Some Aspects of the Contemporaneous Analytical Chemistry A Personal View

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The present state and some perspective trends and tasks of contemporaneous analytical chemistry are discussed and commented.

Analytical chemistry has naturally changed for several times its face and contents during the historical evolution of chemistry. Nowadays we are witnesses of a deep resurgence of analytical chemistry. An interdisciplinary science has been developed with close relations to metrology, chemometry, and information theory, with strong needs of mathematics, physics, electronics, computer and instrumental sciences.

Its position among chemical sciences is rather specific. No experimental chemical science can avoid analytical chemistry since it strongly contributes to the achievements and progress of these sciences. Analytical science, however, *vice versa* evidently needs a solid background of other chemical sciences, especially of physical chemistry and physics. Moreover, it seems sometimes the modern analytical science is often equally close to physics as to chemistry. Beyond all doubt analytical chemistry plays a significant role for the mankind today contributing to solution of many of its key problems. In contrast, the progress in analytical chemistry is considerably stimulated by the needs and problems in particular domains of man's activity such as protection of the environment, production of special technologies, investigation of resources, stimulated food production, the medical and life sciences on cellular basis, the space research, *etc.*

What Is Contemporaneous Analytical Chemistry?

The origin of analytical chemistry is usually attributed to *Boyle* in 1677 [1]. *Ostwald* [2] has laid down the theoretical principle of analytical chemistry but rather considered it as a kitchenmaid for other chemical branches. It is the matter of fact that in the last 35 years the analysts have been intensely thinking about the state, definition, contents, and tasks of analytical chemistry [*cf. e.g.* 4—11, 13—27, 29—32, 199, 237]. A simple and clear characterization of analytical chemistry comes from the Working Party of Analytical Chemistry of Federation of European Chemical Societies [238]. According to that analytical chemistry is a science that develops and applies methods, instruments, and strategies to obtain information on the composition and nature of matter in space and time. In agreement with chemometrics [3, 12, 28, 273], modern analytical chemistry deals with physical and chemical signals being produced during interaction with various kinds of energy in a stochastic system where signals are correlated to the composition and structure of matter. The appropriate evaluation and interpretation of analytical signals resulting during adequate treatment of the analyzed matter give a true and adequate chemical information. Thus, the theory of analytical chemistry decides what kind of chemical information can be deduced from the data being produced by analytical instruments and methods [199].

It is evident that the modern analytical science is close to the information science dealing with chemical and physical processes leading to true and relevant information about the composition and structure of the analyzed objects in gaseous, liquid or solid state in space and time. For this fact, optimal conditions of the methods and procedures and the optimal strategy of analytical approaches are carried out. Hence the optimization of conditions for using analytical methods and procedures as well as studies of processes running

in the system during the interaction with analytical methods or reagents also belong to analytical chemistry.

The interdisciplinary character of the contemporaneous analytical chemistry called up a discussion about a more proper name for this chemical specialization better corresponding with its actual contents and activities. Terms like Analytik, analytics, analytical sciences, analytika were suggested but no agreement has been attained among analysts.

Some Actual Trends in Analytical Chemistry

Inter alia 1. an intensive treatment of physical (instrumental) methods and the introduction of new special methods, *2.* introduction of new sophisticated, computerized and highly automated instrumentation for the analytical practice, *3.* development of effective softwares for operating and self-diagnostifying instruments and for the treatment and evaluation of analytical signals and data, *4.* automation and robotization of analytical operations and procedures to improve continual monitoring and decrease the human factor in the sample treatment, *5.* development of methods of the highest selectivity, sensitivity, accuracy, precision and detection power for analytes in complicated multicomponent systems, *6.* development of ultramicrotechniques for infinitesimal samples, belong to actual activities of analysts.

Some important contemporaneous tasks for analysts are *1.* the analytical treatment of mixtures of analytes containing a large number of organic analytes in complicated real samples, element speciations, metabolites, enantiomers or polymers, *2.* determination and monitoring of residual pollutants and drugs, *3.* determination of biochemically and biologically important substances on the cellular level, *4.* development of sensors and biosensors, analyzers and robots (*cf.* also [32]), *5.* use of hyphenated procedures for elements and compounds such as ICP-MS, GD-MS, GC-MS, GC-FTIR, GC-MIP, HPLC-ICP, HPLC-AAS, HPLC-MS, HPLC-ICP-MS, *6.* development of highly effective chromatographic and electromigration methods for complicated mixtures of analytes in real systems, *7* analytical monitoring of cell and life processes, *8.* analytical problems in high-technology production, semiconductor technics and electronics, *9.* surface and thin-layer analysis, *10.* analysis of remote objects, *11.* ultratrace analysis, *12.* validation and harmonization of analytical methods, techniques, and procedures, processes for total quality control and quality assurance, accreditation of analytical laboratories, *13.* analyses in flow systems with selective membrane separations and multivariate detectors, *14.* new approaches in pretreatment of mineral, biological, and clinical samples. Thus, contemporaneous achievements in analytical chemistry reflect problems of the real world to be solved and the present state of the analytical tools to be used for solving them.

In this paper our opinions are given about the state of art and trends of selected analytical topics and tools suitable for solving actual analytical problems of the contemporaneous world.

Analytical Aspects of Metal Complex Equilibria in Solutions and Organic Analytical Reagents – Withdrawal of Glory?

For many years, studies of analytically interesting complex equilibria in solutions have been an important part of analytical research. Complicated equilibria in solutions during metal ion hydrolysis or interaction of analytes with reagents have been discovered by using spectrophotometric (UV VIS) and potentiometric measurements with subsequent graphical and numerical interpretation. Sophisticated computer programs have been developed for the evaluation of data based on different minimization of least squares procedures or some numerical differentiation using iteration procedures. Such approaches enabled to find all significant equilibria of the analyte in the studied system and to evaluate stability and equilibrium constants and other valuable parameters of the species for broad experimental conditions [186—188, 213, 214, 226]. Hence the conditions for an optimal complex species were selected and used as basis for spectrophotometric determination of particular element [215]. Moreover, the knowledge of chemical equilibria in solution has also been suitable for explaining errors or chemical interferences in the course of various instrumental methods.

Organic analytical reagents have been critically evaluated and a selected number of them recommended as selective analytical reagents and reagents for sensitive spectrophotometric and fluorimetric determination of elements, for the adsorption voltamperometry of traces of elements, for monitoring of inorganic pollutants but also as modifiers in FAAS and ET-AAS. Especially useful are such reagents for the preconcentration of element traces on modified and nonmodified sorbents, during liquid-liquid extraction, or within inorganic HPLC, IC or capillary zonal electrophoresis [189—194, 227, 272, 286].

General Characteristics of Instrumental Methods

Despite of their universal use the instrumental analytical methods are usually relative methods. Highly efficient computer software contributes to the formation of true calibration functions and correction terms for elimination of chemical and instrumental interferences providing reliable standards are available. The absolutization of such methods, free of calibration functions or standards and realized by direct calculation of unknown analyte concentration, sensitivity

and limits of particular signals and basic physical and chemical constants, is still an actual problem. It requests to know all processes and reactions joint with the applied method including equilibrium constants and values of particular parameters of all chemical and physical processes. This is particularly difficult if the sample must be transformed into the plasmatic state or when unknown mutual interactions between the analyte and matrix take place in complicated samples. The sampling matrix and the sampling itself may be sources of serious problems during evaluation of analytical signals. Recently promising results with regard to absolutization were obtained for AAS [162, 165].

Important paradigms of each analytical method or approach are the precision, accuracy or trueness, robustness, sensitivity, detection or determination limits, traceability, and selectivity. With respect to them the analytical approaches are validated in the frame of total quality control, GLP, and laboratory accreditation. Moreover, studies of chemical equilibria and physical and chemical processes should be, of course, an important part of such validation.

The detection and determination limit of analytical methods or approaches are still matter of discussion in spite of IUPAC recommendations [51, 97—99, 155]. For an instrumental method, these limits are influenced by the detector system, the precision and accuracy of measurements of analytical signals, the actual signal-to-noise ratio, and the noise and drift fluctuations. For chemical reactions, these parameters are limited by reaction thermodynamics and kinetics in extremely diluted solutions. In general, experimental conditions, matrix composition, the quality and technical level of the used instrument and the statistical approach for the data treatment considerably influence the above parameters. The limits are accessible from parallel measurements, calibration functions or plots of the relative standard deviation *vs.* analyte concentration [52, 100, 243, 244].

For the selectivity of analytical reagents, reactions or methods, the quantification or evaluation is a problem especially for complicated mixtures of analytes. The selectivity problem is closely joint to chemical and physical interferences among analytes and the resolution power for analytical signals of the particular method and instrument. The nonselectivity causes usually systematic errors during the determination of analytes. In fact, the contribution of signals of accompanying species to the analyte signal estimates the selectivity or nonselectivity degree and is described by different terms with respect to the particular interfering component [101, 102]. The coordination selectivity characterizes the complexing agent against the particular element and depends on the function-analytical group of donor atoms in the reagent, the structure of reagent, the bond type involved between the analyte and the reagent, and the structure and the physical properties of the complex formed. The problem of the selectivity can be solved mathematically *via* calibration matrices or multicomponent multivariate approaches using sophisticated computing software [103—107, 110—112]. However, mathematical expressions for selectivity are usually not sufficiently transparent and have not been currently accepted in practice. In fact, no unified concept of selectivity exists as yet [113].

Electroanalytical Methods – Steady State of Art

No new fundamental trends are observed in electroanalytical chemistry at present. On the other hand, electrochemical automated sensors or biosensors are of particular significance for monitoring the environment, biological, clinical, and industrial systems. A steady analytical attention has been paid to widely spread voltamperometric, potentiometric, and coulometric methods and the development and application of new ISE. The familiar classical polarography has receded into shadow but can be still very useful in organic analysis, for studies of biologically active compounds, drugs and toxic metal species, and for post-column detection of analytes [311]. Various developed techniques, especially the inversion (stripping) and pulse voltammetric approaches are currently applied with a mercury dropping and hanging or glassy carbon electrodes in inorganic trace analysis because of its high detection power for elements. Recently, various kinds of adsorption stripping voltammetry based on metal complexes with organic reagents or various organics were successfully used in trace analysis [245, 246, 312]. Unfortunately the substitution of toxic mercury electrode by carbon was not successful. Carbon paste electrodes have become more perspective as selective sensors [229, 230]. For many years the development and application of ISE has been the object of intense electrochemical research. Recently an excellent survey has been written on ISE, their theory and application [59]. Special attention is paid to electrode miniaturization, development of both, microelectronics and membrane ion-selective technology, to the search for suitable CHEMFET and ISFET sensors and microelectrode arrays. Voltammetric and ISE may also be perspective for monitoring processes in living organs when suitable microelectrodes have been implanted [59, 231] or for the differentiation among element speciations, complexes, and free ions in the aquatic system [75, 76, 232—234].

Molecular Absorption Spectrophotometry (UV VIS) – No Principal Novelties

Nowadays no principal invention is observed ex-

cept of considerable improvements in instrumentation. Standard procedures and the easily accessible instrumentation make this method highly reliable, fast and broadly spread in routine analytical laboratories dealing with organic, biochemical, biological or clinical analytes, food and environmental analysis. Increased attention has been paid to UV- and far UV-spectrophotometry, the multicomponent multivariate analysis, derivative spectrophotometry or to studies of kinetics and fast reactions in biochemically active systems. UV VIS spectrophotometry in various types of flow cells is frequently used for monitoring analytes in flow systems, column chromatographies or electromigration.

The analytical use of photoacoustic spectrometry [247] is far from previous expectations. Some positive significance is only for measurements in highly concentrated, colloid, turbid solutions producing high absorbances.

Spectrometry of Atoms and Ions – New Challenges

The spectrometry of atoms and ions in gaseous and plasmatic state after various kinds of atomization and ionization of elements or molecules represents main contemporaneous trends for the multielemental determination of elements leading to extremal detection limits.

The *atomic absorption spectrometry* (AAS) has reached its development top and is widely used in contemporaneous laboratories [159, 160]. At present ET-AAS and HG-AAS are the prevailing techniques for the determination of trace elements and their speciations. For the simultaneous determination of elements with ET-AAS in several channels, the temperature and time gradients belonging to particular elements had to be averaged among optimal conditions and for wavelengths with no spectral interferences [164]. Unfortunately, there is no true multicomponent application of AAS. Recently an enormous effort has been spent in order to develop chemical modifiers the effect of which during AAS processes is multinumerous [167, 168]. The degree of atomization of element is increased, the matrix effects decreased, the overlapping of particular sample steps avoided or their sequence changed in the course of ET-AAS. The transversally heated graphite cuvette with an integrated platform of pyrolytic carbon is an effective innovation in AA-spectrometers. In such case the matrix effect is diminished and the uniformity of the sample evaporation improved [153, 154, 166]. Graphite atomizers are still perspective because of increased degree of atomization but tungsten atomizers have also been successfully used in argon—hydrogen gas mixtures for the atomization of elements forming thermostable carbides [313]. The present state of ET-AAS in graphite furnaces has been commented recently [163]. Studies in sampling of microamounts or microvolumes, slurry sampling or sampling of filter fragments or suspensions are getting more popular [248, 282, 283]. The simple Zeeman splitting of absorption lines in longitudinal or transversal magnetic fields is assumed to be the best way for the elimination of high background for biological and clinical samples [171, 181—184]. The elimination or decrease of considerable background is an important task for the ET-AAS in the trace analysis [161]. Moreover, various kinds of on-line preconcentration of elements using semi-permeable membranes or special probes and discs are now recommended (*e.g.* [249, 268]). A current interest is paid to procedures with volatile hydrides of elements. The previous preconcentration of the hydride under liquid nitrogen and its decomposition in a graphite furnace or heated fused silica tubing prior to determination is most often recommended [129, 170, 250].

An effective emission of atoms in the graphite furnace may be achieved under glow discharge (GD) at reduced pressure and 2100—2700 K in the presence of argon (*furnace atomic nonthermal emission spectrometry*, FANES) [156, 157]. A high-resolution spectrometer must be, however, combined with the furnace to eliminate the considerable background. Ions and oxide molecules are also partly excited in the gaseous state [157]. Unfortunately, the use of this technique in practice is rather limited.

The present state and contemporaneous trends in *emission plasma spectrometry* are discussed by *Boumans* [61], *Hieftje* [71, 148], *Brockaert* [147], and *Varma* [251]. The dominant technique is the radiofrequency induction coupled argon plasma (ICP) (27—60 MHz) combined with a high resolution echelle grating spectrometer, the perpendicular prisma separator of wavelength orders, and silicon plane CCD or CID detector [158]. In fact, ICP spectrometry is a widely used routine technique based today on a rich and sophisticated instrumentation. Studies of conditions for optimal plasma production, sample nebulization, transportation phenomena, and the topography of plasma with regard to sensitivity and the origin of chemical and spectral interferences are, however, still actual and intensely followed. The main advantage of this technique is to realize fast and sufficiently sensitive multicomponent determination of elements where calibration functions are linear over a wide concentration level [149, 150] and the detection limits are in the $\mu g/cm^3$—ng/cm^3 level. Pneumatic and ultrasonic nebulizers are still widely used but other ways of sample introduction into the plasma such as microwave or graphite furnace desolvation or laser ablation have got attention at present. The previous hydride formation is also readily used for the ICP determination of a couple of elements. On the other hand, *direct current plasma* (DCP) is scarcely used although its properties and detection limits are similar to ICP but higher backgrounds were observed. It is worth to mention

that the plasma spectrometry is still not free from insufficiencies. Residual matrix and spectral interferences, signal fluctuations for various nebulizers and spray chambers, plasma tailing and inhomogeneous zones, insufficient acquisition of the signals against internal standards and the mutual interferences in mixtures of analytes can introduce errors [71].

The *induction coupled helium or argon microwave plasma* at reduced or atmospheric pressures is highly suitable as element specific detector in combination with GC, when element speciations are studied. The plasma production in capillaries is of great advantage for gaseous microsample analysis [252—254]. Traces of metals may also be determined by microwave plasma spectrometry after electrothermal vaporization of sample solution in argon [287]. The *capacity coupled microwave plasma* is less often used in spite of the fact that it can be operated with higher power, the plasma burner has a robust construction and water vapours make little troubles. The spectra have, however, higher background and spectral interferences appear [145, 146]. The combination of a graphite furnace with the capacity coupled plasma torch (argon or helium) at atmospheric pressure may be useful for elemental analysis even in the form of monoxides or monohalogenides [151] but is not commonly used.

On the other hand, the significance of the *glow discharge spectrometry* (GD) [294] is still underestimated especially with respect to the bulk analysis. The discharges at reduced pressure (10 kPa) are highly effective for the excitation and ionization of atoms because of the high electron temperature of the excited atoms against neutral atoms. Especially pulsed microsecond discharge gives intensive atomic spectra [145, 152].

In contrast, the production in metallurgical industry is almost exclusively controlled by *automatic emission* (UV VIS) and *X-ray spectrometers*. The UV VIS spectrometers have Paschen—Runge gratings of high resolution power, semiconductor or photoelectric detectors and use electric discharges for excitation and ionization of atoms. Unfortunately, UV VIS spectrographs containing photographic plates as multicomponent detector practically disappeared from analytical laboratories.

X-Ray emission (fluorescence) spectrometry holds its position among most important methods for multielemental analysis of main and subsidiary elements in samples of various consistence usually without previous destruction. Complicated mathematical expression enables to manage the increased mutual influence of components in the sample and introduce corrections during the signal evaluation. The method of fundamental parameters successfully competes with those using internal standards for evaluation. Automated multicomponent X-rays spectrometers prevail for monitoring the production in metallurgical industry. The absolute detection power reaches its optimum value (0.1 μg) for elements around the atomic number 30. Energodispersive X-ray spectrometers with highly resolving multichannel analyzer of X-ray energies and powerful computer begin to predominate in laboratories. Complicated phenomena are involved during interaction of accelerated particles such as protons, deuterons or He^+ (E = 1.0—2.5 MeV) with the sample, *i.e.* Rutherford backscattering (RBS) and X-rays or gamma-rays which are detected with semiconductor detectors. Signals are then evaluated by computer and corrected against scattered particles or radiation. RBS gives information about the surface composition and structure of sample. *Proton induced X-ray spectrometry* (PIXE) is suitable to detect less than 1 p.p.m. of elements in 10 mg of sample. When the proton beam is readily focused to 1 μm, traces of elements (pg, fg) are detectable [172, 176]. Such a proton microprobe is able to analyze aerosols, ashes or biomedical samples on the cellular level.

The *total reflection X-ray spectrometry* (TXRF) is a new perspective variant of energodispersive X-ray spectrometry. Traces of several elements can be determined on a silica plate covered by a homogeneous film of the sample. The matrix or Compton effects are not observed in this case and the detection power is 1000 times higher than with the conventional energodispersive technique. Remarkable results were obtained for histological cuts of clinical or biological samples [177—179]. For some new X-ray techniques with analytical perspective *cf.* [175, 180].

Instruments for *electron spectrometry* such as *photoelectron spectrometry* (ESCA) [173], *Auger spectrometry* [174], *Auger microprobe* combined with *electron* [314], *proton, laser* [89], and *ion microprobes* (SIMS) belong to the standard but expensive equipments of an analytical laboratory dealing with surface and thin-layer analyses [185].

Some Analytical Aspects of Lasers

The introduction of lasers into analytical chemistry has deeply influenced not only the instrumentation but also the effectivity of particular spectrometric methods. Moreover, new methods with extremely high detection power for atoms in gaseous state and organic molecules in solution were created. Besides of commonly used Nd-glass, Nd-YAG, nitrogen, excimer or dye lasers for UV, VIS and near IR, semiconductor *diode* lasers arose particular interest recently [255].

Laser ionization resonance spectrometry with selective laser pulses (RIS) is a special tool for the detection of a low number of atoms in gaseous state [128, 135, 136]. The identification of a single Cs atom in a GM chamber filled with inert gas under reduced pressure is rather of academic significance [128]. Various methods and problems with the indication of a single atom or several atoms have been compared and discussed [137]. The disadvantage for RIS is the necessity of using several lasers producing radiations cor-

responding with the transition energies between the atom, excited and ionized atom as well as the detection of various ions in more complicated systems. In such case, however, the ions formed can be suitably identified by means of an on-line mass spectrometer (RIMS) [127].

The *laser enhanced ionization* (LEI) where laser-excited atoms are ionized by additional collision phenomena in flames, by inert gas atoms (argon), in a thermoionic diode at increased temperature [256] or in a low-energy plasma [257] has more practical use. The method is suitable for several more volatile elements including alkali metals and some transition elements in extremely low concentrations (10^2—10^4 atoms/cm^3) in the presence of inert gas excess [130—132].

Analytically promising is the *laser induced fluorescence* (LIF) in flames [259], graphite furnace [258], low power ICP plasma [141, 257] or GD [142]. Of special interest is the nonresonance fluorescence produced by excited atoms being involved, *e.g.* in collisions with atoms of inert gases (SONRES). For such case the scattering of radiation is mostly eliminated and excellent detection limits are obtained for elements. On the other hand, several metastable levels under the main level in the excited atom readily influence the transition kinetics of the electron and the detection limit for the element dramatically decreases. Elements with increased excitation potential (Se, As, Cd, Zn, Hg) give excellent detection limits. The furnace technique is especially suitable for improving the detection limit to the pg/cm^3 level [138—141].

A *multiphoton soft ionization of molecules* by using laser radiation is remarkable for detecting aromatic polycyclic hydrocarbons. Solutions in alkanes are used and the ionization is followed between two electrodes of the photoionization cell during laser radiation at laboratory temperature. If several lasers with various wavelengths are used extremal detection limits are observed [133, 134].

Single large molecule in solutions can be detected in submicrometer channel prepared by drawing out electrophoresis capillaries where the Brownian motion is reduced. The molecule was moved into the detection capillary by electrokinetic force. The involved fluorescence of a rhodamine associate of such molecule can be observed by a confocal fluorescence microscope [288].

MALDI-TOF is a perspective tool for the characterization of large molecules such as polypeptides, small proteins, nucleic acids, organic polymers and biopolymers, but also of small molecules. When using UV VIS laser pulses a volatilization, degradation, and ionization of molecules take place in the presence of suitable matrices or co-matrices which lower the energy of laser pulse by absorption [124—126]. This method has a high detection power but it is still in development. Possible complications take place because of the decrease of the point-to-point repeatability, the sample-to-sample reproducibility, laser shot-to-shot repeatability and local concentration changes in the sample during interaction with the laser beam. A good experience is demanded for the selection of suitable matrix or co-matrices and during the evaluation of the mass spectrum from the reflectron TOF spectrometer. The quantification of results is rather difficult since nonhomogeneities of sample can appear during the co-deposition of the matrix, the low shot-to-shot repeatability and the nonlinearity of the calibration function. Moreover, the signal of the minor component of the sample may be decreased in the presence of the matrix excess. The commonly used method of internal standard may be influenced by the insufficient mass resolution of the mass spectrometer used, when an isotopically labeled standard is used [123—126, 143].

The absorption of laser radiation in solutions is scarcely used in the analytical practice. Increased attention has been paid to the *thermal lensing spectrometry* in suitable solvents [144, 145]. This method enables to measure extremely low absorbances in extremely diluted solutions of the absorbing species but no decomposition of such species must take place. Moreover, no commercial instruments are available on the market.

Analytical Aspects of Mass Spectrometry

Mass spectrometry (MS) of inorganic and organic ions bestows the direct and absolute detection or determination of species in trace and ultratrace amount. In spite of limited resolution power quadrupole mass spectrometers prevail in the analytical practice but an increased attention is paid to the reflectron time-of-flight (TOF) spectrometers and to the ion trap. The analytical efficiency of MS is influenced by the kind of sampling and ionization process. The detection power for analytes currently concerns picograms or even femtograms or zeptomoles in special cases. The TOF MS or ion trap joined with MALDI or laser microprobe is particularly used for the identification of large biomolecules. The quadrupole ion trap has been widely proved for the storage of ions previously obtained by electron impact ionization, chemical ionization, laser photoionization or other soft ionization techniques [115—117]. For organic species the electron capture – negative chemical ionization technique and the production of negatively charged ions are of particular importance [260]. The tandem MS-MS or generally MS^n gave remarkable results for environmental, pharmaceutical, drug analysis or peptide sequencing because of its extreme detecting power (pg—fg/g or cm^3). In the first stage of MS^n the precursor ion is selected, in the second MS stage the fragments or products of the precursor are separated and detected. The dissociation or splitting of the precursor is done by collisions with inert gas atoms in the interface between both MS stages [114, 121]. The intro-

duction of ion traps offers new challenges to MS/MS device such as the differentiation in time for particular steps. In the first step only the parent ions are stored in the trap which are then dissociated by collisions and finally purged into the detector and the daughter ions are scanned. Such process can be repeated in the next step where selected daughter ions become parent ions for the succeeding new dissociation. The collision among ions and neutral molecules leading to imperfect and nonreproducible spectra is partly eliminated in the ion trap of new generation. The ionization is realized in an external source under standard conditions and a suitable amount of ions are introduced by pulses into the trap. A special course of electrodes potential enables to expel all ions from the trap except of the parent ones which are then submitted to dissociation in a further MS/MS experiment [205]. Several ionization techniques are available today for the elemental MS in multicomponent systems, *i.e.* ICP, GD, MIP, the sputter neutral atom technique with high-frequency discharge, the thermoionic source, graphite furnace or laser ablation of gaseous atoms to be subsequently ionized [116]. Increased attention has been paid to the various modes of direct sample insertion in the electron impact ionization chamber. Hydrophobic membranes, *e.g.* from dimethylpolysiloxane are mentioned in this connection [317].

Especially effective is the on-line hyphenation of MS with some instrumental and separation systems such as ICP, GD, laser or graphite furnace for the determination of elements in various speciations, or GC, HPLC or CZE for the determination of organics [261]. Sophisticated interfaces are necessary when complicated organic, biological or environmental samples are analyzed. Laser ablation and laser microprobe coupled with a reflectron time-of-flight spectrometer are highly effective tools for trace analyses of solid samples and surfaces [89].

ICP-MS is doubtless the most often used method for trace multielemental analysis often considered an approach with the highest detection power for elements. It is realized by a coupling of ICP supplied with a horizontal burner with a quadrupole or time-of-flight mass spectrometer. Using some suitable instrumentation even both, the m/z^+ ion characteristics and the emitted radiation of selected wavelength could be simultaneously recorded in perpendicular direction. The calibration plots are usually linear over 6—7 concentration orders and the detection limit in ng—pg/cm^3. The internal standardization by isotopes is suitable for the evaluation of signals. Unfortunately, even this method is still not free from matrix and spectral interferences and signal drifts which may cause deviations in reproducibility. Since the signal fluctuations may be fast enough they may influence results for time-dependent and transient samples. The use of TOF spectrometer instead of quadrupole one seems to be more suitable for the on-line coupling with ICP [33].

The hyphenation of capillary GC with MS is currently used for the determination of volatile organic components in complicated mixtures and matrices. Matrix interferences may appear when mass spectrometers of limited resolution power are used. In such case the use of GC-MS-MS is more economical than the use of high-resolution MS [121] but the detection limits are decreased.

At present, the hyphenated HPLC-MS is currently used. This combination, however, requires more complicated interfaces to remove the opulent mobile phase, to transform the organic species in the gaseous phase to ions and to involve a soft ionization technique for organic molecules. In addition, the transition from the atmospheric pressure for the chromatographic mobile phase to the high vacuum of the mass spectrometer (10^{-2} Pa or less, depending on the length of flight) must be realized. From various ionization techniques the electrospray with APCI is probably the most perspective technique used today which softly give positive or negative ions of organic molecules and is suitable for the determination of element speciations, metabolites, and large biochemical molecules [118—120].

Chromatographic Techniques – Large Field of Analytical Application

The capillary gas chromatography (GC) based on sophisticated instrumental technique with a choice of a great number of detectors and element specific detectors has reached its top of development and is currently used as standard technique for the analysis of complicated mixtures of organics, element speciations, drugs and residuals of suitable volatility in environmental, biological or clinical samples. The status, trends, significance, challenges, and limitations were frequently reviewed in literature [62, 63, 204, 218, 262, 305]. It is a recognized method of the first choice for the analyst when faced against complicated samples. Moreover, hyphenated systems such as GC-MS, GC-MIP or GC-FTIR enlarge the capability of this technique for the identification and determination of organics and organometallic species in complicated mixtures [79, 81].

On the other hand, the HPLC is the prevailing separation technique for nonvolatile organics, drugs, metabolites or toxic residuals and element speciations using isocratic and gradient elution being still in progress [306, 308]. The RP-HPLC, ion-pair HPLC, ion, ion-exchange HPLC or sometimes size exclusion chromatography [307] are currently used and developed in practice. The HPLC based on ion exchange, chelate formation, and ion interactions is highly suitable for the separation and determination of inorganic species or ions [303, 304]. Nowadays, a special attention is paid to the separation of enantiomers or stereoisomers and the separation of complicated mix-

tures of organics [218, 219, 310]. The post-column mass spectrometry is the most powerful detection technique but other detection modules or principles are developed for separated organic species including post-column reaction detectors, post-column derivation or pyrolysis. Element-selective detectors such as AA-, ISP-, and mass spectrometers are hyphenated and frequently used for the determination of element speciations of different toxicity or biological activity in the atmosphere, aquatic system, food, biological material [79—81]. In the environment, the chromatographic studies are often combined with various voltamperometric approaches and ion exchange studies with the aim to differentiate free ions and complex species [75, 76, 232—234] since the total elemental analysis loses significance at present [77, 78]. The supercritical fluid chromatography in capillary columns [82, 88, 309] combines the advantages and disadvantages of both, the GC and HPLC and is occasionally used but no principal breakthrough is expected. The HPLC in microbore and capillary columns packed with hydrophobic sorbents and with various post-column detection techniques is another useful mode of the HPLC [197, 270, 271, 274]. Various modes of ion chromatography (IC) using conductivity, spectrophotometric or post-column reaction detectors are versatile and sensitive approaches for the determination of a variety of cations and anions on the trace level and in complicated mixtures [83—85, 90, 272, 277, 302]. Especially for the separation and identification of mixtures of anions this approach successfully competes with the capillary zonal electrophoresis.

There are still discussions about processes on the boundary sorbent surface—mobile phase, the influence of mobile phase composition and the properties of the sorbent in various variants of HPLC [289, 290], which, however, does not hinder the broad application of HPLC. The retention of analytes on the sorbent is in general the result of complicated chromatographic and electrokinetic interactions on the boundary sorbent—mobile phase. The structure of chemical double layer and the zeta-potential on this boundary is without doubt of essential significance. Thus, the ion-pair retention and the dynamic ion-exchange models bear parallel upon the RP-HPLC in the presence of ion-pair agents. The dynamic modification of hydrophobic sorbent surface by anionic and cationic surfactants is shared successfully by processes in ion chromatography (IC) [87, 275, 276]. The presence of micelles in the mobile phase also influences the processes on the column [216, 217] and enhances sometimes the separation of organic analytes.

In general, the information power of column chromatographic techniques resulting in opulent sets of peaks may for complicated real samples often overpass our capability to evaluate chromatographic peaks qualitatively and quantitatively owing to the lack of suitable and reliable standards.

A real boom has been recorded for methods based on *electromigration in capillaries* [47, 58, 72, 86, 206, 297, 301], especially *capillary zonal electrophoresis* (CZE) and its different modes [91, 92, 96], such as *capillary electrochromatography* [86, 241] or micellar *electrokinetic capillary chromatography* [291], *isotachophoresis* (ITP) [93, 210, 211, 298] or *capillary isoelectrical focusing* (IEF) [292]. CZE can be applied in a high extent for the separation of organics, biologically and therapeutically active substances, element speciation, complexes and free ions but also large charged molecules and chiral compounds in the presence of chiral selectors [94]. Moreover, capillary electrophoresis has recently attracted considerable attention for metal ions separation, especially in the form of complexes [318].

The successful application comes from extraordinarily high separation efficiency of this method, from the use of microsamples, the speed of analysis, the high degree of automation of commercially available instruments with variable detectors, and the use of various sampling techniques. The sensitivity of the method is increased after developing new detection principles. The speed of CZE is highly appreciated in comparison with other electromigration techniques. The present studies of this technique are concentrated on the validation of procedures, selection of background electrolyte and processes on the surface of electrolyte-modified or bare fused silica capillaries. Selectivity can be improved in the presence of micelles, chiral selectors and nonaqueous medium [296]. Problems may be joined with deviations in reproducibility of subsequent electrophoreses, the influence of sample matrix, increased ionic strength, high excess of electrolytes in the sample, high concentration of background components, and the complicated phenomena on the surface of fused silica capillary. Unfortunately, the resolution of CZE decreases considerably during the separation of large molecules and biomolecules. CZE-MS using electrospray as evaporating and ionizing medium or ITP-MS [154] have not yet been widely accepted in routine analysis but are promising for the near future [60, 293, 295]. A couple of years the interest of capillary electrophoresis has been focused on metal and nonmetal ions, especially in the form of complexes and anions [227, 286, 299] which competes successfully with the ion chromatography [300]. Comparing with HPLC, the latter technique enables to separate analytes on the basis of molecular interactions with the sorbent surface but the migration of charged particles is essential in the CZE.

The research interest for the popular ITP declined at present but the method is still frequently used in practice. Remarkable is the combination of CZE with ITP, especially for complicated sample matrices or in the presence of a bulk of inorganic substances. ITP differentiates the sample into several zones and the subsequent CZE com-

pletes the analysis of microcomponents [207, 263, 264, 278].

Remarkable results were obtained for capillary electrophoresis with continuous pH or mobility gradients concerning isoelectrical focusation (IEF) and isotachophoretic focusation regarding the separation of large and biochemically important molecules in complicated mixtures. In addition tapered capillaries were used for the capillary electrophoreses. The resolution of particular peaks is highly improved by suitable pH and mobility gradients with weak and strong electrolytes. During continuous gradient ITP the analyte concentration in the focused Gaussian zones increases approximately by two orders compared to CZE which improves the actual identification limit [208, 209, 212].

Flow Systems in the Analytical Practice

The well proved principle of *flow injection analysis* (FIA) [34—36] is widely used and has reached the top of development in combination with various detection systems or principles, combined reactions in the flow and various separation, preconcentration or pyrolytic modules. FIA is based on a controlled dispersion of the formed analyte species in a continuous flow which leads to narrow and reproducible analyte zones. For this fact, defined experimental conditions, laminar flow and reproducible concentration profiles of the injected sample are obligatory. Combinations of detectors or hyphenated systems such as diode array, FIA-FAAS, FIA-ICP-AES or FIA-ET-AAS are currently used. The hyphenation with the first two methods is rather familiar today but the combination with ET-AAS may bring technical obstacles and requires several operational stages [169]. Mixed reagents in multicomponent FIA and evaluation by multichannel diode array detector with suitable computer software have been one of the trends for metal microanalysis [319]. Separation or preconcentration modules were also inserted into the flow, *e.g.* membrane separation, separation microcolumns with ion exchanger or sorbents or liquid-liquid extraction separators [37—40]. The flow analysis is indispensable for continuous monitoring by using sensors or membranes or for the application of hyphenated systems or for laboratories with a large number of samples.

Extended Chemometrical Approach

Detailed statistical approaches or more complicated chemometrical procedures were developed for the treatment and evaluation of analytical signals and the diagnostics of analytical errors, for the formation of calibration functions and testing of analytical standards and reference materials. This is supported by the explosion of data created by the high resolving power of contemporaneous instruments and by the easily accessible computation technique. Various computation approaches and softwares are now available to use linear and nonlinear multicomponent multivariate calibration [68,108, 109, 315]. Moreover, complicated chemometrical approaches are used for solving analytical problems of samples from the real world [28, 67, 225]. For cases where calibration functions cannot be created, chemometrics offers special approaches such as pattern recognition, cluster analysis, partial least-squares (PLS) approximations, fuzzy logic or artificial neural networks [64—66]. Fuzzy logic may be used for an undefined set of data as well as to express the degree of trueness of available data or to decide the membership of an item to a set of data for solving *e.g.* the calibration with signals or analyte concentrations at some level of error. Broadly applied artificial neural networks simulate the function of the human brain looking for the kind of heteroassociation between the input and output pattern in a sometimes complicated mathematical way, *e.g.* optimal parameters without any knowledge about the relationships among the patterns. Artificial neural networks can recognize similarities among objects, classify them and transform complicated relations into simpler presentation without losing any information. No *a priori* knowledge about the rules governing the phenomena being studied is necessary. Applications of such networks are now currently done in spectrometry, chromatography, ion-selective electrodes, capillary electrophoresis, *etc.* With artificial neural networks the optimal conditions for analytical reactions or methods can be reached more reliably and efficiently than with single variable approach or with the trial-and-error approach commonly used in practice. The artificial neural networks may also be used for pattern recognition, modelling and prediction, process control and multicomponent analysis [224]. The application of neural network replaced in fact simple optimization procedures such as simplex or the method of the steepest ascent [69, 70]. The last two chemometrical approaches enable to develop and apply expert systems for automatic interpretation of analyses using particular methods [20].

Samples and Sampling – the Everlasting Source of Problems

The sampling in the real world and sample treatment have been underestimated for a long time although they usually introduce a considerable extent of uncertainty and significant errors into analytical results. Although rigorous regulations, automation and robotics were recently introduced into the sampling process, the strategy and theory of sampling call for steady attention [56, 57].

The decomposition and solubilization of complex mineral and biological samples often produce considerable errors in trace elemental analysis, coming from incomplete sample decomposition, contamination, and volatilization of elements. Increased atten-

tion has been especially paid to the decomposition of mineral and biological samples in microwave oven in open air or closed system. Melting, burning, and wet decomposition remain still among the main decomposition procedures. The wet chemical decomposition in high-pressure-ashers or dry decomposition in cool-plasma-asher, *e.g.* under high-frequency low-pressure oxygen plasma at elevated temperature are commonly used for biological samples [46, 48—50, 198].

In spite of many special approaches for sample decomposition classical wet decomposition more or less prevails in open or pressurized systems under focused or nonfocused microwaves.

The isolation or separation of residual organics from composed samples remains a delicate problem. The combination of liquid and solid phase extractions, various kinds of volatilization, or subboiling distillation belong to the commonly used treatments of environmental and biological samples.

Sampling without dissolution has a number of advantages and is increasingly used. During the laser ablation, the inorganic sample is directly transformed to vapours and transported by inert gas to various spectrometers, *e.g.* ICP, ICP-MS, MS or GF-AAS [41—45, 196, 284]. Sample surfaces and thin layers are examined in this way but bulk of metals or powders have also been treated successfully. The laser ablation is, of course, a complicated phenomenon since neutral and ionized particles are desorbed and vaporized and the results are also influenced by changes from sample areas closed to the laser spot. Difficulties appear during quantitative evaluation because of lack of reproducibility coming from fluctuations in penetration paths of the laser beam. Most promising results were obtained with on-line combination of laser ablation and ICP-AES. Various kinds of interaction of laser beam with the sample material may, however, influence the character and intensity of spectral lines in the subsequent spectrum. On the other hand, the spectrometric detection power for elements may increase when laser ablation is used for sampling.

The novel slurry technique of direct introduction of powdered sample into spectrometric atomizers brings a number of advantages against current sample decomposition techniques and its significance increases [248, 282, 283].

Recently an increased attention is paid to semipermeable selective membranes during sampling, sample handling, and preconcentration or separation of gaseous analytes or those in solution. In such case solid or liquid membranes substitute effectively current SPE and liquid extraction techniques but processes on the membrane interface between the donator and acceptor phases may be rather complicated. Supported anchored liquid membranes (SLM) have been frequently used during sampling and sample treatment. In flow systems incorporated SLM are an effective mean for the selective and effective extraction and preconcentration of analytes for their FIA, GC or HPLC determination [200—202, 279, 285, 320].

Why Preconcentration of Analytes?

Preconcentration is often obligatory for separation of residual analyte from complicated sample matrix and to sufficiently exceed the determination limit of the particular analytical method and to reach the optimal analyte concentration interval of such method [53, 265, 266]. In fact, efforts of the analyst to determine less or even the least amounts of matter are limited by increasing technical problems, loss of reproducibility and by the increase of a couple of errors, which makes the preconcentration of analyte to increased concentration levels more attractive.

A considerable attention is now paid to the on-line or off-line application of solid phase extraction (SPE) of microamounts of inorganic and organic analytes or residuals in environmental, biological, and clinical samples or food [54]. Microamounts of inorganic analytes are retained by various types of ion exchangers, especially chelating ion exchangers, modified, derived or nonmodified silica gel [55, 281], chelating glycol methacrylate gels, macroporous organic copolymers coated with organic complexing agents, polyurethane, sorbents coated with liquid ion exchanger or microcrystalline modified cellulose [95]. For traces of organic analytes, hydrophobic organic copolymers, derived silica gel, Tenax®, Florisil®, diatomite materials, aluminium oxide, macroporous XAD Amberlites® Separons® or modified carbon [55, 281] are suitable. Retained substances have been usually released off-line or on-line by selected eluents or by thermal desorption. The previous retention of analytes on sorbent columns is also suitable for their subsequent liquid or supercritical fluid extraction [88, 122, 203, 267]. The sorbent column has been replaced advantageously by extraction membrane discs from PTFE, fibres and polymers or modified silica gel containing C_8 or C_{18} alkyl groups or ion exchanger skeleton [223].

Nowadays, in spite of solid phase extraction the conventional manual or microwave-assisted liquid extraction of organics by solvents of different polarity seems to undergo renaissance. Microextractions (SPME) of volatile and semivolatile compounds from gaseous or liquid samples into stationary liquids (polydimethylsiloxane, polyacrylate, poly(ethylene glycol)) coated or immobilized on quartz fibres are increasingly performed. Organic or inorganic sorbents on quartz fibres coated by stationary phase may also be used. Then analytes may be successfully desorbed by increased temperature into the injection port of the GC or GC-MS or into HPLC column by the mobile phase [280]. The quantitative extraction of the analyte is usually not achieved but a reproducible equilibrium between the aqueous sample solution and the station-

ary phase on the fibre is established [220—222]. The common liquid extraction of analytes from solid samples is readily improved by stirring the solvent (SOXTEC) or by heating through microwaves.

The supercritical fluid extraction (SFE) based on carbon dioxide with various modifiers is now frequently used for the preconcentration of various organic residuals. The properties of liquified gases under supercritical conditions make the SFE especially suitable for the extraction of organic environmental pollutants [88, 122, 203, 267].

Total Quality Control and Validation of Analytical Procedures

At present, one of the most important tasks is the validation and critical evaluation of analytical methods and approaches according to unified and harmonized regulations for reaching the highest degree of quality assurance and quality control. This endeavour culminates now in analytical laboratories. Accredited laboratories with an up-to-dated status of analytical operations result from this endeavour for various areas of the analytical practice. The quality issues from the philosophical and economical concept of perfection which corresponds with previously defined criteria. It must be told that the analytical aspects of quality incorporate the quality of analytical processes and that of resulting analytical data. Moreover, the quality of work inside and outside the analytical laboratory but also the quality of applied chemicals, standards, instruments, and softwares must be taken into account. The quality of analytical peaks or signals, the selectivity, precision (reproducibility), accuracy and trueness, robustness, the detection and determination limits, and the linearity of calibration function belong to the hardly tested parameters during the optimization of a particular analytical method or procedure [73, 74, 316]. Some special attention must be paid to the harmonization and integration of current standards [228].

The quality assurance in the analytical laboratory results commonly from the quality control as a bulk of activities ensuring the analytical quality in the analytical laboratory and the quality assessment coming from the laboratory staff and quality audits to ensure the quality control is done correctly [73]. All-European regulations of the ISO 9000 and EN 45000 series were carried out, standards for all analytical routine laboratories were developed and responsible institution in European countries founded to ensure all these activities. Thus, resulting legislative regulations in various areas of human activities, *e.g.* concerning the environment, industry, production, food, and the man's health, raise from analytical activities. Efforts for quality assurance and quality control result in the bulk of GLP regulations. In fact, routine analytical procedures in all practical domains are above all the subject of accredative treatment for achieving creditable analytical results. Such efforts involve, however, considerable demands for the organization and material and financial needs of the analytical laboratory which is only profitable when large series of analyses are carried out. This creditable endeavour for quality assurance and control is unfortunately accompanied with an extensive paperwork. A shortcoming could, however, rise from the effort to firmly hold just accredited analytical procedures instead of developing new better analytical methods and approaches.

CONCLUSION

Problems and tasks of the contemporaneous society may not be solved without modern analytical chemistry which is one of the main impacts for the ability of man to improve life and the world round him. Moreover, analytical chemistry accentuates a joint work for solving problems.The interests of contemporaneous analytical chemistry have shifted towards physical methods, sophisticated and computerized instruments, and objects of the real world containing complicated mixtures of organic or inorganic species, microamounts or traces of analytes in micro- and ultramicrosamples.

On this background, the state of art of some selected analytical approaches and problems was commented taking advantage of our orientation and experiences. The subjectivity of views, of course, cannot be often avoided. Modern analytical chemistry needs laboratories equipped with sophisticated instrumental technique and well educated and skilled people in them, which is a necessary precondition for solving problems of tomorrow. At present, chemical laboratories and the chemical industry are already provided with multimodular and multidimensional automatic devices controlled by computers and operated by operators, which produce a bulk of analytical data. In these connections qualified analysts in the working team are needed who consider the suitness of provided technique for solving particular problems and evaluate the trueness and qualification of produced analytical data [201], *cf.* also [195]. The interdisciplinarity of modern analytical chemistry has loosed the sharp outlines of this science which sets particular demands on the analyst's education and knowledge. Analytical chemists for the near future should be well acquainted with all perspective trends and needs of modern analytical chemistry having a very solid background of other chemical sciences, mathematics, physics, computer and instrumental sciences but should also be familiar with problems of contemporaneous society and economics. Only in such case the analytical chemist will be a good problem solver and successful searcher after errors and shortcomings. For this purpose the curriculum and education programs in chemistry including analytical chemistry at universities and tech-

nical universities should be considerably rearranged, renewed and improved [235, 236, 239, 240, 242, 269].

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