supercritical and planar chromatography (and also capillary electrophoretic techniques). On the other hand, the on-line preparation of aqueous samples and sample extracts is frequently being carried out by means of Solid Phase Extraction (SPE) using either short precolumns, disposable cartridges, or membrane extraction

TABLE 4
Characteristics of Human Sense Organs and Artificial Devices

Organ	Human	Artificial
Nose	100s–1000s of receptors for different smells Several million cells	“Electronic”, “bionic nose” 1s–10s of metal oxide semiconductor sensors, quartz crystal microbalance sensors or conducting polymer resistance sensors
Ear	20,000 cilia around the cochlea	Sensitive microphones to cover any range of frequency. (Note the Cochlear prosthesis that has 22 electrodes implanted in the cochlea)
Eye	Light-sensitive rods (125 million) and cones (7 million) distinguishing 300 hues at 100 levels of brightness for a given saturation	CCDs in a camera have a wide intensity range and wavelength discrimination, but very poor recognition software
Touch	Nerve endings: millions of cells	Piezoelectric crystal sensors

TABLE 5
A Summary of Milestones in Ssensor Development

I. 1906–1937. pH glass electrode and ion-exchange theory

1906	**Cremer**—dependence emf on pH (glass membrane)
1909	**Haber, Klemensiewicz**—development of glass electrode
1936	**Beckman**—commercial production of pH meter
1937	**Nikolsky**—Nikolsky equation and theory of glass electrode
1937	**Kolthoff**—crystalline “electrode”
1937	**Nikolsky**—crystalline membrane

II. 1961–1969. Conventional ion-selective electrodes and biosensors

1961	**Pungor**—heterogeneous solid ISE
1962	**Seiyama, Taguchi**—semiconductor gas sensor
1966	**Frant, Ross**—LaF_3-electrode
1966	**Simon**—liquid ISE with neural carrier
1967	**Ross**—ion-exchange membrane
1969	**Guilbault, Montalvo**—biosensor
1969	**Baker, Trachtenberg**—chalcogenide glass membrane for ISE

III. 1970–today. Microelectronics in sensor development

1970	**Bergveld**—ISFET
1972	**Shone**—piezoelectric biosensor
1975	**Lundstrom**—gasFET
1976	**Schen**—immunoFET
1978	**Lubbers, Optiz**—opt(r)ode
1986	**Thorn EMI Microsensor**—first commercial production of ISFET

IV. 1970–today. Multisensor arrays and sensor systems

1982	**Persaud, Dodd**—“electronic nose”
1995	**Vlasov, Legin, D’Amigo, Di Natale**—“electronic tongue”

discs. As a result, five coupled-column combinations are of interest today: SPE-LC, SPE-GC, LC-LC, GC-GC, LC-GC.

With respect to the other multidimensional approach, systems are called hyphenated if a separation module is combined on-line with a spectroscopic detection device providing structural information, or, in other words, if the combined set up enables the provisional identification of the analyte(s). As far as LC separations are concerned, there is no doubt that diode-array UV absorbance detection (DAD-UV) with its admittedly limited identification potential but wide applicability, easy availability and user-friendliness, holds the first place. When a sufficient number of interfaces became available, mass spectrometry (MS) and, more recently, tandem MS has become a serious competitor to DAD-UV detection, with the wealth of information being provided easily outweighing the cost and the higher level of complexity of instruments. Of course, in gas chromatography MS has always been the spectroscopic detector of choice, so much so that an analyst is surprised to find out that his routine GC-MS procedures all of a sudden come under the advanced heading of hyphenation. Historically, tandem GC-MS is the first coupled apparatus in common use. The GC-MS technique has been known for more than 25 years.[109] Next to the tandem MS techniques (often ion-trap based), atomic emission detection (AED) and Fourier-transform infrared (FTIR) detection are alternative ways of achieving hyphenation in GC. Quite recently, the FTIR option has also gained some popularity in on-line and at-line combinations with LC. The same is becoming true for nuclear magnetic resonance (NMR) as a detection technique, but here the analyte detectability still leaves so much to be desired that LC-NMR cannot yet be considered a viable way for trace-level analysis. On the other hand, it may suffice to mention the good fluorescence characteristics of the ubiquitous and notorious polynuclear aromatic hydrocarbons (PAH's), and many of their derivatives, to illustrate the usefulness of fluorescence detection. In environmental analysis, the real-time identification of analytes, or, in other words, of microcontaminants apparently present at or above given threshold levels, is becoming more and more important. Consequently, hyphenated techniques are here to stay, and they will be used increasingly for routine applications, i.e., for early warning, screening and monitoring studies.

3. Automation, Robotization, and Computerization 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[110–113] and environmental laboratories.[114] Most analytical instruments used in an environmental laboratory are highly automated. Gas chromatography (GC) instruments, for example, can run 20 to 50 samples in an autosampler and store the data for later interpretation. However, data interpretation remains largely a manual task. As the sample loads increase, the data interpretation and review process becomes a troubling bottleneck in the laboratory. Increasing the throughput of the environmental laboratory by automating sample preparation will require a commensurate automation of the data interpretation process in order to avoid the bottleneck.
- Application of robots in the analytical laboratory.[115–118] A decade ago robots moved into the field of laboratory automation. They started as sample probe-handling devices and have developed into multipurpose pieces of equipment for sample processing such

as pipetting, weighing, mixing and extracting. Supported by user friendly software including pull-down menus, soft-key and/or mouse-driven, robots have changed their status from being a "nice-to-have piece of equipment," as they were called in the past, to well-accepted laboratory "work horses". Equipped with sensor devices, robots made "the dream" of unattended laboratory shifts a reality. There is no clear distinction between automation and robotics in the laboratory and if a robot is considered to be a device which carries out transportation and manipulation, then several longstanding items of equipment have robotic properties. Most often, a robot is considered to be a device that is able to make different programmed movements under computer control, while using tools or sensors to perform transportation, manipulation and measurements. The following potential benefits should be taken into account when considering whether to apply robotics in the laboratory:

- Improvement in precision
- More cost-effective use of staff and resources
- Protection of workers in a hazardous environment
- Improvement in job satisfaction by reduction of repetitive work.

It may be considered that first and second of these are related, in that errors in repetitive work may be attributed to the moods or attitudes of the analyst.

- Development and application of artificial intelligence[119–122] and especially expert systems,[123–130] in analytical procedures. Automated instruments have become essential components of modern laboratories. Unfortunately, however, unattended operation can result in delayed detection of instruments faults and improper sampling. In many cases when such faults occur, the instrument is usable to successfully analyze the current sample or the remaining samples in the batch. For example, an overconcentrated sample may contaminate the instrument and affect the 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 analyzed. 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 analyzing 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—the overconcentrated sample may be reanalyzed successfully 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-error 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.[122] 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 of such instruments are even able to select the most suitable method available, schedule a work program, optimize 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 computerization of analytical expertise, thus providing a vehicle for maintaining and communicating this knowledge. A formal and complete definition of an expert system would be:[129] "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. Expert systems have been applied in various fields of analytical chemistry such as:

- Chromatographic techniques.[125–127,131,132] A knowledge-based system has been proposed that uses experimentally determined relationships between a gas chromatography (GC) system and the properties of a standard test mixture for automated quality control and diagnosis of GC instruments.[131,132] When utilizing this approach, standard test samples are run at regular time intervals, the results are analyzed automatically and the system performance is evaluated by expert system based software. When the GC system is set up for standard tests, four Relative Performance Indices are derived that relate the response of this specific instrument to the chemical or physical properties of the sample of interest. Possible component faults are diagnosed in order to ensure that the system operates under perfect conditions.

- Kinetic methods of analysis[128]
- Quality assurance in an analytical laboratory[123]
- Trace analysis[124]
- Electrochemical techniques (FIA);[133]
- Spectroscopy[134]
- Chemometrics and data management[135]

Artificial neural networks (ANNs) are another tool for artificially encoding intelligence, typically in the realm of pattern recognition based on decision-making processes.[121,122] 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 organization in nets, biological neurons fulfill an unlimited number of tasks related to perception, recognition and learning. The human sensory system is able to recognize 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,[119,120,136,137] 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.

4. Miniaturization of Analytical Instruments

Miniaturization is not a new concept for the separation scientist, as small volume separations have occupied analysts for a number of years. The most important achievements in the field of miniaturization concern:

- Gas chromatography[138–140]
- Liquid chromatography[140–142]
- Electrophoresis[143–151]
- Micellar electrokinetic chromatography[152]
- Chemical microanalysis[153,154]
- Electrochemical methods[84–86, 88,89,155] for example in the form of screen printed electrodes[84–86,88]

Essentially, miniaturization in the field of separation was first accomplished through the use (such as column packing) of particles having micrometer dimensions to achieve improved separation efficiency. The subsequent tendency has been towards open and microparticle-packed columns of reduced internal diameters of 1 mm or less, and therefore termed microcolumns. Both practical and theoretical considerations provided the incentives for these developments. The practical benefits to be gained from scale-down separations include a drastic reduction in the consumption of mobile phases that are often prohibitively expensive or hazardous to the environment, improved capability of analyzing samples having much smaller volumes, and reduced time of analysis. Theory predicts that an overall reduction in the dimensions of flow channels should result in enhancement of analytical performance.

Moreover, the use of narrow bore columns packed with small diameter particles should yield better resolution in a separation than open columns of the same dimensions. Numerous examples in the literature of the last decade substantiate these theoretical predictions. In cases where theoretical separation performance was not fully achieved, technical problems in execution of the experiment were generally found to be the cause. These could often be traced to inhomogeneity in column packing in the case of packed microcolumns, or too large a variation in bore diameter in the case of open capillaries. Injection and detection problems prevailed, with dead volumes of coupling capillaries often too large to retain a reasonable separation resolution. Several authors have noted that the use of microlithographic techniques to fabricate systems would be beneficial.[92,138,139,141,143,156,157] The use of small structures manufactured in this way should facilitate connecting capillary separation systems with each other for two-dimensional separations, or to injectors and detectors with minimum dead volume. In addition to the practical benefits to be gained from small column analyses, the simplicity and possible low cost of fabrication of such structures are advantages which should be noted.

Planar technology or micromachining of silicon or other planar materials, has its roots in the microelectronics industry, and therefore includes a number of well established and accepted techniques. Micromachining is a combination of the following:[142,151]

- **Film deposition** A large variety of metals, inorganic oxides, polymers, and other materials can be deposited. Depending on material deposited, and the deposition method employed, film thickness of a few nanometers to a few micrometers can be obtained.

- **Photolitography** It is the technique by which a pattern of geometric shapes is transferred to a layer of photosensitive material called photoresist, with the pattern itself in the form of a glass mask with dark surface regions defining the design.
- **Etching process** It is a process of transfer of two-dimensional patterns defined on the wafer surface to underlying films and substrates. These processes may be classified as either wet or dry. In wet chemical etching the structure is immersed in an etching solution chosen specifically to etch only the desired material from among those exposed to the solution. Dry etching processes include those carried out in partially or fully ionized gases (plasmas).
- **Bonding** Refers to an assembly of structures, whether it be silicon-to-silicon, silicon-to-oxide, silicon-to-glass or some other combination of materials. Because of planarity of the surfaces used, bonding usually leads to fusion of the assembled structures and a perfectly tight seal.

Micromachining is used to fabricate diverse three-dimensional structures. A variety of materials can be used ranging from glass[143,147–149,158] and quartz to metals, plastics and ceramics. At the top of the list, however, is silicon. It is the most commonly employed a material[138,139,141,142,145,156] for the following reasons:

- High level of purity
- Crystalline perfection
- Low cost (owing to volume production)

Silicon can be micromachined to produce structures having dimensions of the order of a few micrometers, making it very important for miniaturization.

Advances in microengineering now make it possible to fabricate microcomponents such as pumps,[146] sample injection systems,[147,148,158] devices for solvent mixing,[138,143] and valves that are only a few cubic millimetres in size. Current trends suggest that these components might be mass produced easily, using inexpensive materials as polymers. Combining individual components will make it possible to produce microsystems that fulfill useful chemical or biochemical functions (called also “laboratory on a chip”).[140] A very interesting review paper focused on:

- Submersible stripping sensors
- Microfabricated metal sensors
- Hand-held stripping analyzers
- Micromachined stripping analytical systems has been published recently[155]

In a recent line of development separation techniques have been integrated successfully into the concept of the so-called **T**otal Chemical **A**nalysis **S**ystem—**TAS**.[146,150,153,159,160] The combination of all sample-handling and measurements 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 of 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 miniaturized Total Chemical Analysis System has been introduced.[146,150,159,160] A miniaturized 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 utilizing 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:[161]

- Total system size of the same order of magnitude as the transducer part
- 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, e.g., achieved by built-in-alignment of sensor parts
- Standardized waveguides, sensing pads and schemes suitable for a wide variety of applications

There is a continuous drive in information technology to miniaturize its basic components for signal sensing, information processing, and storage, as well as updating. The final goal is to develop miniaturized wires, switches, storage devices, etc., with atomic dimensions.[162–165] Terms like molecular electronics, bioelectronics, nanocomputing, nanosensors, molecular mechanics,, characterize different trends in this rapidly growing field that are determined by two limitations. The first is the lack of concepts and technologies to prepare, manipulate, and analyze devices with atomic dimensions. For selected applications this problem may be solved in the future, and then the limitations on applications will be created by economic factors. The second limitation is one of principles. It is created by the quantum-mechanical uncertainty principle and leads to reduced reliability for very small information-storage devices.

Present and future applications of nanostructures concern different fields of information technology, including in particular chemical and biochemical sensors, electronically controlled nerve actions or drug release in the human body, molecular electronics, and bioelectronics.[163]

Man-made chemical or biochemical sensors represent prototype systems interfacing the technical and the biological world. A specific example may illustrate the functional similarities and the technological differences of the device components which may be based upon either artificial (man-made and "electronic nose") or natural structures (human nose). The two noses are made up of completely different materials. Nevertheless, similar functions formally characterize the components of both systems.

5. In Situ Measurements

The use of *in situ* measurements results in a decrease in the so-called information lag. The instruments used for *in situ* measurements, although generally less sensitive than laboratory instruments, must meet a number of stringent technical requirements. The traditional approach for performing environmental chemical analysis is to acquire field samples that are transported to a laboratory at a later date. This approach is often inefficient and costly. In many cases, the time lapse between sampling and obtaining the results is unacceptable. Novel detection and monitoring applications for environmental chemistry (waste incineration, site remediation fugitive emissions control), law enforcement (drug interdiction, explosives detection), and military uses (mobile engagement, stockpile reduction, treaty verification) are generating a growing demand for "field-portable" analytical instruments.[166] Certain emerging problems in field analyses can no longer be solved with transportable equipment, e.g., mobile apparata[167–169] or mobile laboratories[170] including measurement devices on board of aircraft.[171,172] Presently, man-portability,[173174] or preferably hand-portability,[174–176] is required for fully operational equipment.

Personal dosemeters and personal continuous monitors[177] used to evaluate individual exposure constitute a special class of transportable measurement devices.

This places strict limitations on the weight, size, power consumption, ruggedness, maintainability, and user-friendliness of the devices. In certain applications, strict requirements are additionally imposed on sensitivity, specificity, and speed.

Most portable instruments provide information that is one-dimensional in nature, i.e., the intensities of output signals are measured relative to a single parameter—retention time. The gas chromatograph is the most extensively used portable instrument[167,170,178] and can be compared or evaluated by figures of merit with respect to sensitivity, selectivity, and choice of detector. Detectors that were not capable of providing the "second dimension" served only to produce a record of column eluate during the chromatographic process.

In literature one can find information on instruments for *in situ* measurements that are equipped with modules for isolation and/or preconcentration of analytes from air and water before they are subjected to final analysis.[167,179–182]

This is a relatively efficient manner of expanding the field of practical application of *in situ* measurements.

The utility of GC can be broadened if the detector provides additional information that is helpful in characterizing individual GC peaks. This is the origin of hyphenated techniques[169,170,173–176,181] that provide a second dimension in analysis. Some of the most widely used detectors are mass spectrometers and Fourier-transform infrared spectrophotometers, which have technical limitations concerning portability. The addition of a second dimension into analysis while maintaining portability is desirable in the development of portable GC instruments. Ion mobility spectrometry (**IMS**) is an attractive technique in conjunction with GC for the determination of constituents in a mixture. Ion mobility spectra paired with a GC retention time can result in a powerful combination of analytical information for detection and identification of substances.[170,174–176]

In analyses of air and water pollutants, other types of field instruments are also utilized.[183–187] Special attention should be paid to multigas monitors. Portable gas monitors designed for the continuos monitoring of ambient air quality in the workplace are not new. The technology employed for the different sensors used in gas detection is well documented. The majority of these older models, however, are designed for continuos monitoring of only one or two gas levels. At present, a multitude of new-generation portable monitors exists that can continuously and simultaneously detect the spot concentrations of several kinds of gases (oxygen, toxic gases, combustible gases) in the atmosphere. Multigas capability in these monitors is achieved through the use of specific sensors for each of the gases.[185,186] The latest versions are microprocessor controlled, and are equipped with software allowing for digital display of each gas level. Other features include a data logging capability (which permits data to be downloaded to a computer for storage and further analysis):

- TWA (time weighted average) concentration
- STEL (short-term exposure limit)
- Peak value readouts
- Automatic instrument for self-diagnostic testing

- Meter fault detection and alarms
- Low battery power condition detection

Unfortunately, the reliability of the monitor as an early warning device is still sensor limited. Desirable features of an ideal multisensor portable gas monitor are as follows:[186]

- Fast, specific, sensitive, accurate, and reproducible sensor response
- Microprocessor-controlled
- Data logging capability
- Easy to operate, requires minimum maintenance
- Remote sampling or sensing capability
- Visible and audible alarms
- Easy-to-read, self-illuminating digital display that provides simultaneous readouts for all gases being monitored
- Rugged and durable
- Certified to be intrinsically safe
- Failsafe
- Can be operated using either disposable dry cells that are easily interchangeable or recharchable batteries
- Compact and light

6. Passive Devices

The use of passive samplers (dosemeters) is one of the modern approachs 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 vapors of many compounds.

Passive samplers are also often called diffusive samplers, having been defined as devices that are capable of taking samples of gas or vapor pollutants from the atmosphere, at rate a controlled by a physical process such as diffusion through a static air layer or by permeation through a membrane, but that 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 dosemeters
- 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 dosemeters. They are especially important to those health professionals (surgeons, dentists, nurses, and veterinarians) who use them for determining exposure to waste anaesthetics. Personal charcol tube (CT) samplers that use battery-powered pumps require specially trained personnel in order to obtain valid results and do not fulfill the mobility and sterility requirements in 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 period/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 the state-of-the-art techniques involved, have been comprehensively reviewed.[188,189]

Although diffusive samplers utilizing simple colorimetric principles have been available since the early 1930s, it was not until the early 1970s that the first mathematical model, which attempted to codify the factors controlling the uptake rate in the application of Fick's laws of diffusion, was published. This early work led to the design of a sampler for NO_2, which is generally recognized to be the forerunner of most the devices available today. A major step forward was made with the publication of a paper describing the development of the "Gas Badge" diffusive sampler which recognized the part played by external factors such as wind velocity, temperature, and pressure.

Fairly rapid commercial development followed during the 1970's with the appearance of mercury vapor and organic vapor monitors from the 3M Company, and an organic vapor monitor from the Dupont Company. A more logical extension of the original Palmes work was the emergence of the tube-type sampler in the U.K., sponsored by an industry group and eventually commercialized by the Perkin Elmer Company. During this period of development many other types of devices were introduced, usually variations on either the flat badge or the tube concept, but most of them did not find significant commercial use during this time.

Two events of significance occurred in 1973. First, the publication of a deceptively simple technical paper dealing with analogies between diffusion resistance and electrical resistance and demonstrating that they could be handled in a similar fashion. The second event was the appearance of diffusive samplers having a means of backup or validation, thereby addressing the problem of sample loss or variations in sampling rate over the sampling period.

During the 1980s there was a substantial increase in the use of both sorbent based and colorimetric samplers. Since then, a wide variety of such devices became available from numerous manufacturers both in the U.S. and in Europe. A very comprehensive review of the field was presented in the *American Industrial Hygiene Association Journal* in 1982. In 1983 there was a nearly simultaneous publication of validation protocols by NIOSH in the U.S. and by HSE in the U.K. These represented a serious attempt to provide a set of standards and testing methods that could be used to compare all types of diffusive samplers against common criteria.

The period from 1983 to the present day has been particularly marked by the publications of some key papers dealing with the mathematics of various aspects of diffusive samplers. Of particular significance are the mathematical models of the influence of sorbents on the uptake rate published by two groups in the U.S., as well as the study of transient sampling conditions and numerous studies of comparisons between diffusive samplers and the charcoal tube sampling method published in a variety of technical journals.

Passive samplers are used not only to preconcentrate and determine time-weighted average concentrations of pollutants in indoor air, in working place atmospheres, and in atmospheric air (area monitors), but also to measure personal exposure.

According to one approach, passive samplers can be classified into three basic types:[188]

- **Direct reading reagent-type monitors** rely on the pollutant reacting chemically with the reagent system dispersed on a suitable support to produce a color change, the length or tint of which is proportional to the pollutant concentration.
- **Indirect readout reagent-type monitors** are based on instrumental measurement of weight changes, colour changes or changes in conductivity.

- **Sorption-type monitors** are based on trapping analytes by adsorption, absorption or chemisorption during exposure. The samples are liberated prior to the analysis carried out by means of, e.g., gas chromatography or spectrophotometry.

Diffusive samplers can also be classified as badge type and tube type. The dimensions and the shape of the diffusion path are the only distinct differences between both types.

With respect to the diffusion barrier, passive samplers can be classified into two groups:

- Diffusive samplers, in which a stagnant air layer in which no convection occurs makes up the diffusion barrier
- Permeation samplers—in this case we have diffusion (permeation) through a semipermeable membrane made of a proper material (silicone rubber, Teflon) into a concentrating medium layer.

Passive samplers (diffusive as well a permeation type) have been used to collect many organic and inorganic compounds from the atmosphere. Inorganic compounds involved include water vapor, carbon monoxide, nitrogen oxides, ammonia, hydrogen sulfide, hydrogen fluoride, hydrogen cyanide, ozone, chlorine, sulfur hexafluoride, arsenous hydride, carbon disulfide, phosgene, and mercury vapor.

Passive sampling finds an especially wide use in concentrating organic compound vapors, especially aliphatic hydrocarbons (C_5-C_{12}), aromatic hydrocarbons (benzene, toluene, xylenes, ethylbenzenes, styrene), vinyl chloride, tetrachloroethylene and other chlorinated hydrocarbons, amines, formaldehyde, acetone, methyl- ethyl ketone, cyclohexane, ethyl acetate, vinyl acetate, Freon 12, tetraethyl lead, hydrazine, alcohols, acrylonitrile, methyl methacrylate, butyl acrylate, ethylene oxide, and also halothane and influence (gases used as anaesthetics in operating theatres). During recent years passive samplers have been employed extensively for monitoring low concentrations of organic vapors. The basic advantages and shortcomings of passive samplers used in the field of monitoring of the gaseous media are presented in the Table 6.

The field of practical application of passive samplers is continually expanding. During the last 10 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 prepared recently.[190,191]

TABLE 6
Basic Advantages and Shortcomings of the Use of Passive Monitors

Advantages	Disadvantages
Passive monitors are simple to operate; no moving parts	They can produce only integrated concentration values
These instruments are relatively inexpensive (both in purchase and analytical costs) as long as they are used in large quantities	Exposure times tend to be rather long (days rather than hour) Some systems experience interference problems from other pollutants
They can be used by inexperienced people (e.g., occupants of buildings) and are suitable for mailout monitoring programs	Results may be affected by air currents and temperature

7. Direct-Reading Instruments

Chemical analysis moves from specially equipped laboratories to the sites where samples to be analyzed are located. This is an important trend in modern environments analytics. In the future, the role of stationary laboratories will decrease not only due to the growing potential of process analysis, but also due to the simultaneous increase in the importance of reliable and simple to operate tools for on-site analysis. The development of tools for fast test methods is directly connected with this tendency.[192] There are many phrases used in order to describe this type of action such as[193] test kit, rapid test, test strip, screening test, orientation test, pocket test, ready-to-use kit, and field test. Test (spot) methods of analysis are a fast, simple and cheap way to detect and determine pollutants without trained personnel, sophisticated sample treatment, the use of complicated devices, laboratory equipment, or the laboratory itself. The tools used for this purpose are in many cases portable, light, and for single use only. The general principle of almost all chemical test methods is the use of well-known analytical reactions and reagents under the conditions and in the forms that yield a visual and easily measurable, effect, e.g., the intensity of paper color, the length of the colored part of a tube[194–197] or strips.[88,198] The first information on the application of thin-layer detector tubes instead of the classic detector tubes with bed of reagent on a support has appeared recently.[199] These new tubes are glass tubes the inner surface of which is coated with a thin reactive layer consisting of reagent impregnated support material. The trace component to be determined in the air sample aspirated through the tube diffuses to the walls where it undergoes a gas/solid phase reaction with this layer, thus producing a color change which is, in terms of area and intensity, a measure of the amount of the reacted trace component. Both organic and, less often, inorganic reagents involving different reaction mechanisms are used: acid-base indicators, complex-forming agents, organic compounds with functional groups that are able to participate in reactions typical for organic molecules. There is an indication to use the most selective and sensitive reactions, in practice, however, the most studied and the best known reactions and reagents are usually applied. Reagents are used either as ready made solutions (sold and stored in ampoules or droppers), or immobilized on a solid support.[200–203] Besides the analytical reagents themselves, testing tools usually consists of other components: reductants or oxidants, masking agents, buffer solutions, stabilizers, adhesives, etc.

Evaluation systems include visual (intensity, saturation, length of a colored zone), colorimetric (comparator, colorimeter), photometric (simple portable photometer), reflectometric (portable reflectometer), and titrimetric (counting drops, plastic syringes) estimation methods.

The metrological aspect is significant for the development, preparation, and use of testing tools. The results of tests should be reliable, even when small amounts of substance are being determined. For environmental, analysis tools of various sensitivities are needed, but the tools that are especially important are those characterized by having the detection limit close to the permissible concentration limit of analytes. The precision of visual measurements for color reactions is approximately 10 to 30%. Therefore, in some cases these methods should be considered as semiquantitative. However, they allow fast determination and do not require a well-equipped laboratory or highly trained personnel.

Test methods have been developed for a lot of analytes: metal ions, anions, dissolved oxygen and chlorine, hydrogen peroxide, ammonia, pesticides, nitrite, nitrate, PAHs, petroleum products (in water and solutions), as well as for sulfur dioxide, hydrogen sulfide, ozone, and many other gases (e.g., in air). Short reviews on these test methods can be found in the literature.[193,201,204]

Besides chemical test methods (including enzymatic ones), there are immunological tests and biotests based on the use of living organisms, separate organs or tissues; however, these latter test methods are omitted here. The methods under consideration here serve in many cases for the preliminary estimation of the amount of component present, but as they are improved they will become the sole tool of analysis.

Direct-reading instruments for aerosols have not been as popular within the industrial hygiene community as similar instruments for gases and vapors.[183] There are several reasons for this situation:

- Aerosols have complex properties that are difficult to characterize with a single measurement
- Commercial instruments often do not provide an accurate measure of a useful aerosol property
- Aerosol instruments are relatively expensive for industrial hygiene use

Some typical applications for fast tests include:[193]

- Screening
- Process monitoring
- Setting on analysis strategy
- Analysis of highly perishable samples
- Performing analyses in emergency situations
- Fast clarification
- Health and safety protection

Test kits provide results on-site, which is sometimes absolutely necessary. This means that the sample does not go to the laboratory, but the laboratory comes to the sample. Finally, test kits are very often used because of unavailable laboratory equipment.

8. 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 because they afford the option of rapid warning and proper feedback, while avoiding the errors, delay, 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 concentrates (by a rather subjective selection of examples) on remote "chemical" sensing.

A number of remote monitoring techniques are being developed that do not have the disadvantages of point monitors and are capable of making measurements difficult or impossible to carry out using conventional methods.

The literature on the subject provides the basis for distinguishing the following groups of techniques used for remote measuring of the pollution level in different parts of the environment:

- Remote electrochemical sensors.[88,205–209] Challenging demands for continuous monitoring of water resources or waste sites with toxic metals or inorganic and organic pollutants have triggered a growing interest in the development of submersible chemical sensors for real time monitoring of priority pollutants. Chemical sensors, based on a combination of a recognition layer and a physical transducer, hold great promise for *in situ* environmental monitoring. Fiber optic sensor technology has been widely used for remote monitoring of organic[210] and inorganic pollutants.[211] Recent advances in electrochemical sensor technology should make possible expanding the scope of these devices toward real-time monitoring of a wide range of contaminants. These advances include the introduction of modified electrodes and ultramicroelectrodes, the design of sophisticated biological and chemical recognition layers, molecular devices, and sensor arrays, and the developments in the area of microfabrication, as well as in technology of flow detectors and compact, low-powered, user-friendly instruments

- Remote monitoring of groundwater pollution using geoelectric techniques.[212] The use of surface geophysical techniques in hydrogeological investigations has become increasingly important. This has largely resulted from the increased interest in groundwater for domestic and industrial supply, and from the need to monitor freshwater aquifers for better protection of the resource. In particular, geoelectric techniques have been applied extensively for delineation of pollution plumes from point sources of contamination such as waste disposal landfills or effluent ponds. These techniques have also been used for recharge estimation,[213] in studies of salinity in dry climates,[212] in investigations of saline intrusion at coastal margins,[214] and for estimation of hydraulic properties of aquifers and sediments.[215]

Some of these studies have attempted to relate quantitatively the electrical conductivity (EC) of groundwater to formation resistivities that are determined in the field using surface geoelectric methods. If successful, one could avoid the need to drill extensive networks of observation boreholes for groundwater quality monitoring. Thus, potentially, these techniques offer a more efficient means of impact assessment when combined with a limited drilling investigation.

Literature reports a wide range of application of both DC-resistivity soundings and electromagnetic (EM) studies of pollution plumes.[216,217] It is clear that geoelectric soundings can be useful qualitatively (for example, in determining the approximate extent of groundwater pollution) if not quantitatively.

A range of techniques is available for investigation of groundwater quality in shallow aquifers. A comparison of such techniques as DC-resistivity sounding, magnetotellurics, ground-penetrating radar, and fixed frequency (FEM), and transient electromagnetic (TEM) sounding has been published[218]

- Remote spectroscopic monitoring systems. Following the history of spectroscopic remote sensing that started as early as 1963, it is possible to distinguish two approaches:[219]
  - Direct remote sensing when both the laser and the signal are used along an open (atmospheric) path
  - Indirect remote sensing, i.e., the laser or the signal is brought through fiber optics

First, direct remote techniques is described. More specifically, suitable devices employing a beam of optical, usually infrared or ultraviolet radiation, to detect the gas directly in the atmosphere[220–226] are discussed. Optical remote systems. utilize Raman scattering, fluorescence, or absorption as their measuring principle.[227] Classification of the optic remote measuring system is presented in Figure 4. The remote systems can be divided into active or passive, depending on whether the system contains its own source of radiation or relies on external emissions (such as from the sun). Active systems are currently used. They are generally set up to transmit a beam across the portion of air to be measured.

Remote systems can be classified as either monostatic or bistatic. In the monostatic configuration, the transmitter and the receiver are colocated, and either a topographic target (building wall, ground, vegetation), or atmospheric aerosols and molecules, or a retrore-

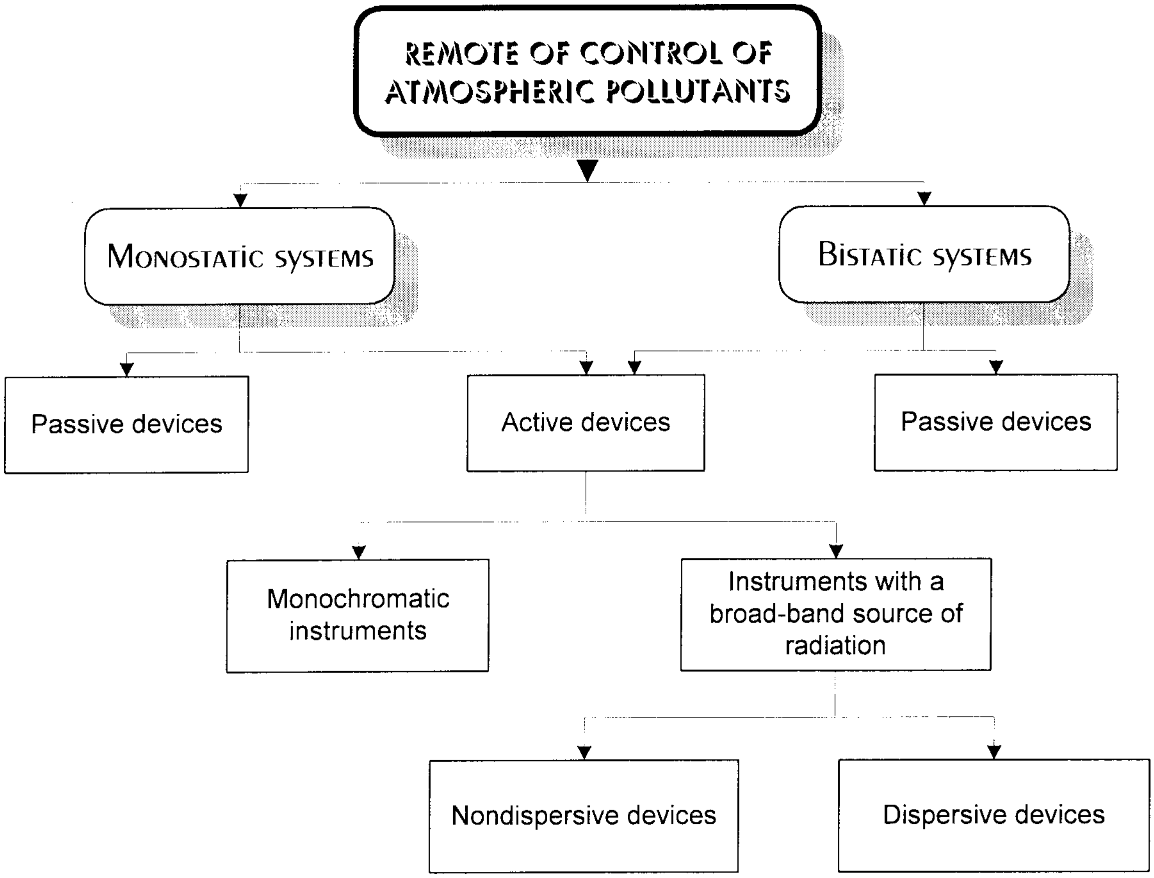

FIGURE 4. Classification of analytical instruments for remote control of atmospheric air pollutants.

flector may be used to reflect the transmitted radiation back to the receiver. In the bistatic configuration, a radiation source (transmitter) is placed at one location, with a sensor (receiver) at another location. The two location define the optical path. In this case, the monitor is an open-path optical instrument.[220-222] The active remote systems can be grouped into two different classes: those with a monochromatic source of radiation and those intentionally equipped with a broad-band source of radiation. The radiation source in the monochromatic instrument is a laser generating a very coherent, monochromatic light used as analytical beam.[223,224] Raman backscatter, resonance fluorescence, thermal radiation and resonance absorption principles have been evaluated by several researchers for use in air monitoring. Although resonance absorption requires retroreflectors or scatterers, instruments utilizing this principle can be operated at safe energy levels to provide high sensitivity over a large range. The principle has the further advantage of being the only method capable of detecting pollutants in their natural airborne state. Recent developments in microwave correlation laser spectroscopy indicate its high potential for measuring certain air pollutants without separating or sampling of the air. The unique spectral lines occurring at high microwave, ultraviolet, and infrared frequencies allow identification and measurement of air pollutants.

Broad-band instruments are subdivided into nondispersive and dispersive. Nondispersive devices do not contain diffraction elements splitting the radiation beam into discrete wavelengths; therefore, they are not specific and have only moderate sensitivity. Nondispersive analyzers have been designed to detect specific constituents of gases only. Concentrations of constituents of gas mixtures are derived from the intensities of incident R/VIS/UV radiation transmitted through paths in the gas mixtures.

Dispersive monitors are used to obtain more information about the absorption spectrum of the air. A more detailed shape of the spectrum can be achieved by means of a diffraction grating. Dispersive instruments (i.e., spectrometers) are speciifc but even at long path lengths their sensitivities are barely adequate to monitor the ambient air quality. Furthemore, they are complicated, fine, and expensive and are not readily utilized for continuous operation.

Very interesting examples of monostatic systems with a monochromatic source of radiation are **D**ifferential **A**dsorption **L**aser (**DAL**),[227] **L**aser **P**hotoacoustic **S**pectrometry (**PAS**),[228] Lidar,[223–236] and **Di**fferential **A**bsorption **L**idar (**DIAL**).[237–241]

Differential **A**bsorption **L**aser is a system in which two laser beams of different wavelengths are passed through a cloud of gas along the same path to a beam return target. If one wavelength is selected to be at the absorption maximum of the gas of interest and the second is a nonabsorbing wavelength, then the difference in absorptions of two returned beams is proportional to the amount of absorbing gas in the beam. Species quantification is possible if there are no interfering gases.

Lidar (**Li**ght **D**etection **a**nd **R**anging) 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.

Different Absorption Lidar (**DIAL**) is a system with a high-energy source of tuneable wavelength radiation. Two pulsed laser beams of different wavelengths are passed through a cloud of gas along the same path. If one wavelength is selected to be at the absorption maximum of the gas of interest and the second is a nonabsorbing wavelength, then the difference in absorptions of two returned beams is proportional to the amount of absorbing gas in the beam. Therefore, it is possible to measure pollutant concentration as a function of the distance from the source along the line of sight of the transmitted beam.

Because the air acts as a very inefficient reflective medium, a pulse source emitting radiation of high intensity and a sensitive detector are required to take accurate measurements. Appropriate sources and detectors are now available and the DIAL technique can be used to make measurements of the concentration profiles over a wide range of gaseous pollutants, i.e., from a few meters to one kilometer.

An example of a remote active system with the spectral broad-band source is OPSIS.[242] This system makes possible the measurement of more than 20 specific gaseous constituents in the beam of light between the transmitter and the receiver. This method is based on optical absorption measurements in the ultraviolet and near infrared range. The principle is known as differential absorption spectroscopy (**DOAS**).[234,238,241] In this case, the sky radiance is used as a distributed light source. Another technique that also employs diffused sky radiance is simultaneous **co**rrelation **spec**troscopy (**COSPEC**).[238,241]

Broad-band absorption yields little spectral structure and therefore it is difficult to differentiate it from scattering by water vapor and other particles. Furthermore, it is impossible to obtain a “clean gas reference spectrum”. Therefore, the DOAS technique takes into account the narrow-band structure and differential absorption, but ignores all broadband absorption.

The literature on the subject contains some information on another remote measuring technique called **Sodar** (**So**und **d**etection **a**nd **r**anging).[243] 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 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.

As mentioned earlier, there is a second approach in the field of remote sensing techniques, which is based on application of fiber optics. The development of fiber optical materials for long distance sensing provides an opportunity to avoid the significant limitations of conventional direct laser remote sensing. Fiber optics have revolutionized a number of fields including telecommunications, endoscopy and physical or chemical sensing. The fiber's flexibility, long-range transmission ability, broad bandwidth, small size and imaging capability allow a wide variety of design options.

Nowadays, fiber optical sensors are adapted to samples varying with respect to both analytes and matrices. Table 7 summarizes the major spectroscopic techniques suitable for fiber optical remote sensing.[219]

A specific example fo the practical application of different types of remote sensing techniques is oil spill observation.[244] Through the use of modern remote sensing instrumentation, oil can be monitored on the open ocean around the clock. With a knowledge of slick locations and movements, the response personnel can more effectively plan countermeasures in an effort to lessen the effects of the spill.

Work continues on extending the applicability of different remote sensing techniques.

9. *Visualization of Exposure*

The quality of air comprising the workplace, indoor, and outdoor environment has important consequences for our health and quality of life. Particularly in the workplace there is a risk of exposure to a wide range of potentially harmful gases and dusts. Preventive measures must be taken in order to minimize exposure. Such exposure is often associated with a specific work site and can vary both

TABLE 7
Techniques Suitable for Fiber Optical Remote Laser Sensing

Technique	Abbreviation	Analytical information
Laser-induced plasma spectroscopy	LIPS	Elemental composition
Laser induced fluoroscence spectroscopy	LIF	Native fluorosphores or fluorescent-labeled molecules
Raman spectroscopy	RS	Inorganic and organic vibrational structure
Laser photofragmentation	LPF	Luminescence from fragments
Photothermal spectroscopy	PTS	Inorganic and organic electronic and vibrational structure
Absorpotion spectroscopy	UV/VIS/NIR	As above

temporally and spatially. Engineering control (e.g., machine design, local exhaust ventilation) and hygiene measures (e.g., personal protection) can be employed to help reduce exposure. Thus, it is necessary to perform some form of workplace air monitoring to ascertain whether such preventive measures are necessary, and, if such measures already exist, whether they are effective.

Conventional measurement techniques, such as sampling followed by analysis and direct-reading instruments, when used in isolation cannot record all the information that is needed for an occupational hygienist (for example) to make an accurate assessment of the situation. However, an exposure visualization system[245–247,248] can help to resolve this problem. The 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. There are two basic systems of visualization:[245,248]

- A two-channel mixer based visualization system. A signal from the video camera filming the work activity and the analog signal from a fast response personal monitor are combined in a video mixer. The signal from the personal monitor is transmitted by radio telemetry to the receiver unit. The mixer displays the exposure measurements as a bar graph at the edge of the video image, the height of the bar being proportional to the exposure. The mixed picture is recorded on a video recorder and viewed on a TV screen
- A computer-based visualization system. This system is able to use the power and flexibility of a microcomputer for more advanced data processing and analysis. Here, the video mixer is replaced by a personal computer.

The information in this medium is presented in a highly comprehensible manner and the correlation between exposure and the work activity is clearly and visibly demonstrated. The video can be used to demonstrate sound working practices and helps to improve the worker's awareness of the potential risks present.

This technique has been used in a number of studies to identify the critical activities associated with high exposure to organic vapor or airborne dust. It can also be readily used for studying the human factors whenever it is important to demonstrate the correlation between physiological parameters, which characterize a work process, and exposure.[247–251]

10. *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 were described in papers published in 1997[252] and in 1998.[14]

Extensive use of GISs in the environmental field has been stimulated by expanding data resources.[253] As a result, global, regional, national, and local users have digital data available on toxic release inventory sites, air monitoring locations, areas unaccessible for air quality measurements, and current and proposed Superfund cleanup sites.[254] GIS is also proving to be useful tool for exploring relationships between geology, soil types, and the results of water-quality sampling from residential wells.[255]

FINAL REMARKS

We should realize that the discussion presented in this article 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 procedures used in analysis of environmental samples;
- Different levels of confidence the 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.

It should be stated here that, independently of the tendencies and developmental trends mentioned above, the tendency to satisfy Quality Assurance and Quality Control is observed also in the area of analytical chemistry.[256,257] Quality has become crucial in the social, economic, technical, and scientific fields. Despite the fact that the concept is as old as human activities, it has become a buzz word only in the last few years. Humans have always striven for exellence. Analytical chemistry as a chemical information science cannot evade this trend. Obtaining still greater amounts of chemical information of higher quality by using less material, time, and human and economic resources has been a major goal of analytical chemistry science the earliest chemical measurements were made.

Quality Assurance (QA) involves actions necessary to satisfactorily perform specific activities and to provide quality data as a results of such activities. Quality assurance is made up of three components, namely:[256]

- Quality Control (QC), which can be defined as a set of specific activities intended to facilitate achieving the analytical quality (organization, management, work, materials, instruments). From this point of view, not only the analytical laboratory, but also the results produced must be controlled
- Quality assessment, which encompasses a suite of specific operations performed by both the laboratory staff and the hired workers (quality audits) with a view of ensuring that quality control is done correctly and efficiently. In general, quality control is performed by laboratory staff and quality assessment by outside personnel
- Correcting activities which are obvious consequences of quality assessment and affect both QC activities and laboratory work, both of which must be adjusted in order to ensure that the results meet requirements in terms of the planned quality parameters

It is now widely accepted that there are three essential elements to laboratory quality assurance which assist the process of facilitating mutual recognition of results. These elements are:[258,259]

- Accreditation of EN 45000 (involving third party auditing)
- Use of validated analytical methods
- Participation in laboratory proficiency testing

There is an analogy between an analytical laboratory and a factory.[260] Samples go into an analytical laboratory—results and reports come out. Parts go into a factory—subassemblies and complete products come out. In an analytical laboratory managed in a modern way the same methods of management and control should be used as in the factory. As management tools one can use:[260]

- **L**aboratory **I**nformation **M**anaging **S**ystems—**LIMS**
- **P**erformance **E**valuation and **R**eview Technique—**PER**
- **C**ritical **P**ath **M**ethod—**CPM**
- Gantt charts

Project management methods are used to find slack in the system. Slack is the amount of time by which the actual completion of an activity can exceed the earliest expected completion time without delaying the overall goal. A laboratory manager might also be interested in deadtime and resource allocation. For example, studies in one laboratory reveal that in chemical extraction, TLC, clinical diagnostic GLC and colorimetric analyses direct labor or supervision is not required 60 to 75% of the total procedure time. An analyst's efficiency is increased if other tasks are scheduled for this time.

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