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PREPARING SAMPLES FOR ANALYSIS - THE KEY TO ANALYTICAL SUCCESS

PRZYGOTOWANIE PRÓBEK DO ANALIZY - DROGA DO SUKCESU

Summary: The article presents and discusses the literature on the individual stages of environmental sample preparation up to the stage of final determinations concerning analytes occurring in low concentrations.
Special attention was paid to:
- ✓ challenges related to speciation analytics,
- ✓ modern techniques of extraction and analyte enrichment,
- ✓ use of ultrasounds and microwave radiation on each stage of analytical procedures,
- ✓ implementation of principles associated with the conception of sustainable development in the procedures used in analytical laboratories.

Keywords: sample preparation for analysis, sample preservation, extraction and/or enrichment of analytes, application of ultrasounds and microwave radiation in analytical laboratory, speciation analytics, green analytical chemistry

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1. Introduction

The recent decades have witnessed a sharply growing demand for information. This also pertains to the information on various material objects that can be obtained in the course of analytical examination of collected samples. Therefore, the analytical information resulting from the work of analysts is a response to society's demands, as is pictured in the diagram shown in Figure 1.

The desire to satisfy the need for analytical data stimulates actions towards:

- developing new analytical methodologies,
- designing and implementing new technical solutions for the measuring instruments used in analytical practice.

Analytical methodologies and measuring instruments are the tools for obtaining reliable data on the composition of the material objects being studied.

The science on the construction and operating rules of measuring instruments is often referred to as “instrumentation”. The consecutive stages of this science development can be easily discerned. Figure 2 presents a diagram of the factors that influence the development of measuring instruments.

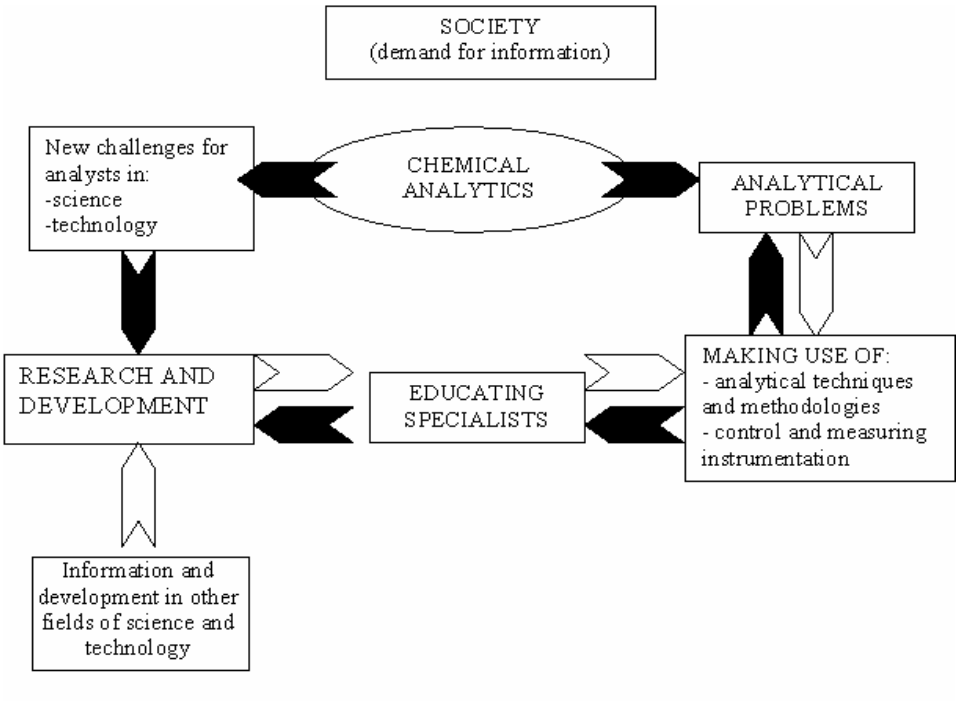

Fig. 1. Demand for analytical information as a stimulus for the development of analytics

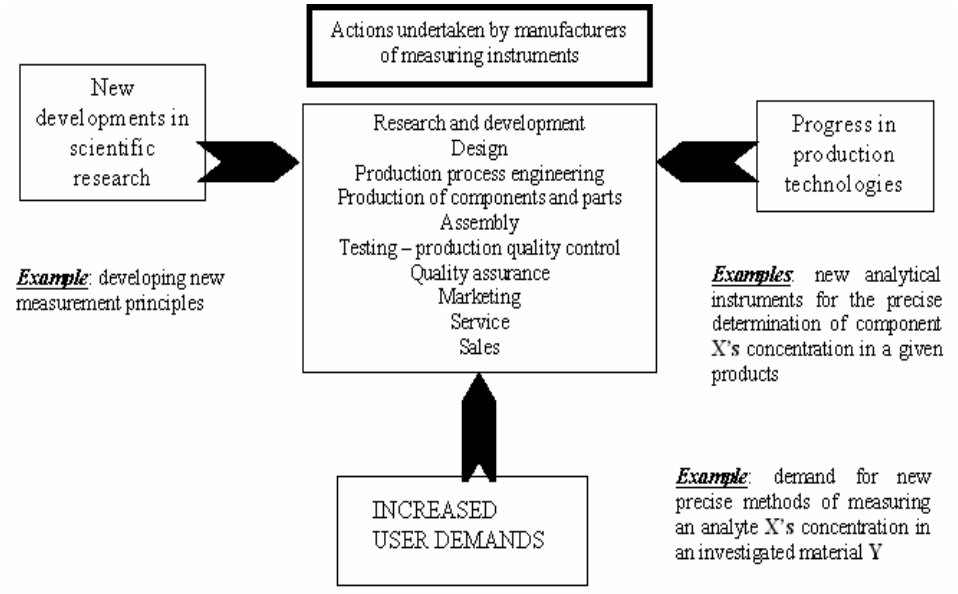

Fig. 2. Factors that influence the development of instrumentation

Access to a variety of information sources facilitates decision making not only in politics, but also in the economy and technology (related to control over the processes of manufacturing consumer goods). A new type of market arose, where information is bought and sold [1].

Analytical data on the studied material objects are a specific kind of information. This information is not usually obtained through an analysis of the whole object, but is based on the analyses of appropriate samples. Therefore, the samples have to be collected in such a way that the most important criterion is met, *ie* representativeness.

In order to satisfy the growing demand for analytical data, more and more intense research is taking place with the aim of developing new methodological and instrumental solutions so that the analytical results are a source for as much information as possible, that is - in other words - are characterized by the greatest information capacity possible.

Measurement results must be reliable (credible), that is, they must accurately (both precisely and truly) reflect the real content (amount) of analytes in a sample that is representative of the material object under research. This leads to the conclusion that all developments in analytical chemistry are derived from the desire to obtain in-depth analytical data. Analytical chemistry uses a very broad spectrum of measurement methods and techniques. Table 1 presents the basic classification only.

Table 1

The basic classification of modern chemical analysis methods

Basis for Categorization	**Types of analytical methods**	**Additional explanation**
1	2	3
Relation to the current international system of units SI (location in the comparison chain ensuring traceability)	primary methods	used for direct measurement of units in the SI system
	relationship methods	Isotope Dilution Mass Spectrometry (IDMS)
	secondary methods	
Measurement principle	absolute methods	based on such units as mass, volume, time, electric current intensity, which do not require calibration
	relative methods	by comparing signals from analytes in the model sample and in the examined sample; the calibration stage is necessary
Means of examining the sample	direct methods	an appropriate measurement device (sensor) is placed directly in the examined object in order to obtain analytical data (measuring of pH and electrical conductivity)
	indirect methods	in most cases used because of: - very low analyte concentration levels - complicated matrix composition and the presence of INTERFERANTS; it is necessary to prepare the sample properly, and measuring analyte concentration is done in an appropriate extract

1	2	3
Type of analytical data	methods for determining the momentary concentration of analytes in the examined material object	methods used in examining the quality of the environment and determining individual exposure
	methods for determining time-weighted concentrations while taking the sample	
Location of the analysis process	methods of making *in situ* measurements	appropriate mobile laboratories, movable or portable measurement devices are used
	laboratory methods	
Means of obtaining analytical data	methods using devices which can read the amount/concentration of analyte directly	usually used in field research, in order to quickly obtain analytical data (often semi-quantitative)
	methods with previously prepared samples and the amount/concentration of analyte calculated based on laboratory measurements	
Means of taking a representative sample	sedimentation methods	a sample of analytes is collected by way of free migration of analyte onto the collecting surface
	isolation methods	sample is put into a container (probe) with a specified volume
	aspiration methods	analyte samples are collected by running a stream of medium through a trap (*eg* sorption tube)
Level of automation	manual methods	most of the operations and actions (both in field and in laboratory) connected with preparing the sample are performed manually
	automatic methods	all or part of the operations are performed without the participation (intervention) of an operator (analyst)
	monitoring methods	specific type of automatic methods; the devices used must have the following features: - they must be able to obtain data in real time or with only a slight time delay - they must be capable of performing continuous measurements - they must be able to operate autonomously for extended periods of time

Depending on the objective of the measurement, a procedure has to be chosen from two main (Fig. 3). The first is the classical procedure recommended and even required by the official text for regulation monitoring, based on sampling and laboratory analysis, including several steps between sampling and analysis: conditioning, storage, transportation and pretreatment. The other procedure, carried out on site, is based on the existence of on-line measurement systems or on the use of field-portable devices or test kits. Actually, the two approaches are often combined, taking into account either the

scientific relevance of some practices (*eg* on-site measurement of dissolved gases and temperature), or the availability of systems for on-line monitoring [2].

The problem of preparing samples for analysis has been discussed in a vast number of both original and review publications [3-29]. These publications present universal problems in chemical analytics as well as problems and challenges concerning properly preparing samples of certain materials for analysis, and specific requirements in preparing samples for analysis using a specific analytical technique [30, 31].

- It must be remembered, however, that despite further development in instrumentation (the science of building measuring instruments, and their operating principles) and the availability of many complex hyphenated devices on the market, the basic principle that a device should only be a necessary and useful tool in the process of obtaining analytical data is often forgotten. Possessing the tool itself will not solve any analytical problems. Without understanding the chemism of the analysis process, no reliable and credible results can be obtained. People who treat the analytical device as a typical black box deserve to be called "operators of analytical devices" rather than "chemical analysts". In this case analytical misinformation may occur easily, despite the amount of work and time spent in the process of analysis.
- Educating specialists who will be able to make use of these innovative methodologies and devices.

Figure 4 diagrammatically presents the division of technical competences in a research laboratory.

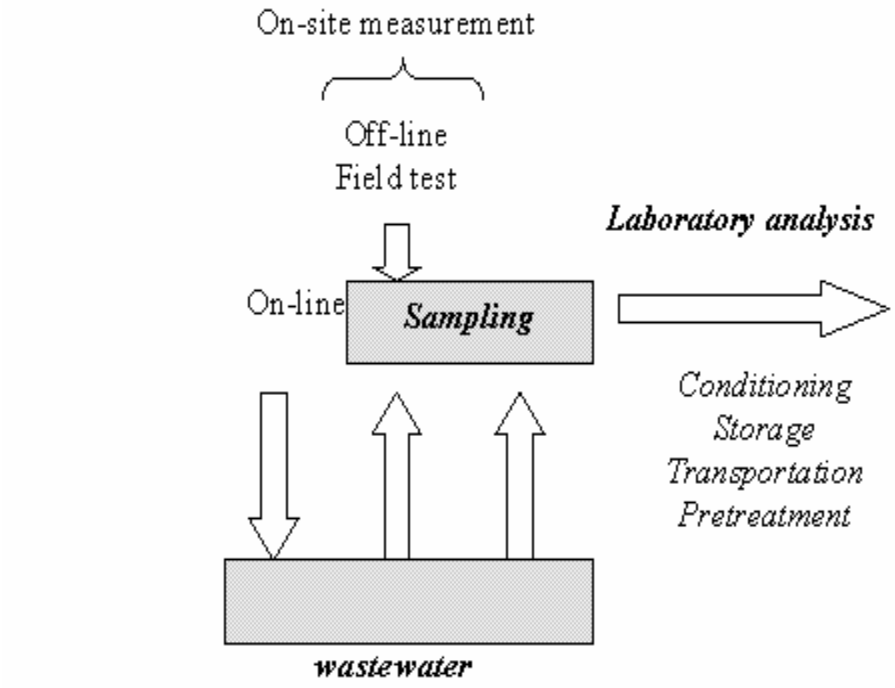

Fig. 3. Measurement procedures for wastewater quality monitoring

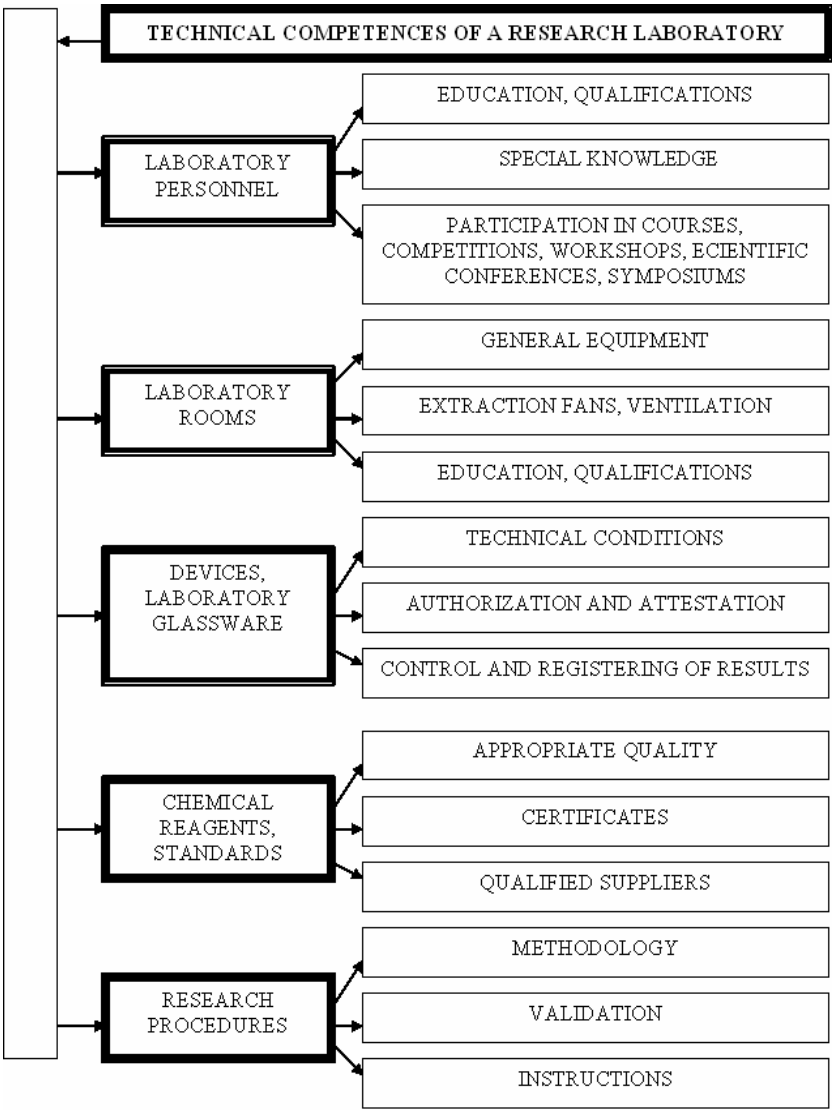

Fig. 4. Division of technical competences in a research laboratory

Analytical research draws on various procedures and analytical techniques. Some of the measurement devices used are referred to as “monitors”. These devices should have the following operating parameters:

- high measurement sensitivity,
- delivery of analytical information about the investigated or with only slight time delay,
- high resolution of results characterized by a short response time,
- long period of unsupervised operation.

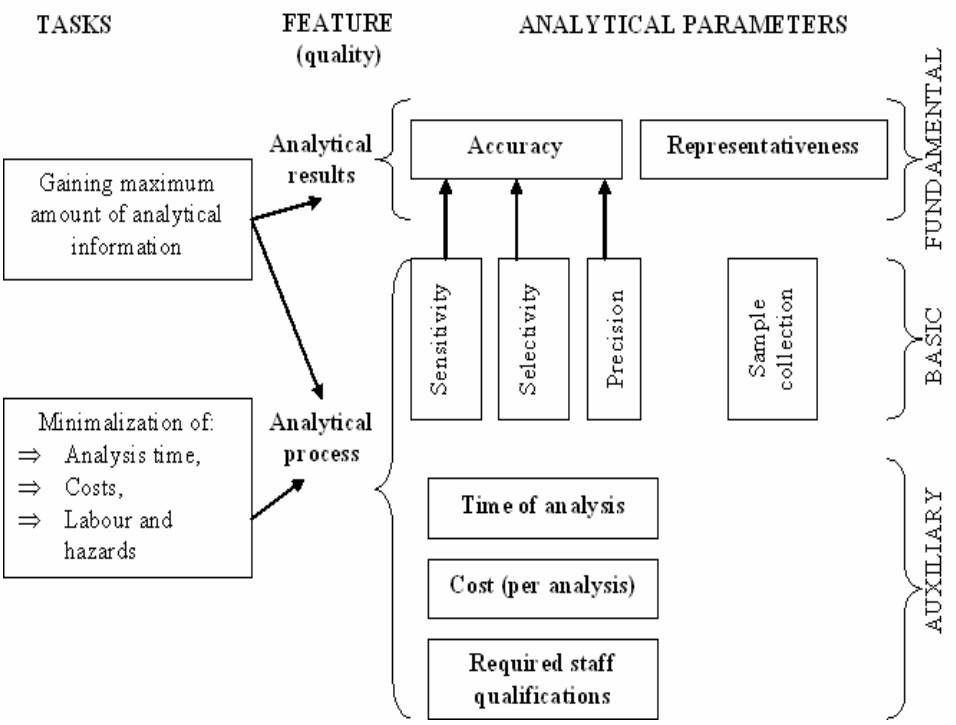

Fig. 5a. Main tasks of analytics and their dependence on quality of analytical process and analytical parameters

Qualitative data

1. Is the analyte present in the sample? YES/NO

Quantitative data

1. Is the level of analyte present in the sample higher than acceptable? YES/NO
2. What is the amount/concentration of analyte in the sample?
3. What is the physical or chemical form of analyte in the sample?

↓

SPECIATION ANALYTICS

4. In what part of the examined object is the analyte present?

↓

DISTRIBUTION ANALYTICS

5. What are the time-fluctuations related to analyte concentration?

Fig. 5b. Types of analytical data contained in the analytical results

Next, monitoring poses several requirements concerning:
- instrument zeroing and calibration,
- protecting the instrument against power surges,
- providing the instrument with an independent power supply,
- automatic filing up with solution and reagents (electrochemical monitors),
- installation of devices preventing the flame from extinguishing (in certain detectors, *eg* FID and FPD),
- exchange and regeneration of spent filters.

Figure 5 diagrammatically shows two main tasks of analytics and their dependence on quality of analytical process and different analytical parameters.

2. Types of analytical data

Data obtained through analysis of samples may prove useful in various fields of science, technology and human life. They play a particularly vital role when it is necessary to:
- describe the condition of the examined material object and find out what changes it undergoes,
- confirm a new theory or scientific hypothesis,
- make a decision concerning the law, the economy or in court,
- plan and implement educational campaigns in order to raise social awareness.

Various types of data may be obtained as a result of analyzing samples.

There is no doubt that quantitative data (amount or concentration of analyte in the sample) are most important in the majority of cases. Therefore it is worth learning the basic terminology of chemical metrology with reference to the quantitative determination of analytes. The diagram in Figure 6 will help put these terms in the correct order on the analyte concentration axis (expressed in the same units as the standard deviation of analytical noise (δ)).

Many elements and compounds occur in a variety of matrices at levels that were undetectable, for analytical methods that were first developed in the nineteenth century. As analytical technology improved, and it became known that elements were present at these very low levels, the term “trace” was coined to describe them. Although modern analytical methods allow accurate, repeatable determination of elements at such low levels, the generic terms “trace” and “trace element” are still in use.

The boundaries of trace analysis are described by the definition of “trace element” in the IUPAC Compendium of Chemical Terminology, second edition: “Any element having an average concentration of less than about 100 parts per million atoms and less than 100 μg/g”. As analytical techniques have become more sophisticated, detection capabilities have improved and, in several fields, this upper boundary of the definition of “trace” is now too far away from the capabilities of analysis that new terms such as “ultra-trace analysis” are in common use. There is no agreement about the range of ultra-trace analysis and no rigorous definition. Within the literature, the term is used for the definition of elements at mass fractions less than 10^{-6} and 10^{-8} (1 ppm and 10 ppb).

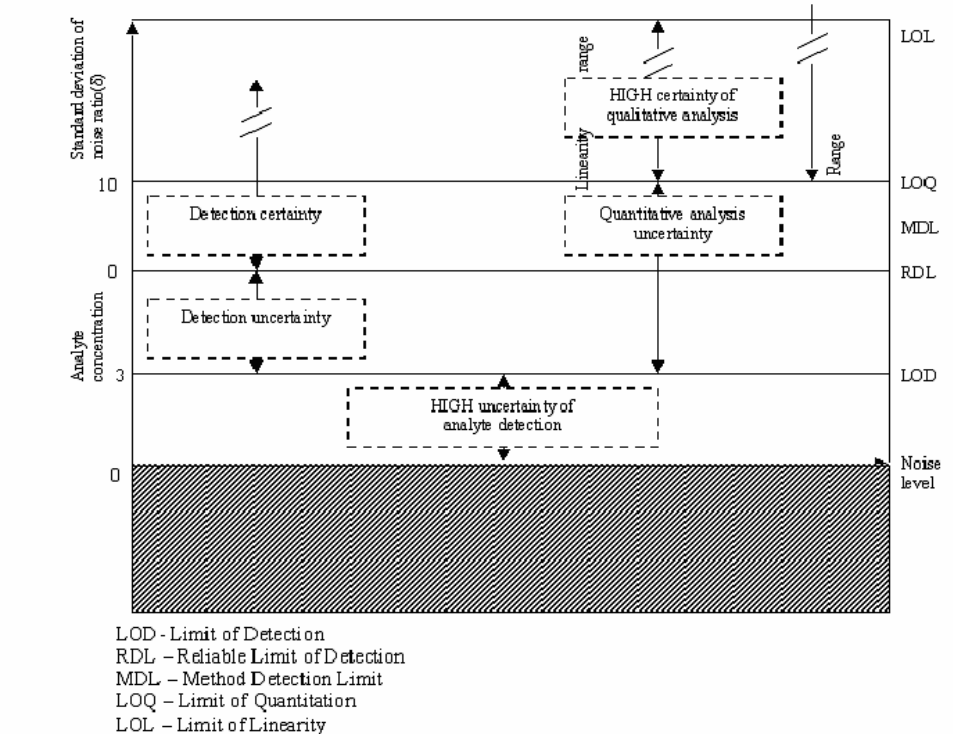

Fig. 6. Basic metrological terminology related to the quantitative analytics of trace elements

3. Speciation analytics - an important task for analytical chemists

Attempts at environmental 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. Species alterations have to be avoided or minimized. Information on the degree of possible species changes must be elucidated [32-39].

In general, there are at least three approaches in use of term “speciation analytics” in the analytical context:

- local concentration differences of a particular element or compound in a given structure of a material,
- physical distribution of an element or compound in different phases that are in contact with each other,
- presence of different chemical conditions or binding states of a particular element within a single phase.

Initially, speciation analytics was only associated with biogeochemical cycles of metal in water environments. Even in the 1950’s, geochemistry distinguished between two forms which metals could assume:

- metals in dissolved form,
- metals bound to suspended matter.

At that stage, filtering water samples through a filter with pores 45 µm in diameter was sufficient to properly separate the two phases. Later, due to the development of electrochemical analytical methods, it was possible to identify different forms which metals assumed in a dissolved state - free metal ions and complex ion forms.

Simultaneously conducted simulation studies on the possible equilibria between ions and organic or non-organic ligands have lead to the conclusion that a wide variety of chemical compounds in metals could exist in water environments. In this day and age, speciation analytics deals not only with metals, but also with other elements and in different types of tests.

It is well known that the toxicity of many elements depends on the physico-chemical forms which they assume. Determining the total content of a certain element in a sample is definitely not sufficient to determine its toxicity for example. A good example may be selenium, which in small amounts is essential for the human body. However, transition from the necessary amount (about 70 µg of selenium per day for an adult person) to a toxic dose (about 800 µg of selenium per day) is comparatively easy.

For instance, a fatal dose of Se(IV) compounds for a rat amounts to 3.2 mg/kg of body mass, while for dimethyl selenide it is 1600 mg/kg of body mass. Non-organic selenium compounds [Se(IV) and Se(VI)] are believed to be the most toxic ones, whereas in the environment selenium occurs most commonly bound to amino acids (selenomethionine and selenocysteine). The least toxic forms seem to be the volatile methyl compounds of selenium, which are metabolites of a detoxication process.

The question concerning what "speciation" means is very often asked. The answer can be found in IUPAC recommendations.

In Table 2 the most often used terms are presented.

Table 2

The terms connected with speciation analytics

Term	Definition
Chemical (species)	Specific form of an element defined according to isotopic composition, electronic or oxidation state, and/or complex or molecular structure
Speciation	Distribution of an element amongst its chemical species in a system
Speciation analysis	Analytical activities of identifying and/or measuring the quantities of one or more individual species in a sample
Fractionation	Classification process of an analyte or a group of analytes from a certain sample (according to physical size, solubility) or chemical (bonding, reactivity) properties

Generally, speciation analytics plays a very important role in:

- studies of the geochemical cycles of elements and chemical compounds,
- determination of the 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.

Different chemical species and its physical forms behave differently in geochemical, ecological and metabolic cycles. This refers particularly to:
- deposition,
- accumulation,
- mobility/transportation,
- phase transfer,
- (re)mobilization,
- (bio)availability,
- resorption/excretion,
- essentiality/toxicity.

Physico-chemical properties of particular species strongly influence their behaviour in complex multiphasic systems such as specific ecosystems. Special attention should be paid to:
- solubility → mobility, remobilization, resorption, deposition,
- volatility → phase transfer, transportation,
- oxidation state → bioavailability, essentiality, toxicity,
- reactivity → remobilization, bioavailability,
- polarity/charge → accumulation, bioavailability,
- molecular weight → mobility, phase transfer, deposition.

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

3.1. Physical speciation

Physical speciation takes place when different forms of the same chemical species have to be determined in a sample. Examples include adsorbed forms, dissolved forms, complex forms, etc.

3.2. Chemical speciation

Chemical speciation occurs when different chemical species should be determined in the sample under investigation.

It is possible to distinguish five types of chemical speciation:
- *screening speciation* means detection and determination of one particular analyte, for example one known for especially high environmental toxicity;
- *group speciation* determination of the concentration level of a specific group of compounds, or of elements existing in different compounds at a specific oxidation level, and their physical forms;
- *distribution speciation* takes place when the same chemical species needs to be determined in different compartments of the material object under investigation;
- *chiral speciation* determination of the enantiomers of the given chemical compound;
- *individual speciation* is the most difficult type of speciation analytics, involving the broadest range of analytical work. Its purpose is to separate, detect, determine and identify all species of an element in a sample.

Specialists in speciation analytics are interested in various chemical specimens and the physical forms which certain elements assume. Here are the examples of physico-chemical forms of trace element species in water bodies:

dissolved:
- simple hydrated ions,
- inorganic complexes,
- organic complexes,
- molecules and polymeric compounds,
- ion-pairs,

colloidal:
- mineral substances,
- products of hydrolysis and precipitation,
- biopolymers,

suspended particles:
- mineral substances,
- precipitates and agglomerated colloides,
- plankton,
- bacteria and microorganisms.

There are a set of important factors affecting the formation, stability and transformation of dissolved elemental species in the samples under investigation. They are as follows:

- shift of pH,
- change of redox-potential,
- presence of reactants (*eg* inorganic and organic ligands),
- catalytic effects,
- presence of particulate matter and micro-organisms (adsorption and biotransformation).

Speciation Analysis is dealt with mainly in environmental, nutritional and biomedical research. The sample matrices are generally highly complex and requirements for reliable (trace) element determinations are high (even for total amounts).

The most important challenges are connected with such issues as:

- concentration of the individual species often being very low,
- large concentration differences amongst the elemental species,
- small structural differences in elemental species,
- low thermodynamic and kinetic stability of the species,
- preserving the integrity of the sought species throughout the analytical procedure,
- existence of not (yet) identified species,
- non-availability of suitable reference materials.

There is some specific analytical methodology for speciation analytics. The most common are:

- direct *in situ* detection of species (*eg* Ion Selective Electrodes, Electron Spectrometry),
- chemical derivatization of individual species (Optical Molecular Spectrometry),
- separation of individual species and element-specific detection (extraction, sorption, ion-exchange, gas-permeation, electrolysis),
- separation of all species and their determination (chromatographic and electrophoretic methods).

Chromatographic techniques constitute the techniques of choice for speciation analytics. In specific cases, there is a need for the application of non-chromatographic

techniques with respect to the characteristic properties of the analytes. They are as follows:

- differentiation of oxidation states of inorganic metal compounds:
  - electrochemical methods,
  - selective derivatization and molecular spectrometry,
  - ion exchange separation of anionic and cationic species;
- separation of inorganic ions from organic species:
  - solvent extraction,
  - solid phase extraction using reversed phase materials;
- separation of volatiles from non-volatiles:
  - (isothermal) distillation,
  - dynamic headspace analysis (purge-and-trap);
- separation of low and high molecular weight compounds:
  - membrane techniques (dialysis, ultrafiltration).

Speciation is one of the driving forces of development in the field of chemical analytics and instrumentation. New approaches in this field can be distinguished:

- highly resolving separation techniques in hyphenation with high-sensitivity detectors (two dimensional separations),
- separation techniques in hyphenation with elucidation of the structure of organo-metallic compounds (ESI-MS, MALDI-MS),
- new *in situ* techniques with enhancements in sensitivity and selectivity (sensors based on molecular imprinted polymers),
- selective sampling for species, making use of “biological receptors”,
- (new) reference materials and round robin tests for quality control.

4. Problems associated with the trace element analysis

The task that many analysts face is to determine the content of trace and micro-trace components in samples with complex and often varying matrix compositions. There is no doubt, then, that this kind of analytical work poses a special challenge. The end result of analysis is influenced by a number of additional factors, which are not taken into account when the presence of higher content components is determined. These issues have been discussed in a great many publications [40-52]. The lack of awareness of those specific requirements when performing analytical research on various types of samples for trace elements may lead to situations where the obtained result, instead of being a source of analytical data, will cause disinformation.

Contamination of the sample with the analyte and/or losses of the analyte from the sample are the most important systematic errors that can occur during preparation steps such as [53]:

- sampling,
- storage,
- sample pretreatment,
- separation of constituents,
- final determination.

The first steps of analytical procedures have been a largely neglected area in trace analysis for a long time. Research was mainly focused on the development of sensitivity and selectivity. Over the last 20 years, analysts recognized more and more that the majority of systematic errors might be introduced during the analytical step at the beginning of a combined analytical procedure, and not during final measurements. A good analytical strategy also includes a sampling procedure free of contamination and losses, and proper stabilization and storage of the sample. As analytical chemistry is a discipline that helps other disciplines solve their problems, close cooperation is necessary.

In practice, the analytical chemist is often not involved in the sampling procedures; the analyst is mostly not even informed of the origin of the sample. Therefore, severe systematic errors in these first steps of an analytical procedure are the consequence.

The influence of contamination and losses on the analytical results becomes increasingly important with decreasing concentrations of the analyte (tab. 3). These effects depend not only on the concentration range, but also on the nature of the analyte. One should keep in mind that contamination and/or losses can never be completely eliminated, but they must be reduced to an acceptably low level.

Table 3

The basic sources of sample contamination for liquid samples

Source of errors	**Physico-chemical process responsible for contamination**
Phase transition	Solvatation Crystallization Transition into vapor
Component transformation	Hydrolysis Crystallization Reduction Adsorption
Component degradation	Radiolysis Autocatalysis Photolysis Return to equilibrium
Component release	Vaporization Permeation Diffusion Rinsing the gaseous space over the liquid

In Figure 7, the sources of error that can destroy the results of determination of trace components in liquid samples are presented schematically.

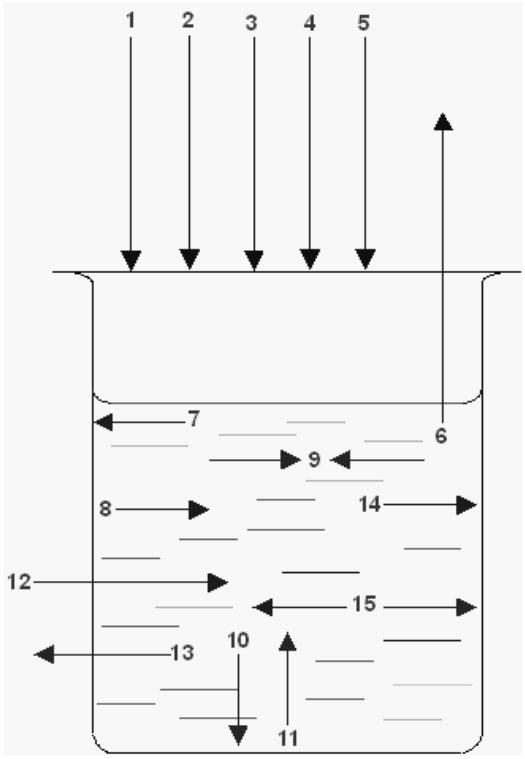

Fig. 7. Diagrammatic presentation of factors that can affect concentration levels of trace components in a liquid sample: 1 - contact of sample with laboratory air, 2 - residues of dishwashing mixture components, 3 - distilled water, 4 - reagents and solvents employed, 5 - contact with analyst, 6 - vaporization of the most volatile components, 7, 8 - process of adsorption-desorption (the wall memory effect), 9 - adsorption of analytes on suspension, 10 - precipitation of sediment, 11 - leaching of component's tram vessel, 12, 13 - permeation of solution components through vessel walls, 14 - reaction of analyte with vessel material, chemical reaction among solution components

The intensity of the processes and phenomena shown in the Figure 7 can depend on:
- the temperature of the liquid sample and its changes,
- the presence and intensity of solar radiation,
- the presence of living organisms in the sample.

Contact of analytes present in liquid mixtures with the walls of vessels, tubing and appliances can crucially affect the concentration levels of trace and ultratrace components. It is the result of adsorption and desorption processes of the analyte on the surface of the solid. These phenomena destroying the sample composition are described as the "wall memory effect" and "cross-contamination".

The materials of vessels and tools are of great importance in trace element analysis. Contaminants can be leached out of the materials or desorbed from impurities on the surface of vessels and tools. Table 4 shows preferred materials and their use in trace element analysis [54].

Table 4

Preferred materials and their use for trace element analysis

	PE and PP	**FEP (≤ 200°C)**	**PFA (≤ 250°C)**	**TFM (≤ 250°C)**	**PTFE (≤ 250°C)**	**Vitreous silica (> 500°C)**	**Glassy carbon (> 500°C)**
Storage containers	+	+				+	
Beakers and flasks	+	+			+	+	
Separatory vessels	+	+				+	
Vessels for wet digestion					+	+	+
Vessels for bomb digestion		+	+		+	+	+
Vessels for microwave digestion			+	+	+	+	
Crucibles							+
Boats						+	+

In Table 5 some measures which should be undertaken when one wants to reduce the intensity of factors likely to affect the concentration levels of trace constituents in a liquid sample are listed.

One by one, new publications appear which present results of research into specific sources of errors connected to the analytics of trace components. The following examples can be named:

- the Midas touch effect [55]. The most common type of contact between two different materials that can transfer micro-amounts of one material to another occurs with the use of human hands and fingers. Among many elements constantly used in industry, the rarest ones are the noble metals. Therefore, investigations into the ubiquity of gold and silver should be particularly informative as to their transfer and the role of human fingers,
- influence of factors in the reagents used on the unreliability of trace component measurements [56, 57],
- migration of volatile organic components from plastic pippetes (HDPE, PEX, PVC) into a liquid medium (*eg* water) [58],
- sorption and adsorption processes of organic constituents of water sample on surface of plastic materials [59], and on suspended mater [60],
- reducing interactions between the analyte and the vessel walls polystyrene coated glassware use a means of reducing metal losses in trace metal speciation [61],
- influence of the sampling marine waters traction of particulate trace metals [62],
- artifact formation during:
  - storage of samples in different conditions [63],
  - extraction (fractionation) of different groups of analytes from water use of solid sorbents [44, 64],
- reduction of matrix effect connected with the use of different techniques at the final determination step for analytes [65],
- changes in the amounts of volatile organic compounds in water samples and stored standard solutions [66],
- influence of the quality of water used as an analytical medium [50].

Table 5

Ways of eliminating or reducing the influence of factors affecting concentration levels of trace components in a liquid sample (see Fig. 8)

Factor affecting concentration of trace components in a liquid sample	**Countermeasures**
1. Contact of sample with laboratory air	- making all activities and operations air-tight - use of clean boxes and clean rooms to carry out operations involved in sample preparation for analysis
2. Residues of dishwashing mixture components	- use of proper dishwashing agents and suitable (tested) procedures of cleaning, washing and drying of vessels
3. Water used in sample preparation operations	- proper techniques of water preparation (deionization, distillation etc.)
4. Reagents and solvents employed	- use of high purity reagents (HPRs) - use of reagents from sample manufactures unit - addition of reagents in justified excess - reducing scale of determinations - use of the so-called solvent-free techniques for sample preparation
5. Contact with analyst	- use of protective clothes (headgear, gloves, etc.)
6. Vaporization of volatile components	- making sample preparation operations air-tight - storage of solutions and samples in vessels filled up to stopper - use of vessels with an appropriate capacity
7-8. Processes of adsorption-desorption of trace components on walls (the wall memory effect)	- use of vessels made of suitable materials - special preparation of vessel surface (deactivation) through: a) electropolishing b) electropassivation c) silanization - lowering of storage temperature for samples and solutions - rinsing of vessels with a bit of sample or solution
9. Adsorption of components (primarily organic analytes) on the surface of a teflon-coated mixer	- changing method of the sample mixing - use of a glass-coated mixer
10. Adsorption of analytes on suspension	- preliminary suspension removal through: a) decantation b) filtration c) centrifugation
11. Precipitation of sediment	- acidification of sample
12. Leaching of components from vessel material	- use of vessels made of suitable materials
13. Permeation of air components into solution	- use of vessels made of materials with a low permeability to gases
14. Permeation of solution components outside	- use of vessels made of materials with a low permeability to solution components - use of thick-walled plastic vessels
15. Reaction of analytes with vessel material	- special preparation of vessel surfaces as with points 7-8
16. Chemical reactions among solution components	- lowering of solution temperature - preliminary sample preparation through derivatization of reactive components
17. Photodegradation	- storage of samples in the dark
18. Biodegradation	- addition of biocides

5. Sample handling

Analytical data on material objects are usually obtained through analysis of samples which represent a minute part of material objects. Therefore, for the obtained measurement data to be a good source of information, and not analytical disinformation, the samples taken must be representative of the whole material object. There are four basic criteria that determine representativeness of samples [32, 67-72]. Examples of locations from which isolated samples that make up the aggregate sample are taken.

This process, called random sampling, allows the user of the resulting analytical data to make statistical generalizations based on probabilities. Selecting truly random samples is difficult, for random in this context does not mean haphazard. A recommended method for a population consisting of units such as pharmaceutical tablets is to use random numbers selected by use of a random number generator[1]. Bulk materials may be divided into random of real or imaginary segments; the segments may be areas on a two-dimensional surface, or volumes for a three dimensional population.

Data obtained by measurements on random samples can be analyzed by statistical methods to identify whether systematic relations between results exist due to trends or biases in the measurements. A Geiger-Müller tube is interfaced with a computer and the time between successive pairs of radioactive decay is measured and provided as bytes.

A proper way of homogenizing and reducing the mass (volume) of the aggregate sample in order to obtain a sample for analysis is crucial part of the sample handling. Figure 8 presents the hierarchy of terms related to collecting samples.

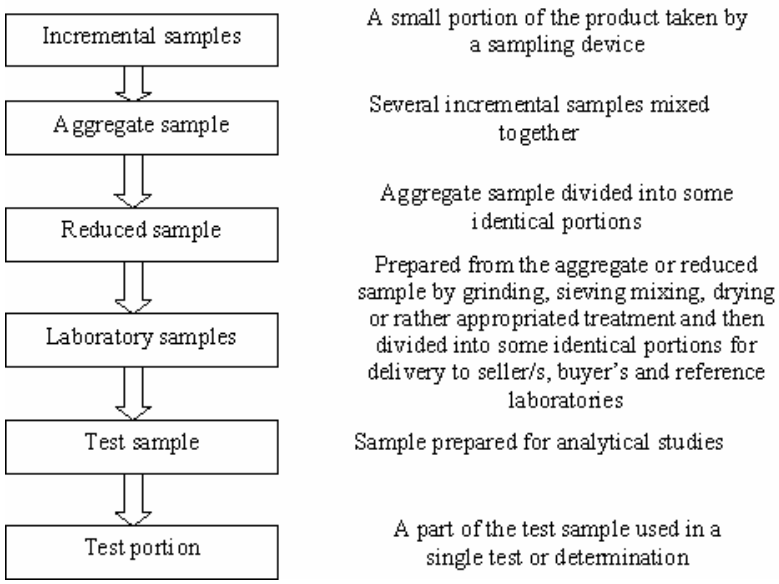

Fig. 8. Hierarchy of sampling terms

[1] Random numbers may be obtained from several sources on the Internet. A good example is www.fourmilab.ch/hotbits, which generates sequences of random numbers based on radioactive decay of krypton-85

Stable composition of samples during the entire period from handling of samples to analysis of the test portion - at this point, it is necessary to stress the importance of appropriate sample transport, maintenance and storage techniques.
In chemical measurement, the term "taking samples" can be understood in two ways:
(a) as taking a representative portion of material from the examined object;
(b) as taking *n* portions of material from a sample delivered to the laboratory.

Consequently, in order to meet a client's requirements and to ensure their full satisfaction and trust, the laboratory ought to unambiguously discuss with the clients the aims of the study and explicitly define the measured quantity. It should also be settled which measuring method will be used, what the size of the sample will be and how the sample will be taken. A decision has to be made at this stage to determine whether the results will pertain to the sample delivered to laboratory only or to the whole material object. In the first case, the laboratory is responsible only for the delivered sample and should state in the report that the results and the unreliability assigned to it are applicable to the delivered sample only, and cannot be applied to the entire object.

Nonetheless, any endeavors by the laboratory are legitimate in order to understand the problems clients deal with and the aim of the studies. Even if the laboratory does not participate in taking samples from a given object, it can actively support clients in negotiating the arrangements related to the research and the required unreliability of the measurements. It is worth defining, with the help of the clients, what the aim of the measurement is, whether knowledge of the delivered sample's properties (up-to-date information) or knowledge of the whole examined object's properties is significant. In the latter case, an appropriate way of sampling the object (when and where the samples were taken) has a significant influence on what decisions are made on the basis of the results obtained.

In this context, the term „SAMPLE" can have two meanings, as a sample in possession of the laboratory, *ie* a portion of the examined object delivered by the client, or as a sample in its natural state, *eg* soil in a field, water in a running stream, or grain in a train car. If the portion of material delivered to laboratory is supposed to represent an object, the basic requirement is that the sample should be representative of the features of the examined object.

Table 6

Classification of analytical techniques with regard to the need for sample pretreatment

Classification of analytical techniques	**Definition**	**Examples**
Direct techniques	Allow direct sample analysis	X-ray fluorescence Neutron Activation Thermogravimetry Spectrographic techniques Ion Selective Electrodes Immunoassays
Indirect techniques	Sample preparation prior to final determination of analytes is needed	All other techniques

Following this, it is worth remembering that extracting samples and the related unreliability may pertain to the process of extracting a representative sample of material from

the examined object (sample in the natural state), or the process of extracting *n* portions of material from the delivered sample (sample in possession of the laboratory).

There are only a few analytical techniques that allow introduction of the sample to the analytical instrument without any preparation. Classification of existing techniques with regard to the necessary omission of the sample preparation step is presented in Table 6.

At present, we can still not state that the utilization of chemical analysis always attains the needed quality level in this field, In this respect, it is first necessary to adapt an analytical strategy, represented by the following points:

- rigorous definition of the problem to investigate,
- selection and collection of samples related to this problem (sampling),
- appropriate sample preparation,
- accurate determination of elements associated with the initial problem,
- validation and evaluation of analytical results,
- interpretation of results as a function of the investigated problem,
- relevant conclusions.

In a usual chemical analysis, the objective of the sample preparation stage is to bring all available means into play in order to determine as readily as possible the elements to be investigated. These means are:

- conversion of the sample to a form compatible with the measurement technique utilized (generally a dissolution),
- destruction and simplification of the matrix (mineralization: wet digestion, dry ashing),
- analyte separation or preconcentration (topics not discussed here).

It is evident that the sample preparation steps are of paramount importance in ensuring good quality for the whole analysis. Contamination risks increase with temperature, pressure, long-term contact of solutions with the vessels and with decreasing analyte concentration. To minimize them, a number of principles must be fulfilled:

- consult established procedures specified in the literature and take into account the real objective of the analysis. The most complex procedure is not always the best,
- ensure a clean environment in the laboratory (hoods, ovens, muffle furnaces, microwave devices…),
- for grinding, milling and homogenization, use devices made of appropriate material to avoid sample pollution,
- limit the mass of the sample to be analyzed and the volume of the vessels to be used (to minimize contact area with the solution),
- use only water and reagents of high purity and reduce the amounts used,
- carefully clean all vessels (a soak in acids followed by a liberal rinse with deionized water),
- do not use old vessels in order to avoid adsorption phenomena of trace elements on any worn-out surfaces,
- simplify handling; avoid filtrations and transfers of solutions if they are not absolutely necessary,
- perform several blank procedures with the same reagents, vessels and operating conditions to evaluate possible contaminations and correct the results,
- check recoveries for the whole procedure using reference materials of similar composition to those of the samples analyzed. If recoveries are incomplete, find the

reason by distinguishing preparation steps (responsible factor: procedure) and measurement steps (responsible factor: interference).

Table 7 presents basic documentation related to the stage of extracting environmental samples (air, water, soil, bottom deposits, biota) for analysis [73].

Table 7

Main documentation related to the environmental sample extraction stage [73]

Characteristics of the sample extraction stage	Sample labels	Chain-of-custody
Matrix of the sample Sample extraction techniques Sample extraction sequence Types of probes used Identification numbers Type of preservative used Parameters measured during analysis Parameters measured while extracting the sample (temperature, pH, electrical conductivity, etc.) Calibration data of instruments used in field work Carrier and method of delivering samples to the laboratory Internal temperature of cooled containers (at the extraction and transport stages)	Name of probe Sample extraction data Extraction time Sample number Location of the sample extraction point Sample type Analytes Preservation method	Sample number Sample extraction date Sample extraction time Sample type Sample identification method Number of sample containers Analytes Signature

6. Preservation and storage of samples

6.1. Sample preservation

Selection of an appropriate method for sample preservation before subsequent steps, that is, transfer to laboratory and storage, may reduce unfavorable sample changes. Changes of particular sample components differ depending on the degree and rate of the reaction. The reactions usually proceed very quickly and can change sample composition in a very short period of time. Therefore, it is recommended to take individual samples only for determining a given parameter. Several research groups have tested different sampling techniques and sample pretreatment procedures to revise the probability of degradation of any contaminants in water samples. The main aim of this study was to find out the maximum time between sampling and analysis in which sample changes are negligible considering the composition of the sample and the accuracy of the data monitored. Special care was taken with the experimental design in order to control the experimental arrangements and to eliminate differences which could interfere with interpretation of the results. However, preventing the samples from changing composition appears to be difficult, and no single universal method to preserve water sample composition has yet been established. The preservation method should be compatible with the analytical technique to be used for final determination of components of interest. [43, 74]. Suitable preservation techniques play a vital role in speciation analytics [75-78].

6.2. Physical preservation

Application of passive preservation techniques is highly advantageous. No chemical compounds are introduced into the sample, so therefore its composition reflects the real state of the medium studied. Physical preservation is achieved by:

- selection of a container and its preparation method appropriate for the kind of compounds to be determined,
- proper filling of containers (filling containers to the top is generally recommended so that no air bubbles are present between the water surface and the container stopper),
- maintaining appropriate temperature: sample cooling down to a temperature of 2°C to 5°C, freezing to a temperature of –20°C, or deep freezing to –70°C,
- sample filtration or centrifugation to remove suspended solids, deposits, algae, and other micro-organisms (filtration is usually performed with 0.40 to 0.45 µm filters);
- exposure to UV rays for sterilizing the sample (it can pose a threat of photodegradation of other chemical compounds present in the sample and thus change sample composition).

6.3. Chemical preservation

Changes of trace and ultratrace concentrations of the sample components may also be prevented by adding a small amount of chemical reagents to the sample. Among the most important methods of chemical preservation of water samples are the addition of acids, sulfides, solvents, toxic metal ions, azides, formaldehydes, and others. The acidification of the sample to pH = 2 through the addition of acid (HCI, H_2SO_4, HNO_3) prevents precipitation, flocculation, complexing of sample components which are the same, and inhibits the growth and biological activity of microorganisms. When storage of samples at low temperatures is not possible for any reason, the addition of compounds inhibiting the biological activity of microorganisms (biocides) is nowadays often applied. Among a variety of additives used for sample preservation, the most common are:

- mercury chloride ($HgCl_2$) - this agent acts by inhibiting the growth of bacteria in water samples. It is, however, highly toxic and the International Standardization Organization (ISO) recommends the use of mercury compounds as preservatives only where it is indispensable,
- chloroform - it is also a perfect preservation agent, inhibiting biological processes in the sample. It prevents chemical hydrolysis and biological degradation of compounds through the extraction of analytes. Chloroform may, however, be a source of carbon for duplicate types of bacteria that stimulate their growth and, in consequence, the biodegradation of other sample components. Also, when determining phosphates, the use of chloroform is not recommended,
- formaldehyde - this chemical compound also inhibits the biological activity of microorganisms; it can be applied for the determination of low-molecular aromatic hydrocarbons,
- thymol - in professional literature - mentions were made of the application of thymol as an effective biocide. No significant changes have been observed in the

composition of precipitated water samples preserved with thymol and stored for a period of 50 days.

When determining specific sample components, the addition of other reagents is necessary for their preservation, for example, the determination of oxygen, typical cyanides, and sulfides requires an appropriate compound to already be added at the stage of sampling (*in situ*). In practice, the addition of the following reducing reagents is mostly used: iodocyclohexanol (indicates the presence of oxidizing substances); salts, for example, copper nitrate $Cu(NO_3)_2$ or sodium thiosultate; gold, which, due to its ability to form an amalgam with silver, stabilizes the sample through amalgam formation; and also reagents influencing water surface tension.

6.4. Physico-chemical preservation

Storage of samples is replaced with storage of their concentrates of many organic analytes received after their separation and enrichment. Storage of extracts is advantageous in many aspects. The extracts have lower volumes (10 to 1000 times) than the original water samples. In such an approach, the water sample matrix is replaced with an appropriate solvent, or the analytes, in adsorbed form, are stored on the solid sorbent. Among the numerous techniques of separation and enrichment of organic analytes from the water samples, the following methods are worth mentioning: Liquid-Liquid Extraction (LLE), Solid-Phase Extraction (SPE), Solid-Phase Micro-Extraction (SPME), lyophylization and derivatization.

Liquid-Liquid Extraction (*LLE*) is a commonly used method for the separation and enrichment of the organic compounds from the water samples, and consists of shaking the sample together with the organic solvent immiscible with the sample. The analyte extracts in organic solvents are more stable than the water samples preserved chemically or stored at low temperatures due to the inhibition of development of microorganisms that can cause degradation of analytes.

Solid Phase Extraction (*SPE*) is a method of receiving an extract of organic compounds adsorbed on the adsorbent placed in a column or disk. Because the sizes of columns or extraction disks used in this method are small, they can be easily transferred in greater numbers to the laboratory and stored in a refrigerator. After sorption, the columns and disks are to be carefully dried to prevent possible hydrolysis reactions and the development of microoganisms.

Solid-Phase Micro-Extraction (*SPME*) is a type of solid-phase extraction.

Lyophylization of water samples is another method contributing to stabilizing the tested compounds. After being lyophilized and stored at a temperature of –20°C for 3 months, the water samples in which pesticides were present did not show any changes in pesticide content.

Derivatization of the water sample before its transport to the laboratory and storage may be an alternative to chemical preservation of the sample. Aldehydes such as formaldehyde, acetaldehyde, and others may be subjected to derivatization just after sampling, and stored in a container with *O*-*2*,*3*,*4*,*5*,*6*-pentafluorobenzylhydroxylamine. The stability of samples preserved in this way is comparable with the stability that occurs when biocides are added.

Table 8
Methods for the preservation of water and wastewater samples for the determination of inorganic compounds and physico-chemical parameters

Type of preservation and storage of samples	Parameters		Holding time max.	Ref. *
Cooling to 2÷6°C	Ammonium nitrogen, Kjeldahl nitrogen, free and ionized ammonia		6 h	ISO
	Odor, iodide		24 h	ISO, EPA
	BOD, cationic, surfactants, nitrate, nitrite, phosphate, color, turbidity, solids (settleable)		48 h	EPA
	Solids (total and suspended)		7 days	EPA
	Acidity and alkalinity		14 days	EPA
	Silicate, silica, conductivity, sulfate, bromide, chlorine, chloride, fluoride		28 days	EPA
Acidification pH < 2	H_2SO_4	Permanaganate index	48 h	ISO
		Ammonium nitrogen, Kjeldahl nitrogen, free and ionized ammonia, nitrate, COD, oil and grease, organic carbon, organic halides total (TOX), phosphorus total dissolved	28 days	EPA
	HNO_3	Metals, total hardness	6 months	ISO, EPA, UKSCA
Addition of sodium hydroxide to pH > 12	Sulfide, total cyanide, iodide		28 days 14 days	APHA EPA
Addition of organic reagents	Chloro-form	Nitrate(V), nitrate(III), suspension	A few days	UKSCA
	Formal-dehyde	Non-ionic surfactants	48 h	ISO
Addition of copper sulfate	Phenol-index		24 h	ISO
Addition of zinc acetate or cadmium acetate	Sulfide		7 days	EPA

*EPA - Environmental Protection Agency, ASTM - American Society for Testing and Materials, APHA - American Public Health Association, UKSCA - United Kingdom Standing Committee of Analysis, ISO – International Standarization Organisation

6.5. Preservation techniques of water and wastewater samples for determination of inorganic components and physico-chemical parameters

The water and waste samples intended for the determination of inorganic components and other physico-chemical parameters must be kept in containers made of polymers: polyethene (HDPE), polypropene (PP), fluorinated ethane propene copolymer (FEP), perfluoroalkoxy polymer (PF A), or of glass (*eg* Pyrex borosilicate glass). Generally, for the preservation of water and wastewater samples, one of the following methods (or an equivalent one) are recommended:

- cooling to a temperature of 2 to 5°C,
- acidification with sulphuric acid to pH < 2,

- alkalization with a sodium hydroxide solution to pH > 11,
- addition of chloroform or formaldehyde.

Table 8 shows the suitability of each of the above methods for water and waste sample preservation. Recently, a detailed specification of the preservation techniques actually used has been published [79].

6.6. Preservation techniques of water and waste samples for determination of organic compounds

Due to the intensive growth of industry, different waters become more and more polluted with toxic compounds, either organic or inorganic. Major sources of water pollution with organic substances are industrial, domestic, and agricultural wastewater. Among the organic compounds most frequently found in wastewater are aliphatic and aromatic hydrocarbons, polycyclic aromatic hydrocarbons, pesticides, phenols, and halogenated compounds. The organic compounds, dangerous to human beings as well as to fauna and flora, are the most common anthropogenic water pollutants. Therefore, permanent monitoring of water polluted with such compounds is necessary. Various methods of preservation and storage of the water samples to be subjected to analysis for organic compounds are nowadays applied by analysts. The choice depends on the type of organic compounds taken into consideration [80].

7. Stages of the analytical procedure

Every analytical procedure is a series of stages which occur in a specific sequence. So, analytical procedure can be compared with a chain made up of a great number of links, where it is obvious that the entire chain is as strong as its weakest link. This is presented diagrammatically in Figure 9.

The last step (interpretation and evaluation of analysis results) should eventually provide an answer to the starting problem, generally stated by a client of the laboratory. If the answer is not satisfactory, the analysis cycle can be followed again, after a change or adaptation of one or more steps. Sometimes this leads to the development of a new method or (part of it) procedure in order to, for example, achieve better separation of certain components, or to attain a lower detection limit for specific compounds.

Generally in a chain of chemical analysis the weakest link in an analytical process is not the one usually recognized as a part of chemical analysis such as chromatographic separation or spectrometric detection, but rather the preceding steps, often taking place outside the analytical laboratory such as the selection of object(s) to be sampled, the design of the sampling plan, and the selection and use of techniques and facilities for obtaining, transporting, and storing samples [81].

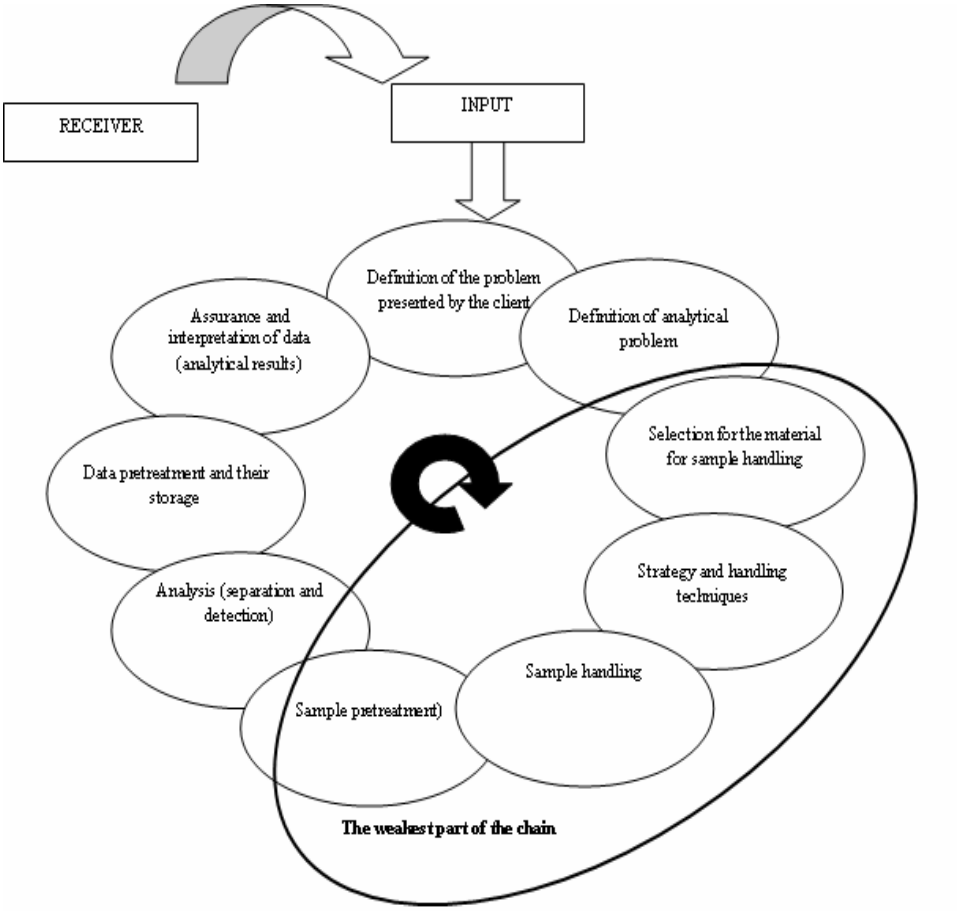

Fig. 9. Graphical representation of the analytical procedure in chain form, where subsequent links are particular stages and operations

When the analytical laboratory is not responsible for the sampling, the quality management system often does not even take into account these weak links in the analytical process. Furthermore, if preparation (extraction, clean-up, etc.) of the samples has not been carried out carefully, even the most advanced and quality controlled analytical instruments and sophisticated computer techniques cannot prevent the results of the analysis from becoming questionable. Finally, unless the interpretation and evaluation of results have a solid statistical base, it is not clear how significant these results are, which in turn greatly undermines their merit. We therefore believe that quality control and quality assurance should involve all the steps of chemical analysis as an integral process, of which the validation of the analytical methods is only one, though an important, step. In laboratory practice, quality criteria should concern rationality of the sampling plan, validation of methods, instruments and laboratory procedures, the reliability of identifications, the accuracy and precision of measured concentrations, and

the comparability of laboratory results with relevant information produced earlier or elsewhere.

Based on many opinions, it can be stated that extracting and preparing samples for analysis are the weakest links of this chain, presented in Figure 9. This leads to one very obvious conclusion: it is necessary to pay particular attention to these two stages, so that the outlay of time, labor and money produces the desired effect, *ie* reliable analytical data, which is in great demand. The extracted samples must be appropriately prepared for the final stage of analysis. The various operations performed *in situ* and/or in the laboratory result in a sample for analysis which is characterized by appropriate values of the following parameters:

- size (mass, volume),
- state of matter,
- analyte concentration range,
- presence of interferants.

Table 9

Typical operations and measurements from the sample preparation stage

Operations and activities	Sample type		
	Gaseous samples	**Liquid samples**	**Solid samples**
Carried out *in situ*			
- Dust removal	+		
- Drying	+		
- Removal of interferences (*eg* deoxygenation)			
- Suspended particulate matter (SPM) removal	+	+	
- Preservation (chemical)		+	
- Derivatization		+	
- Isolation and/or preconcentration	+	+	+
- Transport	+	+	+
Carried out in laboratory			
- Drying		+	+
- Grinding			+
- Homogenization and mixing	+	+	+
- Preservation (thermal and/or chemical)		+	+
- Sieve analysis			+
- Mineralization		+	+
- Isolation and/or preconcentration	+	+	+
- Derivatization	+	+	+
- Analyte extraction	+	+	+
- Purification and removal of interferences	+	+	+
- Sample fractionation and partioning	+	+	+
- Calibration and verification of the instrument and methods	+	+	+
- Sample introduction to the instrument	+	+	+

Figure 10 diagrammatically presents the different portions of the preparation stage (preparing samples for analysis) within the entire uncertainty budget and the analysis duration. The information used for preparing the above diagrams has been collected in a questionnaire sent to over 250 respondents (analytical laboratories in Central European countries).

Table 9 compares typical operations and measurements from the sample preparation stage.

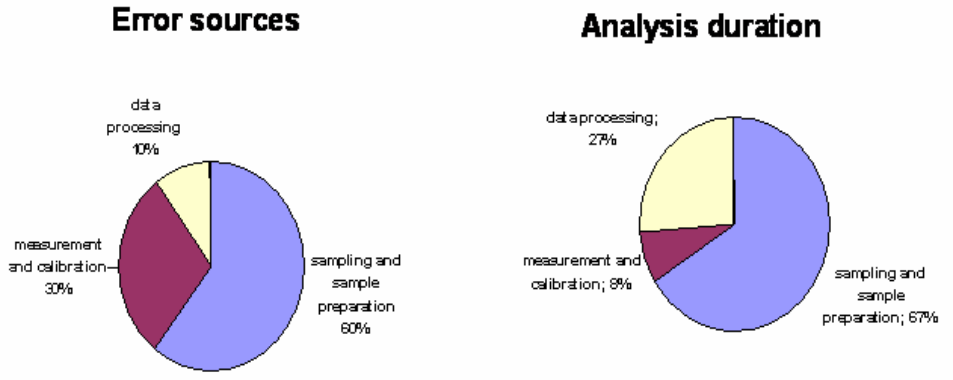

Fig. 10. Portions of the sample preparation stage within the whole uncertainty budget and the analysis duration

Table 10

Main tasks of sample preparation for chromatographic analysis

Aim	Operation
Assuring sample stability and homogeneity during sample transportation and storage	• Grinding • Homogenization • Sieve analysis • Drying • Freeze drying • Chemical preservation • Thermal preservation
Removing interferences	• Dust removal from gaseous samples • Drying of gaseous samples • Oxygen removal from gases • SPM removal from water
Analyte conversion into a form suitable for: Isolation and concentration, Separation, Detection.	• In-situ derivatization • On-column derivatization • Post-column derivatization
Matrix exchange for instrument compatible one	• Analyte extraction using: - Gas stream - Supercritical fluid - Organic solvent • Membrane processes • Thermal desorption to transfer analytes from solid sorbent bed to chromatographic column
Increasing analyte concentration to an instrument detectable level	Isolation and preconcentration of analytes to increase concentration with respect to matrix components (effectiveness characterized by concentration factors)
Reducing solvent consumption	Solventless sample preparation

Table 11

Information on selected isolation and/or enrichment techniques for organic compounds

Extraction technique	Description
Gas-phase extraction headspace (HS) techniques	HS is based on the partition of analytes between the liquid phase. The concentration of analytes in the condensed phase is determined by analyzing the headspace - the gaseous phase in contact with the sample. The most effective release of analytes is achieved for volatile and semivolatile nonpolar or moderately polar organic compounds [82-84].
Static headspace	Both phases are in contact - aqueous (sample) and gaseous (receiving matrix) are stationary. The analysis proceeds in two steps: the examined sample is placed in a closed container at a constant temperature, the system is brought to thermodynamic equilibrium, and a sample of headspace is collected manually or automatically.
Dynamic headspace (TLHS)	The gaseous phase is passed continually through or over a sample (concurrently or countercurrently) and the analytes carried with it are retained in a trap with a sorbent (*eg* water). This technique is often combined with direct aqueous injection (DAI) onto the GC column of a chromatograph equipped with an electron capture detector (ECD).
Purge and trap (PT)	A stream of gas is bubbled through the analyzed liquid sample. The purged analytes are then retained in a trap, from which they are subsequently released, most often thermally, into a gas chromatographic column. This technique is widely used for the determination of volatile and semivolatile organic compounds in a variety of aqueous matrices.
Distillation techniques	These techniques are used for the isolation of volatile, more polar compounds from liquid matrices. They enable the determination of analytes in a sample with a high content of inorganic or high-molecular-weight organic compounds, which would otherwise require an extensive pretreatment procedure prior to chromatographic analysis. The basis for the separation of a mixture into components is the diverse partition of individual components between the liquid phase and the gaseous phase equilibrated with it. The gaseous phase is enriched in more volatile components, which following condensation becomes a concentrate of these components - distillate. Thin layer distillation (TLD) permits analyte transfer from the matrix in a flow injection configuration [85].
Liquid-liquid extraction (LLE)	The principle of isolation is based on partition of analytes between the liquid phase (sample) and an organic solvent. Solvents immiscible with water are used for extraction. The analytes dissolve better in the solvent than in water. This technique is used for semivolatile and nonvolatile compounds [86].
Solid-phase extraction (SPE)	Solid phase extraction involves transfer of analytes from a liquid sample to a solid sorbent, followed by their release using extraction with a solvent of high elution strength or, less frequently, thermal desorption. A large selection of solid sorbents ensures the obtainment of proper selectivity and an optimal enrichment factor of the analytes. Typical sorbents used for analyte retention include: porous polymers, such as styrene-divinylbenzene copolymers; carbon sorbents; and silica gels with chemically bonded stationary phases containing various functional groups. SPE enables isolation and enrichment of analytes with a wide range of volatility and polarity [87-102].
Solid-phase microextraction (SPME)	In SPME, the sorption medium constitutes a layer of liquid or solid coating on a fused silica fiber. This ensures a rapid transportion of the analyte from the sample to the sorbent and simplifies introduction of analytes into a chromatographic column [103-105].

Table 12
Advantages and drawbacks of the most commonly used techniques of isolation and/or enrichment of volatile organic compounds from liquid samples

Technique		Advantages	Drawbacks
Liquid-liquid extraction (LLE)		- simplicity; - inexpensive apparatus;	- tediousness; - need to use large volumes of solvents of high purity; - an often small enrichment factor of the analyte; - low selectivity of the process; - possible formation of emulsions which are difficult to separate; - difficulties with handling large-volume samples;
Solid phase extraction	Solid-phase extraction (SPE)	- possible to store enriched analytes on the solid sorbent (analytes sorbed on the solid sorbent can be transported and stored); - reduction of the volume of toxic solvents used; - emulsion formation not a problem; - much larger enrichment factor of the analyte compared to LLE - ease of automation;	- possibility of low analyte recovery (due to either matrix-sorbent interactions or breaking through of the sorbent bed); - sometimes poor reproducibility resulting from differences in various batches of the sorbent; - clogging of the sorbent (both in columns and in extraction disks) by particles suspended in the sample;
	Solid phase microextraction (SPME)	- elimination of solvents; - short analysis time; - simplicity of operation; - low cost; - ease of automation;	- sensitivity of the PDMS fiber to the presence of suspensions; - low efficiency of the process resulting from the small amount of stationary phase present on the fiber;
Gas extraction	Static headspace analysis	- simplicity of operation; - ease of automation; - elimination of solvents;	- relatively low sensitivity;
	Dynamic headspace analysis	- low detection limit; - relatively short analysis time; - good precision of determinations; - elimination of solvents from the procedure; - possibility to analyze large volume samples and complex organic matrices; - ease of automation;	- expensive apparatus; - problems with foaming samples;

Keeping proper documentation is a significant element of the sample preparation stage [73].

Chromatographic and related techniques play a vital role in chemical analytics. They should be regarded as a tool of a very high decomposition potential. Appropriately

prepared samples for analysis may still extend the practical range of applications for chromatographic techniques. Table 10 presents the basic tasks of the sample preparation stage for chromatographic analysis.

In analytical practice, analytes in organic samples, which are often characterized by very complex and changeable matrix compositions, are isolated and enriched using a wide spectrum of techniques based on the mass transport phenomenon [106, 107].

In Tables 11 and 12 basic information on selected techniques for the isolation and/or preconcentration of organic analytes and their advantages and drawbacks are presented, respectively.

Figure 11 schematically/diagrammatically presents the practical applications of the known extraction techniques before chromatographic determination of a broad spectrum of organic components.

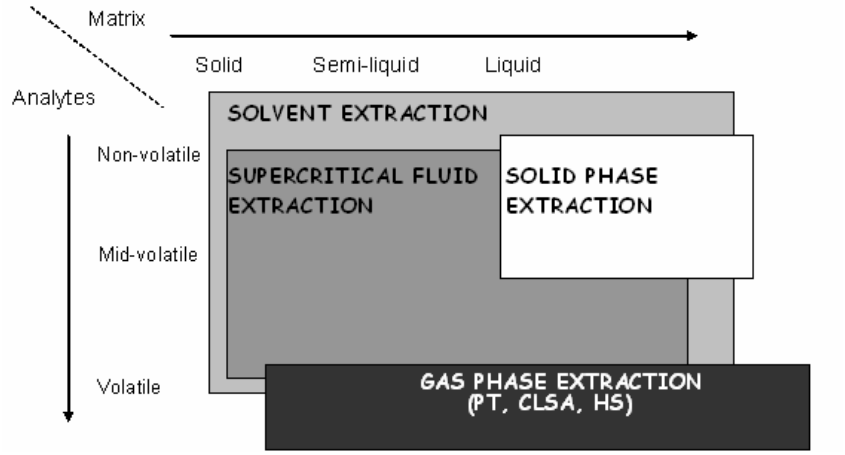

Fig. 11. Practical application of the known analyte extraction techniques before chromatographic separation and determination

8. New methodological developments in preparing samples for analysis

Table 13 compares published information on the new methodological solutions for preparing samples with complex matrices for final determinations.

Table 13

General information on new methodological developments in preparing samples for analysis

No.	Innovation examples (new solutions)	Operations related to the sample preparation stage	Literature reference
1	2	3	4
1.	Cloud point phenomenon (Cloud Point Extraction - CPE)	Extracting analytes (both organic and inorganic) from water samples	108-115
2.	Pressure assisted chelating extraction (PACE)	Novel technique for the digestion of metals in solid matrices	116

1	2	3	4
3.	Sequential solid phase extraction (SSPE)	Extraction of nonsulfonic acids from coastal water samples	59, 117, 118
4.	Development of matrix solid-phase dispersion (MSPD) concerning: - new sorbents, - temperature and pressure of extraction, - clean-up of extracts, - miniaturization	Extraction of organic xenobiotics from a variety of solid, semi-solid and viscous environmental and biological matrices	119-124
5.	Application of pressurized hot water (subcritical water) as the extraction medium	- Extraction of moderately and non-volatile thermally stable organic pollutants from a variety of solid and semi-solid environmental matrices - Extraction of metals such as copper and lead from used industrial oils with acidified PHWE	125-127 128
6.	New achievements and development of new techniques: Pressurized Liquid Extraction - PLE (Accelerated Solvent Extraction - ASE, Pressurized Fluid Extraction - PFE)	Extraction of different microcontaminants in a variety of semi-solid samples	126, 129-134
7.	Microemulsion mediated *in situ* derivatization - extraction (INDEX)	Derivatization - extraction of acidic compounds in water matrix with alkylbromides in homogenous a reaction mixture generated by mixing water, hydrophilic alkyl bromide and co-solvent	135
8.	Enzyme catalyzed esterification of phenolic acids in a surfactantless microemulsion system (SLME)	Derivatization of phenolic acid in water prior to its chromatographic determination	136
9.	Application of UV radiation at different stages of sample preparation	Post-column UV irradiation in order to destroy the structure of organic compounds leasing the chromatographic column Oxidizing organic matter contained in the sample Hybrid photocatalysis/membrane treatment of water UV digestion of the sample	137 126, 138 139 140
10.	New achievements in wet digestion techniques	Sample matrix digestion with use of chemical agents	140-144
11.	New application of supercritical fluids	*In situ* derivatization reactions prior to SFE with CO_2 Sequentional Supercritical Fluid Extraction (SSFE) for estimating the availability of PAHs in a solid Supercritical water oxidation technology (SCWO) applied to the treatment of industrial wastes and sludges	145 146 147

1	2	3	4
12.	Application of ultrasound (sonochemistry)	Ultrasonic treatment of wastes and waste activated sludges	148, 149
		New ultrasound-assisted extraction techniques for both an inorganic and organic sample constituent under investigation	31, 34, 150-158
		Ultrasounds assisted cold vapor generation	159
		Focused sonic probe for speciation analytics	157
		Mineralization of organic compounds by a heterogeneous ultrasound/catalyst process	160, 161
		Ultrasonic atomization technique applied to the removal of Endocrine Disrupting Compounds (EDC's) from an aqueous environment	162
		Sono-sorption as a new technique for the removal of lead ions from an aqueous solution	163
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		Permeable Environmental Leaching Capsules (PELCAPs) for *in situ* evaluation of contaminant immobilization in soil	176
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		Chromatomembrane cells as a unit for advanced sample pretreatment for the monitoring of different types of organic compounds in water	192
15.	Derivatization of analytes with the use of new agents	Optimization of different derivatization approaches for the determination of pentachlorophenol (PCP) in wastewater irrigated soil	193
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		Application of the Stir Bar Sorptive Extraction (SBSE) technique in environmental analytics	204-210
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		Evaluation of multi-walled carbon nanotubes as an adsorbent for trapping volatile organic compounds from environmental samples	226-228
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1	2	3	4
		Hemicelles and admicelles based solid phase extraction of linear alkylbenzene sulfonates (LAS's) and phthalate esters from water	232, 233
		Application of Colorimetric Solid Phase Extraction (CSPE) in speciation analytics	234
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9. Application of membrane techniques

In the simplest approach, a membrane can be treated as a selective barrier between two phases. The phase in which mass transfer takes place is called the donor phase, while the other phase is called the acceptor phase [106].

A general principle for the separation of liquid mixture components using membranes is shown schematically in Figure 12.

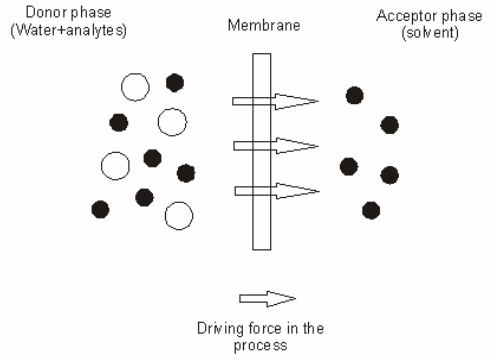


Fig. 12. Schematic representation of transport through membranes

The main factors affecting mass transfer across the membrane are:
- type of membrane,
- driving force of the extraction process.

There are a number of criteria used for the classification of membranes. The ones most often taken into consideration when characterizing membranes are [106]:
- membrane state,
- membrane morphology (closely related to porosity and internal structure),
- membrane shape.

A diagram illustrating membrane classification according to the above criteria is shown in Figure 13. Information on the morphology of various types of membranes which could find use in environmental analytical chemistry is compiled in Table 14.

Table 14

Information on the morphology of membranes used processes

<table>
<tr><th colspan="2">Porous membranes</th></tr>
<tr><th>symmetric</th><th>Asymmetric</th></tr>
<tr><td>• capillary or irregular pores;
• identical porosity in the direction perpendicular to external surfaces;
• preparation methods:
- sintering,
- radiation with etching,
- phase inversion.</td><td>• increase in porosity perpendicular to the surfaces;
• smallest porosity in the surface layer;
• separation layer - surface layer;
• support layer (reinforcing)
- the rest of the membrane;
• methods of formation:
- thermal gelation,
- vapor adsorption,
- Loeb-Sourirajan phase inversion
• Composite asymmetric membranes
- two- or multilayer;
- different composition of individual layers;
- formed by coating a layer of selective properties onto a porous protective layer.
• Dynamic asymmetric membranes
- formed dynamically;
- formed by coating colloids or macromolecular compounds onto a porous bed under pressure;
- support - filtration foil made from an organic material; plate, tube or molder made from a ceramic, carbon or metal sinter;</td></tr>
<tr><th colspan="2">Nonporous membranes</th></tr>
<tr><td colspan="2">• lack of conventional pores (pores of molecular dimensions);
• continual variations in the number, size and location of pores as a result of thermal molecular motions in the membrane material.</td></tr>
<tr><th>solid</th><th>liquid</th></tr>
<tr><td>inorganic membranes:
• material: metals, metal alloys, sintered ceramics, glass
Organic membranes:
material: natural and synthetic polymers, eg cellulose acetate, silicone rubber, polyethylene.</td><td>• thin liquid layer with a dissolved mediator;
• separates a donor solution from an acceptor solution;
• kinds:
- thick-layer,
- emulsion,
- reinforced.</td></tr>
<tr><th colspan="2">Ion-exchange membranes</th></tr>
<tr><td colspan="2">• nonporous, microporous and porous membranes of symmetric or asymmetric structure;
• kinds:
- cationic (cation exchange) - cations pass towards the cathode through a constant electrical field and exclude anions,
- anionic (anion exchange) - anions pass towards the anode through a constant electrical field and exclude cations.</td></tr>
</table>

Separation of components in the membrane process results from differences in the transfer rate of chemical compounds across the barrier. It is a nonequilibrium process, in which the flow of a component depends on the driving force. Some basic information on the driving forces for the membrane processes is given in Table 15.

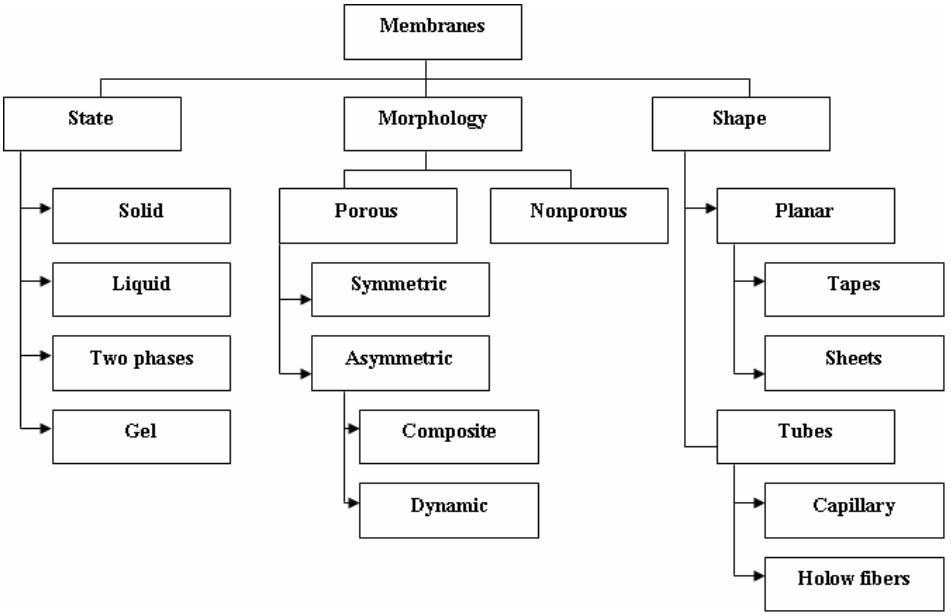


Fig. 13. Classification of membranes with respect to their state, morphology, and shape

Table 15

Basic information on the driving forces in membrane processes

No.	Driving force of the extraction process	Name and mathematical form of the equation used to describe mass transfer	Membrane techniques in which the mass transfer equations are used
1	Concentration gradient	Fick's law of diffusion: $J_m = -D^* A(dC/dx)$	dialysis, membrane extraction
2	Pressure difference	Hagen-Poiseuille equation: $J_v = -K^{**} A(dP/dx)$	filtration
3	Potential difference	Ohm's law: $J_c = -R^{***} A(dE/dx)$	electrodialysis

* - diffusion coefficient
** - hydrodynamic permeability
*** - resistance
A - diffusion surface (membrane surface)

Various analytical techniques make use of both porous and nonporous (semipermeable) membranes. For porous membranes, separation of components is accomplished as a result of a sieving effect (size-exclusion), *ie* the membrane passes through molecules with diameters smaller than the membrane pore diameter. The selectivity of such a membrane is thus dependent on its pore diameter. The operation of nonporous membranes is based on differences in solubility and the diffusion coefficients of individual analytes in the membrane material. A porous membrane impregnated with a liquid or a membrane made of a monolithic material, such as silicone rubber, can be used as nonporous membranes. Basic information on membrane techniques used in analytical practice is provided in Table 16.

Table 16

Basic information on types of membrane techniques

Technique	Kind of membrane	Principle	Driving force	Mainly combined with
Filtration	porous	size-exclusion	Pressure difference	LC
Dialysis	porous	size-exclusion	concentration gradient	LC
Electrodialysis	porous	size-exclusion and selective ion transport	Potential difference	CE
Membrane extraction	nonporous	difference in partition coefficient	concentration gradient	LC, GC, CE

9.1. Filtration

The general term “membrane filtration” includes four processes:
- microfiltration,
- ultrafiltration,
- nanofiltration,
- reverse osmosis.

The driving force behind these processes is the pressure difference across the membrane in a membrane module. Under the pressure gradient applied and due to selective operation of the membrane, some components of a solution penetrate the membrane, while others remain in the solution [252-255].

Individual membrane filtration processes differ with respect to:
- the size of molecules retained by the membrane,
- the kind of membrane used,
- the kind of solutions being separated,
- the magnitude of the pressure difference across the membrane. The classification of membrane filtration techniques with respect to the sizes of molecules being separated and the range of pressures used is shown in Table 17.

The membrane filtration techniques are often discussed in papers dealing with membrane extraction; however, it should be pointed out that they are not strictly membrane extraction techniques.

Table 17

Classification of filtration techniques based on the size of the molecules being separated and the range of pressures applied

Filtration technique	Size of molecules being separated [nm]	Pressure gradient [MPa]
reverse osmosis	0.1÷1.0	> 1
Nanofiltration	~ 1.0	~ 1
Ultrafiltration	1.0÷10.3	0.2÷1
Microfiltration	10.3÷10.5	< 0.2

Filtration benefited significantly from developments in synthetic chemistry that added new polymers for filter manufacturing. These new materials have properties that are more suitable for filtration. Examples are polymers having a low adsorption of particular analytes (*eg* polyethersulfones or polytetrafluoroethylene (PTFE) that have a low adsorption of proteins) polymers with a high resistance to solvents (*eg* PTFE),

which is practically insoluble in any solvent), very pure polymers that have no residual chemicals to act as contaminants, etc. Paper filters, impregnated with a stabilized silicone that lends a hydrophobic property to the filter to allow the retention of an aqueous phase while passing the solvent phases through. Such a filter can be used for the separation of a mixture of water and a hydrophobic solvent, giving a solvent phase that is completely free of the aqueous phase.

A list of common filter materials used today in sample preparation is given in Table 18. As seen in this table, old materials such as cellulose, cellite, and porcelain are still used together with new polymers as filtration materials. Further progress in materials science has also helped filtration technology. The manufacturing of membranes with homogeneous pores, and with "unidirectional pores," as found in asymmetric membranes, allows faster and better filtration, less adsorption of macromolecular materials in filters, and sharper differentiation of molecules based on their size by ultrafiltration [256].

Table 18

Common materials used for filters

Filter material	Solution type	Pore size [µm]	Application*
Cellulose	Water, organic	1, 5, 10, 20	Prefiltration
Cellulose acetate	Water	0.22, 0.45, 0.80	Biological fluids, MF, UF
Cellulose triacetate	Water	0.22, 0.45, 0.80	Biological fluids, MF, UF
Cellulose nitrate	Water	0.2, 0.45, 0.8	Biological fluids, MF
Glass microfiber	Any	Various	Prefiltration
Mixed cellulose ester	Water	0.22, 0.44	Biological fluids, MF
Nylon	Water, organic	0.22, 0.45	Water or solvent solutions, MF, UF
Polyacrylonitrile	Water, organic		Water, solvents, UF
Polycarbonate	Water etc.	0.2, 0.4 etc.	MF
Polyesters	Organic, water		MF
Polyethersulfone	Water	0.1, 0.22, 0.45	Biological fluids, MF, UF
Polyimides	Water		Biological fluids, MF
Polypropylene filaments	Organic, water	1, 5, 10, 20	Water, solvents, MF
Polypropylene hydrophilic			MF
PTFE hydrophobic	Organic	0.45, 0.50	Aggressive solvents, MF
PTFE hydrophobic**	Organic	0.45, 0.50	Aggressive solvents, MF
PTFE hydrophilic	Organic, water	0.45, 0.50	Water or solvent solution, MF
Polyvinyl chloride	Water	0.45, etc	Water solution, MF, UF
Polyvinilydene fluoride	Water	0.22, 0.44	Biological fluids, MF, UF,
Porcelain			Water or solvent solutions, MF
Regenerated cellulose	Water, organic	1, 5, 10, 20	Prefiltration
SiO_2, cellite, diatomaceous earth, celatom, Fuller's earth	Organic, water	Various particle size	Prefiltration, water or solvent solutions
Surfactant-free cellulose acetate	Water	0.22, 0.45, 0.80	Biological fluids, MF, UF

* MF = microtitration and UF = ultratitration,
** Bonded with polyethylene

9.2. Membrane extraction

The membrane extraction process mostly makes use of nonporous membranes. Such a membrane can be a liquid or a solid phase (polymer impregnated with a liquid), which is placed between two other phases, usually liquid, but sometimes also gaseous. Based on literature available, it can be concluded that the term "membrane extraction" includes the following apparatuses and procedures [106, 257-260]:

- supported liquid membrane extraction (SLM),
- microporous membrane liquid-liquid extraction (MMLLE),
- polymeric membrane extraction (PME),
- membrane extraction with a sorbent interface (MESI).

Basic information on these techniques is provided in Table 19.

Table 19

Basic information on the membrane extraction techniques which find use in the analysis of liquid samples

Acronym	Name of technique	Type of membrane	Combination of phases used Donor/membrane/acceptor
SLM	Supported liquid membrane extraction	Nonporous	Aqueous/organic/aqueous
MMLLE	Microporous membrane liquid-liquid extraction	Nonporous (microporous)	Aqueous/organic/organic Organic/organic/aqueous
PME MASE	Polymeric membrane extraction, Membrane assisted sorbent extraction	Nonporous	Aqueous/polymer/aqueous; Organic/polymer/aqueous; Aqueous/polymer/organic
MESI	Membrane extraction with a sorbent interface	Nonporous	Gaseous/polymer/gaseous; Liquid/polymer/gaseous

10. New aspects of the liquid-liquid extraction technique

Solvent extraction is another field in which progress in new materials has helped significantly [256]. Although most extractions are still carried out with solvents such as methylene chloride or *tert*-butyl methyl ether, a continuous effort is made to eliminate these organic solvents. Among the new types of extraction media is the aqueous polymeric solution.

Table 20

Examples of new materials used in an aqueous solution as an extraction media

Agent	Type	Solvent system	Application
Palmitoyl modified poly(propylene imine)	Dendrimer	Water/supercritical CO_2	Extract anionic species
Fluorinated acrylate/ functionalized styrene	Dendrimer	Water/supercritical CO_2	Extract copper and europium ions
Poly(*N*-isopropylacrylamide)	Temperature responsive polymer	Water/polymer	Hydrophobic species separation
Anionic surfactant (dodecyl sulfate, dodecylbenzenesulfonic acid, etc.)	pH responsive agent	Water/surfactant	Pyrene, polycyclic aromatic hydrocarbons

The precipitated polymer can incorporate organic compounds such as polycyclic aromatic hydrocarbons (PAHs), alkylphenols, chlorobenzens, chlorophenols, phthalate

esters, and steroid hormones, yet hydrophilic compounds such as inorganic ions and polysaccharides remain in the bulk aqueous solution, allowing separation. The solution of the polymer in the hydro-organic mobile phase of an HPLC system does not typically influence separation. A few new polymeric materials used in LLE are shown in Table 20.

10.1. Matrix solid-phase dispersion - MSPD

In 1989 solid sorbents were used in the extraction of analytes from solid samples for the first time. Samples were placed in a glass mortar and blended with modified silica [14]. Sorbent was added in order to [261]:

- grind the sample evenly (sorbent acts as an abrasive material),
- bind solvents that cause lysis of cellular membranes for biological material,
- improve mechanical properties of the sample blended with sorbent, which enables to provide a possibility of performing fractionated extraction of analytes (the mixture of sample and sorbent is a new type of filling).

The liquid extraction technique from ground solid samples may be used to isolate analytes from solid. This extraction method is particularly useful when extracting analytes from dense materials, such as food samples, plant and animal tissue samples, or fat samples.

The extraction column with a paper filter at the bottom was filled with sample prepared as described above. The deposit was secured with a paper filter at the top as well and the whole was compressed with a special piston. Next, the column was filled with a known volume of solvent for extraction. The solvent flow was forced by using a rubber pipette syringe and the solvent was collected in special receivers. A scheme presenting the extraction method with the MSPD technique is shown in Figure 14.

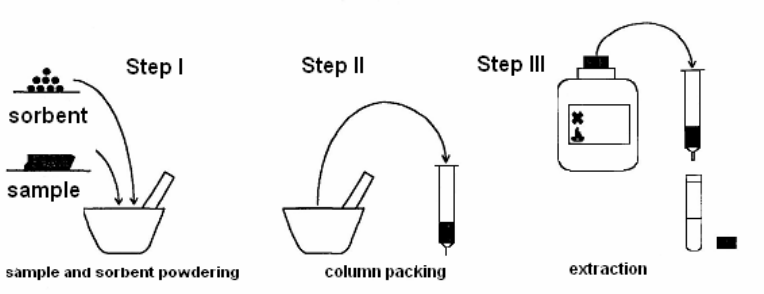


Fig. 14. Representative scheme of MSPD extraction

This method of extraction is different from solid phase extraction (SPE) in that for SPE the samples put in the column must be in the form of a liquid solution. Interactions between particular components of the dispersed sample are stronger and partly different compared with SPE. Specific interactions among all elements of the system, *eg* analytes, interferants, the sample matrix, the solid sorbent added to the sample and the solvent used for extraction, have been observed. The obtained extracts were purified using SPE

or were subjected to final analysis using chromatographic techniques without purification.

The described extraction technique is similar to classic sample homogenization techniques, which usually consist of grinding, pounding or crushing samples. The effects of mechanical grinding are often enhanced by adding solvents, acids, alkalis, detergents or chelating agents, which usually leads to the partial extraction of analytes - an unintended effect. The extracted compounds may adsorb on the walls of the vessels and instruments used. Forming emulsion may be another negative effect. In such a case it is necessary to centrifuge and re-extract analytes from the sample, which is an additional obstacle to carrying out an analytical procedure. **M**edium **P**ressure **L**iquid **E**xtraction (MPLE) is an extraction technique between MSPD and ASE. In this case, the ground sample mixed with solid sorbent fills the chromatographic column through which the solvent is pumped with a special, low-pressure pump. Column discharge (extract) may be subjected to final analysis without further purification.

10.2. Supercritical fluid extraction - SFE

A supercritical fluid is a substance resulting after the exceeding of the so-called critical point, when it shows characteristics of both a gas and a liquid at the same time, being neither one nor the other. Figure 15 presents a diagram explaining the notion of a supercritical fluid. The first researchers to use supercritical fluid for analytical purposes were Klesper, Corwin and Turner (in 1962). Supercritical fluid was used in high-pressure fluid chromatography, where it was part of the mobile phase. Extraction with supercritical fluid was first accomplished in 1978, and since then the SFE technique has been undergoing active development, finding many applications in laboratory analysis and industry [262].

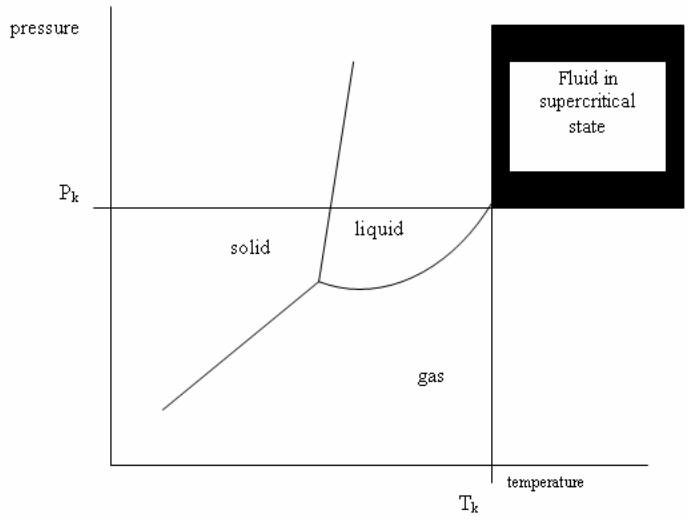


Fig. 15. Phase diagram explaining a concept of fluid in supercritical status

After exceeding the critical point the substance shows certain characteristics of both a gas and a liquid at the same time, but also a number of properties characteristic only for this form of matter, which are as follows:

- it does not subject itself to condensation,
- it does not boil,
- it does not form a meniscus (property characteristic of gases); it is marked by the capability to dissolve, which is characteristic of liquids,
- high "diffusibility": dissolved substances spread in supercritical fluid with speeds between liquids and real gases,
- lack of surface tension, because of which supercritical fluid penetrates even the smallest pores of the sample matrix,
- low viscosity of supercritical fluids ensures effective penetration of the entire sample.

A combination of the aforementioned properties of supercritical fluids accounts for the fact that they penetrate the sample matrix like gas and at the same time dissolve analytes like liquids. Physical properties characteristic of liquids, supercritical fluids and gases are shown in Table 21.

Table 21

Physical properties of liquids, gases and fluids in supercritical status

Physical feature	**Liquids**	**Fluids in supercritical status**	**Gases**
Density [g/cm^3]	1	0.2÷0.9	10^{-3}
Viscosity [g/(cm·s)]	10^{-2}	10^{-4}÷10^{-3}	10^{-4}
Diffussion coefficients [cm/s]	$<10^{-5}$	10^{-3}÷10^{-4}	10^{-1}

Every substance has its own, individual values of critical pressure and temperature that are often difficult to obtain in laboratory conditions. Because of this, despite attempts to use various substances as extraction media during the development of SFE, most of those substances have proven useless.

Table 22

Critical parameters of selected substances used as fluids in supercritical status

Substances	**T_{cr} [°C]**	**P_{cr} [atm]**	**P_{cr} [10^3 kg m^{-3}]**
CO_2	31.3	72.9	0.47
N_2O	36.5	72.5	0.45
SF_6	45.5	37.1	0.74
NH_3	132.5	112.5	0.24
C_2H_6	32.2	48.2	0.2
n-C_4H_{10}	152	37.5	0.23
n-C_5H_{12}	197	33.5	0.23
Xe	16.6	58.4	1.1
CCl_2F_2	112	40.7	0.56
CHF_3	25.9	46.9	0.52
H_2O	374	227	0.35
CH_3OH	239.4	79.9	0.27

Table 22 lists critical parameters of substances most commonly used as solvents in SFE. Properties that need to be taken into account while selecting supercritical fluids for

extraction using SFE (apart from those mentioned in Table 22) are: combustibility, toxicity and price.

A substance that has favorable critical parameter values and best matches the other aforementioned criteria is carbon dioxide (CO_2). The critical temperature of carbon dioxide is +31.3°C, which is especially important for thermally unstable analytes, and its critical pressure of 72.9 bar (1 bar = 10^5 Pa) is easy to obtain in laboratory conditions. Moreover, carbon dioxide is non-flammable, non-toxic, does not pose any additional, serious threat to the environment, and is relatively inexpensive. For *on-line* solutions it is important that CO_2 is compatible with most chromatographic detectors.

Because CO_2 has weak dissolving capabilities, it is suitable as an extraction medium in SFE only for compounds of small and medium molecular mass and low polarity. As a result, suitable modifiers must be added in order to extract polar substances. Modifiers are polar organic solvents *ie* with non-zero dipole moment (methanol, acetonitrile, tetrahydrofuran or water are most commonly used) which enhance the diffusibility of polar analytes in nonpolar extraction mediums such as CO_2.

SFE is carried out above the solvent critical point, and the properties of a supercritical fluid depend on pressure and change along with its density. These criteria determine the selectivity of the extraction medium. One fluid can therefore be used to extract a whole series of compound groups (depending on the pressure in the system, temperature, extraction medium volume flow, and extraction time), and to separate the obtained extract into appropriate fractions. Selective fractionation is used for example in separating olfactory and gustatory substances in the extraction of hops for beer production.

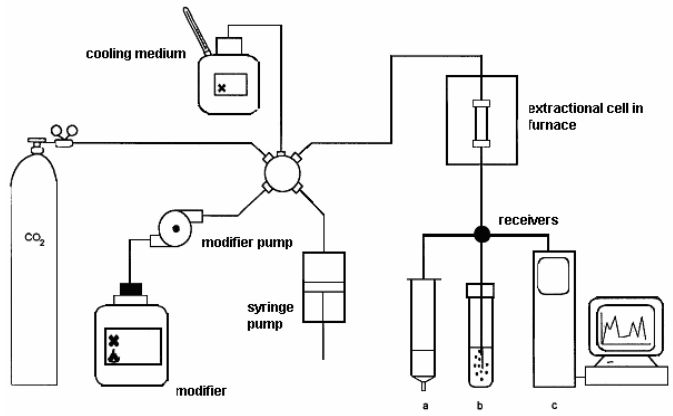


Fig. 16. Scheme of apparatus used for SFE

Fractions of three groups of substances used in beer production are extracted from hops using supercritical CO_2. The first fraction, the so-called oil essence, was obtained via extraction with CO_2 at a density of 0.30 g/cm^3 and a temperature of 50°C. Bitter substances were collected as the second fraction at a CO_2 density of 0.70 g/cm^3 (50°C); that fraction scarcely coincided with the third and last fraction of neutral fats, extracted at a CO_2 density of 0.90 g/cm^3 (50°C).

The extraction medium in SFE is supplied from a cylinder to a pump where it is compressed to a desired pressure of critical range. Next, in this form, the fluid reaches the vessel with a sample situated in a chamber heated to the critical temperature. Here, the substance, already in the supercritical fluid state, extracts analytes, and the extract is collected in a special receiver. A diagram of the instruments used for SFE is shown in Figure 16.

The sample for extraction is situated in a special container which is then driven into the chamber. These are the two preparatory stage measures taken before sample extraction. For solid samples, an additional homogenization stage is necessary, which facilitates the diffusion of analytes in the whole sample volume. Desiccants, such as Na_2SO_4 or $MgCl_2$ are often added to a sample in order to remove moisture. Soils and sediments usually contain certain amounts of organosulfur compounds which decompose under the influence of temperature, and products of this decomposition may cause fluctuations in flow volume and even choke the outflow from the extraction chamber. To avoid such complications, acid-cleaned copper granules, which react with organosulfur compounds to produce copper sulfide, are put in the sample-containing chamber.

Supercritial fluid extraction may be carried out in both *off-line* and *on-line* systems. In the off-line case, the receiver can be an empty container, a trap, an analytical column with which further analysis will be performed, or a container with the solvent. There exist several variants of SFE in an off-line system: extraction in a dynamic or static system, or in a supercritical fluid recirculating system.

Extraction in static conditions consists of flooding the sample with a supercritical fluid, where it is 'drenched' for some time, and then the solvent, together with enriched analytes, is taken to a receiver. The “drenching” stage is useful when the analytes are difficult to isolate from the matrix due to a small dissolution rate or a compact structure of the sample. In a supercritical fluid recirculating system, one dose of a solvent is pumped many times through the sample container. After some time, the solvent with the isolated analytes is entirely or partly collected in the receiver. For *on-line* SFE, the extract in the container is not collected in the container, but is directly supplied into the analytical apparatus.

In a dynamic extraction system, the supercritical fluid is pumped through the container with the sample to the receiver only once. In the receiver, the liquid is subject to vaporization, leaving concentrated analytes which are then dissolved in a small volume of the solvent. Such extracts are subjected to analysis, the aim of which is to determine the selected analytes. This manner of extraction is effective if the analytes dissolve well in the solvent and the sample matrix is penetrable. Apart from the aforementioned possibility of fractionated extraction, SFE has many other advantages as a result of the special properties of supercritical fluids:

- a considerable reduction in the amount of solvent (compared with “classical” methods of extraction such as extraction by shaking, or Soxhlet extraction) which are usually harmful to the environment and human health,
- small samples for extraction; shorter extraction duration,
- decrease in the costs of the process (compared with “classical” techniques),
- usage of low temperatures (which favors extraction of thermally unstable compounds).

11. Unique phase separation behavior of surfactant micelles

Aqueous solutions of neutral (*ie* non-ionic or zwitter-ionic) surfactants can form micellar assemblies in which a certain number of surfactant molecules aggregate to form an assembly possessing a central core region comprised of long alkyl (or alkylaryl) hydrocarbon chains with their more polar polyethyleneoxide (or zwitter-ionic) headgroups extending outward and interacting with the bulk water [263].

Aqueous solutions of neutral surfactants have two particularly important properties (*ie* their solubilization ability and phase separation behavior) that can be exploited in order to develop a new viable extraction-preconcentration technique.

Firstly, it is well known that micellar aggregates in water can solubilize and bind hydrophobic solute molecules that are typically insoluble or only sparingly soluble in bulk water. For example, whereas the solubility of pyrene and anthracene in water is in the 0.1÷0.6 micromolar range, their solubility can easily be increased to the 10 millimolar range by the presence of micelles. The amount of solute solubilized and bound to the micellar aggregate in an aqueous solution is typically proportional to the surfactant concentration up to the limiting value.

In view of its superior solubilizing power, the addition of a known volume of solution containing micellar surfactant to either a given volume of an aqueous sample solution or a given mass of a solid sample provides micelles capable of binding and concentrating (in the former) or desorbing and then binding (in the latter) in the micellar entity the organic species which was originally present in the aqueous or solid sample. For the extraction technique for solids, an aqueous concentrated neutral surfactant micellar solution *is* merely put in contact with or passed through the solid sample containing the organic component(s). The organic solute(s) present is desorbed and solubilized into the micelles in the bulk solution which are then further enriched (as will be described shortly) by the phase separation behavior of the surfactant solution. The desorption process is thought to be similar to the molecular mechanism reported for the solubilization of water-insoluble solids by micellar solutions, which involves direct micelle diffusion to and from the surfactant-modified solid surface, in series with interfacial steps including adsorption and desorption of the micellar-organic species [264-266].

A significant advantage of this bulk micellar extraction technique is that once the initial “extraction” from the solid matrix has been performed, the organic component(s) now present in the extractant micellar solution can be further enriched and preconcentrated prior to final quantization of the workup (as can be any organic species originally present in an aqueous borne sample to which a small amount of a concentrated surfactant micellar solution has been added). This preconcentration is made possible by the phase separation ability of micellar solutions. Aqueous solutions of neutral surfactant micellar compositions can exhibit the so-called critical phenomena and clouding upon temperature alteration. That is, upon increasing the temperature of such isotropic aqueous micellar solutions, a critical temperature is eventually reached at which the aqueous solution suddenly becomes turbid (clouding point) due to a diminished solubility of the surfactant micelles present in the bulk water. After some time interval (which can be speeded up by centrifugation), separation into two transparent liquid phases occurs (*ie* formation of a wet surfactant-rich micellar phase in equilibrium with almost pure water

with the same surfactant molecules). Any organic species present which can bind and partition to the micellar entity will be extracted into and thus concentrated in the small volume element of the surfactant-rich micellar phase. This property forms the basis of surfactant micelle phase separation, or the cloud point extraction technique which is schematically depicted in Figure 17.

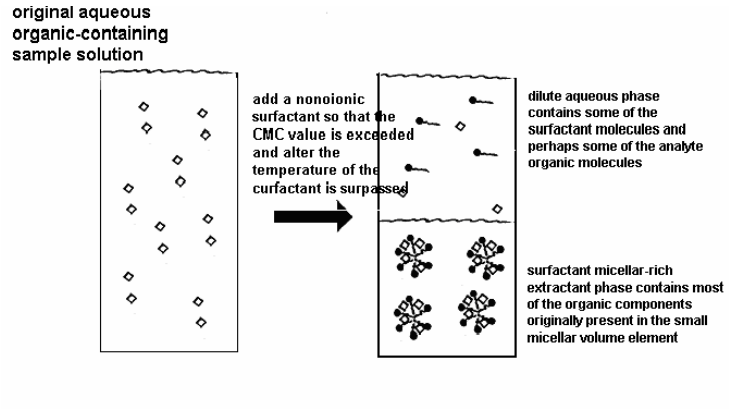


Fig. 17. Schematic representation of the proposed cloud point extraction scheme using a non-ionic surfactant micellar system

A plot of the temperatures required for clouding *vs* surfactant concentration typically exhibits a minimum in the case of non-ionic surfactants (or maximum in the case of zwitter-ionics) in its coexistence curve, with the temperature and surfactant concentration at which the minimum (or maximum) occurs being referred to as the critical concentration and temperature, respectively. This type of behavior is exhibited by as well as others not non-ionic surfactants, shown, *ie* non-ionic polymers, *n*-alkylsulfinylalcohols, hydroxymethyl or ethyl celluloses, dimethylalkylphosphine oxides, or most commonly, alkyl (or aryl) polyoxyethylene ethers. Likewise, certain zwitter-ionic surfactant solutions can also exhibit critical behavior in which an upper rather than lower consolute boundary is present. Previously, metal ions (as metal chelate complexes) have been extracted and enriched from aqueous media using such a cloud point extraction approach with non-ionic surfactants. Extraction efficiencies in excess of 98% for such metal ion extraction techniques were achieved with enrichment factors in a range of 45÷200. In addition to metal ion enrichments, this type of micellar cloud point extraction approach has been reported to be useful for the separation of hydrophobic from hydrophilic proteins, both originally present in an aqueous solution along with a preconcentration of the former proteins.

12. Microwave enhanced chemistry - MEC

The literature underlines the increasing importance of microwave radiation in chemical laboratory. 2450 MHz radiation was first applied in microwave ovens, but some time later it was observed that this radiation can be used to warm different liquids

and solids. It may be said that microwave ovens were the precursors of this new direction in analytics. In an analytical laboratory, in different stages of preparation of samples for analysis, microwave radiation [28, 267] supports the process of analyte extraction. Microwave-assisted extraction was introduced to the scientific community in 1986 [43]. Microwaves, initially used in the food and agricultural industries for conditioning food products, have been used for sample digestion since the mid-1980s. They have even more recently been used in the solvent extraction of organic analytes from a solid sample. Enhancement is based on the absorption of microwave energy by molecules of chemical compounds. The solvents most used include dichloromethane and acetone-hexane mixtures.

Microwave-assisted extraction can be performed in two ways:

- Pressurized MAE in closed vessels. This first technique employs a microwave-transparent vessel for the extraction and a solvent of high dielectric constant (electric permittivity). Such solvents absorb microwave radiation, and thus are heated to a temperature exceeding the solvent boiling points under standard conditions. Boiling does not occur because the vessel is pressurized. This mode of operation is very similar to ASE - elevated pressure and temperature facilitate extraction of the analyte from the sample,
- Atmospheric MAE system. The second technique employs solvents with low dielectric constants. Such solvents are essentially microwave-transparent, and thus absorb very little energy, and therefore extraction can be performed in open vessels. The temperature of the sample increases during extraction, because it usually contains water and other components with high dielectric constants: this leads to an enhancement of this process. Because extraction conditions are milder, this mode of operation can be used to extract thermolabile analytes.

This technique is called Focused Microwaves (FMW), and it also gives satisfactory results for polycyclic aromatic hydrocarbons, polychlorinated biphenyls, organochlorine pesticides, and alkanes with the same advantages of security and ease of manipulation.

Microwave heating is very efficient and can basically be explained by the interactions of an electric field with charged particles and polar molecules in a solution involving two mechanisms of energy absorption, that is, ionic conductance and dipole rotation. However, problems arise in MAE when using apolar solvents, because microwave energy can only be effectively absorbed by molecules having the dipole moments. For the extraction of organic contaminants this is a drawback, but this problem can be solved by increasing the polarity.

The most important instruments for microwave extraction are: a microwave radiation source, a waveguide, a resonant cavity and an energy source. Thanks to waveguides made of materials that strongly reflect electromagnetic waves (*eg* metal foils or metal sheets), microwave radiation is led from a magnetron to the receiver (resonator). The resonant cavity (resonator) is a part of the microwave apparatus from which microwave radiation is repeatedly reflected from its walls. The container with the sample for extraction is placed in the resonator. The MAE technique may use both solvents that absorb the microwave energy and have a high dielectric constant, and those with a low dielectric constant which do not absorb microwave energy [268].

Table 23 presents properties of several of the most frequently used organic solvents, important in microwave radiation applications.

Table 23

Characterization of solvents used in MAE extraction

Solvent	Dielectric constant	Boiling point [°C]	Temperature at closed vessel[a]
Hexane	1.89[b]	68.7	-
Dichloromethane	8.93[c]	39.8	140
Acetone	20.7[c]	56.2	164
Methanol	32.6[b]	64.7	151
Acetonitrile	37.5[b]	81.6	194
Cyclohexane	2.02[b]	80.7	-
Ethanol	24.3[c]	78.3	164
2-propanol	18.3[c]	82.4	145
Acetone-hexane (1:1 v/v)	-	52	156
Acetone - cyclohexane (70:30 v/v)	-	52	160
Acetone - petroleum ether (1:1 v/v)	-	39	147

[a] - pressure 175 p.s.i. (2.54 kPa), [b] - temperature 20°C, [c] - temperature 25°C

In analyte extraction, using solvents with a high level of microwave radiation absorption (with a high dielectric constant value), the extraction process takes place in high temperatures. The solvents' temperature, due to high pressure in the extractive container, usually exceeds the boiling point of the solvent, even up to 300°C. Given that, the container with the sample and solvent, must have special properties. One ought to pay attention to: (1) the chemical and thermal resistance of the material the container is made of, (2) its permeability to microwave radiation, and (3) its resistance to the action of the solvent. The aforementioned requirements are fulfilled by containers made of polytetrafluoroethylene (PTFE), quartz and some composite materials.

Microwave-assisted extraction has several advantages:

- shorter heating and extraction time,
- compact devices,
- easy control of the sample-heating process,
- reduction of the amount of solvent used for extraction,
- efficient energy use (energy is used exclusively to heat the sample and solvent).

It should be pointed out that several additional operations must usually be performed before the final determination:

- separation of the extract from the matrix (by filtration or decantation),
- concentration of the extract (removal of excess solvent),
- purification, drying of the extract.

Using the dynamic approach for extraction is generally advantageous, especially with respect to partitioning the solvent into the extraction media. This can be highly efficient when fresh solvent is continuously introduced into the extraction cell, that is, the rate constant for description need not be large compared with the rate constant for the adsorption for efficient removal of the target solute.

Dynamic microwave assisted extraction has been found to be an efficient technique.

Another new approach is combining MAE with the use of an aqueous surfactant solution as the extracting phase. This new technique is called microwave assisted micellar extraction (MAME). This procedure is based on the well-known solubilization capacity of aqueous micellar solutions toward water-insoluble or sparingly soluble

organic compounds. As a general rule, non-ionic surfactants are usually the most effective, showing larger solubilization capacities that rapidly increase with solubilization kinetics as the cloud-point temperature of the solution is raised.

Table 24 presents information on the application of microwave radiation as an enhancing factor for other operations associated with sample preparation for analysis.

Table 24

Applications of microwave radiation in sample preparation for analysis

Sample preparation operation	References
Desiccating	The process may be carried out both under normal pressure and in a vacuum. Polar water particles are selectively heated [249, 269] and water evaporates [270, 271]
Water (moisture) content determination	Special instruments are used - microwave scale dryer
Quick sample heating	
Microscopic sample preparation	Microwave radiation greatly enhances the fixing process of biological material
Sample incineration and melting	Microwave ovens use ceramic heaters, which are remotely heated with microwave radiation [270]
Plasma incineration	Plasma induced by microwave radiation (pressure of 10 mbar [1 kPa]) significantly decreases the temperature of incineration
Activation of sample components in plasma	To this end, the Microwave Inducted Plasma (MIP) is used
Performing chemical reactions including derivatization	Microwave radiation may be used to accelerate the rate of chemical reactions [112, 272, 273]
Steam distillation	[148, 274]
Pyrolysis	[74, 275, 276]
Digestion of sample	Oxidation takes place in the environment of active reagents (nitric acid, hydrofluoric acid, hydrogen peroxide) [277-281]
Evaporization of aqueous solutions	[270]
Microwave thermal inertisation of wastes	Applied to asbestos containing waste [282]
Heating of GC column	It is possible to employ negative temperature programming for an enhanced separation of compounds during the separation process [283]
Microwave assisted extraction MAE of samples	Because of the high efficiency of this type of extraction process, it can be applied to the extraction of a wide spectrum of analytes from various matrices [72, 284-289]

The main characteristics of commercially available focused-microwave technology are:

- safety due to operation at atmospheric pressure,
- a handling of large samples that can generate a huge amount of gas, mainly when working with organic materials,
- the use of various types of materials to construct reaction vessels, such as borosilicate glass, quartz, and PTFE,
- a programmable addition of reagents (or samples as it will be discussed later on) at any time during the digestion, which allows a sequential acid attack,

- a low-power focused-microwave field can be employed either to accelerate leaching of organometallic species without affecting carbon-metal bonds, or to extract organic compounds (specific examples will be discussed). The focused nature of the microwave energy lends high efficiency and avoids the need for high power,
- multiple methods for different samples can be simultaneously applied, allowing the possibility of operating each reaction vessel independently.

13. Application of ultrasounds (US) in the sample preparation process

Sound waves are mechanical vibrations in a solid, liquid or gas and are intrinsically different from electromagnetic waves. While the latter (radio waves; infrared, visible or ultraviolet light; X-rays; gamma rays) can pass through a vacuum, sound waves must travel through matter, as they involve expansion and compression cycles traveling through a medium. Expansion pulls molecules apart, whereas compression pushes them together.

Ultrasound (US) is simply sound with a frequency higher than the range audible to humans (> 16 kHz). The lowest US frequency is normally taken to be 20 kHz. The top end of the frequency range is limited only by the ability to generate the signals, so frequencies in the gigahertz (GHz) range have been used in some applications.

The use of US in scientific areas has increased in recent years, including areas such as medicine and industry, where US has had the most impact. This increase is continuing, and new uses are frequently appearing. Analytical chemistry has not been excluded from using US energy, as analytical chemists have exploited two aspects of it [109]:

a) for facilitating the development of different steps in the analytical process, mainly related to the preliminary steps involving solid samples, and,
b) for improving detection or even using US as the means of detection.

There are two common US devices for sample-preparation applications: bath and probe units. Although US baths are more widely used, they have two main disadvantages that substantially decrease experimental repeatability and reproducibility [290]:

a) a lack of uniformity in the distribution of US energy (only a small fraction of the total liquid volume in the immediate vicinity of the US source experiences cavitations); and,
b) a decline in power with time.

US probes have an advantage over US baths in that they focus their energy on a localized sample zone, thereby providing more efficient cavitations in the liquid. It has been demonstrated that, because standing waves form, the local intensity in a flask fixed in an US cleaner is highly susceptible to changes in experimental conditions, so precision is considerably affected as a result. Most US-assisted sample-preparation applications are developed in discrete systems; nevertheless, continuous approaches mean that a given step can be automated, as it can be interfaced with others that are also automated.

The performance of baths and probes in US-assisted digestion under soft or strong conditions depends on various factors that are rarely optimized in developing US-assisted digestion methods. Variables affecting US-assisted digestion common to baths and probes are [291]:

- the shape of the vessel containing the target chemical system; a factor which is usually ignored. Flat-bottomed vessels (*eg* conical flasks) are preferred because the energy transfer is more efficient,
- stirring the target suspension can be advantageous, because this ensures effective contact between the solid and the liquid during sonication,
- the temperature of the medium can have a strong influence on assisting digestion. In the case of thermolabile analytes, operation over very short periods of time or circulation of thermostate cold water in the tank can be alternatives in controlling temperature,
- the influence of pressure on US-assisted digestion has hardly been studied at all. There are only a few cases of chemical reaction acceleration where high pressure has been applied in closed ultrasonic reactors. These devices can also be used as ultrasonic digestors,
- solvent properties affect US-assisted digestion, as they impose a cavitation threshold above which sonochemical effects are "felt" by the medium. Therefore, any phenomenon altering same solvent property can modify such a threshold,
- radiation amplitude is directly related to the amount of energy applied to the system. Exhaustive treatments require high irradiation amplitudes, for which probes are more suitable than baths,
- particle size is a key variable, and so digestion mechanisms are influenced by particle diameter. In fact, depending on particle size, simultaneous microstreaming and microjetting or same other effect can dictate the efficiency of US-assisted digestion to a variable extent.

There are other specific physical variables that influence digestion assisted by an ultrasonic probe, namely [291]:

- the depth of immersion into the sample vessel or bath containing the transmitting liquid has a decisive influence on the effect of ultrasonic probes. This is because virtually no sonication exists alongside the tip or above it. Therefore, if the probe is only slightly immersed, it will cause foaming at the liquid surface, resulting in a loss of US energy. On the other hand, if the probe is immersed to an excessive depth, the energy supplied will be inadequately transmitted through the liquid and digestion efficiency will suffer as a result,
- the probe-tip/sample-cell distance should be considered when the probe is not inserted into the sample vessel. The shorter the distance, the less attenuation occurs and the higher the energy applied to the sample as a result,
- when ultrasonic energy is applied in a pulsed mode, pulse duration can be an important variable.

Ultrasound can be used as an enhanced agent during different steps of sample preparation for analysis:

- extraction of analytes [168, 204, 221, 292, 293] US-assisted extraction is an effective way of removing a number of analytes from different types of samples, as it combines several effects, namely:
  a) extremely high effective temperatures, which result in increased solubility and diffusivity,

b) high pressures, which favor penetration and transport at the interface between an aqueous or organic solution subject to US energy, and an organic or aqueous phase, or a solid matrix (which is more common), and
c) the oxidative energy of radicals created during sonolysis of the solvent (hydroxyl and hydrogen peroxide for water).

- digestion [283],
- dissolution [294],
- homogenization and emulsification [133, 206]
- filtration [295],
- analytical reactions (*eg* derivatisation) [186],
- reagent generation [36],
- slurry formation [109],
- cleaning [46],
- degassing [296].

It is worth emphasizing two main constraints in using US in the field:

a) US energy can lead to undesirable deterioration of sample components, so special care must be taken to ensure that only the desired effect is produced in a US-treated system,
b) the use of the appropriate US device is key to obtaining a given effect which cannot be produced by devices designed for other, different tasks. For example, US baths may be designed for cleaning purposes, for which power stability or uniformity in the distribution of US energy is not mandatory.

Even considering that microwave technology has improved some traditional operations in chemistry, there is still a long road ahead since only some 10% of laboratories thoughout the world are equipped with laboratory-designed microwave ovens [280].

14. Green chemistry - introduction of conception of sustainable development to chemical laboratories

14.1. History

The term green chemistry was first used in 1991 by P.T. Anastas in a special program launched by the US Environmental Protection Agency (EPA) to implement sustainable development in chemistry and chemical technology by industry, academia and government. In 1995, the annual US Presidential Green Chemistry Challenge was announced. Similar awards were soon established in European countries. In 1996, the Working Party on Green Chemistry was created, acting within the framework of the International Union of Applied and Pure Chemistry. One year later, the Green Chemistry Institute (GCI) was formed with chapters in 20 countries to facilitate contact between governmental agencies and industrial corporations with universities and research institutes to design and implement new technologies. The first conference highlighting green chemistry was held in Washington in 1997. Since that time, other similar scientific conferences have been held on a regular basis. The first books and journals on the subject of green chemistry were introduced in the 1990s, including the *Journal of Clean*

Processes and Products (Springer-Verlag) *Green Chemistry*, which was sponsored by the Royal Society of Chemistry. Other journals, such as *Environmental Science and Technology* and the *Journal of Chemical Education*, have devoted sections to green chemistry. The actual information may also be found on the Internet.

The concept of green chemistry appeared in the United States as a common research program resulting from the interdisciplinary cooperation of university teams, independent research groups, industry, scientific societies and governmental agencies, each of which have their own programs devoted to decreasing pollution.

Green chemistry incorporates a new approach to the synthesis, processing and application of chemical substances in such a manner as to reduce threats to health and the environment. This new approach is also known as:

- environmentally benign chemistry,
- clean chemistry,
- atom economy,
- benign-by-design chemistry.

Green chemistry is commonly presented as a set of twelve principles proposed by Anastas and Warner. The principles comprise instructions for professional chemists to implement new chemical compounds, new syntheses and new technological processes [83].

Green chemistry is not a new branch of science. It is a new philosophical approach that, through its application and extension of principles, can contribute to sustainable development. It is easy to find many interesting examples of the use of green chemistry rules. In addition, in chemical laboratories new analytical methodologies are still being developed which may be realized according to green chemistry standards. They are useful in conducting chemical processes and in the evaluation of their effects on the environment.

14.2. Green analytical chemistry

The irony is that the analytical methods used to assess the state of environmental pollution and analytical chemists in laboratories, through uncontrolled disposal of reagents and solvents or chemical waste, may in fact be a source of emission of a great amount of pollutants that negatively influence the environment. This is connected with the necessity of using considerable amounts of chemical compounds in successive steps of applied analytical procedures. Sampling and especially preparation for their final determination is frequently connected with the formation of large amounts of pollutants (vapors, reagent and solvent wastes, and solid waste). Therefore, it is necessary to introduce the rules of green chemistry into chemical laboratories on a large scale.

Considering the Twelve Principles of Green Chemistry, it is easy to indicate the directions that may decide the “green” character of analytical chemistry. The following issues should be treated as priorities [297, 298]:

- eliminating or minimizing the use of chemical reagents, particularly organic solvents, from analytical methods,
- eliminating chemicals with high toxicity and ecotoxicity from analytical procedures,

- reducing steps that demand a lot of labor and energy, in particular analytical methods (per single analyte),
- reducing the impact of chemicals on human health.

Development of analytics and environmental monitoring leads to better knowledge of the state of the environment and the processes that take place in it. Due to the introduction of new methodologies and new measuring techniques for the identification and determination of trace and micro-trace components in samples with complex compositions into analytical practice, discovery of the following important facts has been enabled:

- acidifying particular elements of the environment,
- the existence of a stratospheric ozone depletion phenomenon,
- designation of long-term trends in the changes of trace components in atmospheric air,
- increased concentration levels of the so-called persistent organic pollutants (POPs), *ie* compounds belonging to dioxins (PCDD, PCDF), polychlorinated biphenyls (PCBs) and others,
- examination of pollutant bioaccumulation in the tissues of organisms on different steps of the trophic chain.

This branch of analytical chemistry creates many challenges. The most important are as follows:

- low and very low concentration levels of analytes,
- the existence of time and space fluctuations of analytes in the investigated media,
- a broad range of concentrations of analytes belonging to the same group of compounds,
- the possibility of the presence of interfering compounds, frequently with similar chemical structures and properties.

The techniques of sample preparation, extraction (isolation) and/or preconcentration of analytes are usually used in the analysis of trace components of gaseous, liquid, and solid samples. During this operation, the transport of analytes from primary matrices (donors) to the secondary matrix (the acceptor) takes place. Nevertheless, it should not be forgotten that the extraction and preconcentration steps can be a source of environmental pollution. Techniques of sample preparation introduced in the article have the following advantages [299]:

- they are solvent free or virtually solvent free - solvent usage per one analysis is reduced to a minimum,
- the transport of analytes to the matrix is characterized by simplicity of composition compared with primary matrices, and more suitable and compatible with the analytical technique used at the final determinations step,
- removal, or at least reduction, of interferences as a result of selective transfer of sample components to the acceptor matrices,
- increased concentration of analytes in the acceptor matrix to levels over the limit of quantitation for the chosen analytical technique.

There is an urgent necessity to evaluate the used analytical methods not only with respect to the reagent, instrumental costs and analytical parameters, but also to their negative influences on the environment. A good tool for such evaluation may be the Life Cycle Assessment (LCA).

Introduction of the Life Cycle Assessment technique as a tool in examining the environmental burden of various analytical techniques may revolutionize the field of analytics. In rating analytical techniques according to their influence on the environment, one should apply a holistic approach and include:

- the output of raw materials,
- production of reagents and energy,
- transport of raw materials and final products,
- the influence of a given reagent on the environment in the process of its usage,
- storage and utilization of chemical waste and out-of-date reagents.

It can be stated that green analytical chemistry is the essential element of green chemistry. The constant development of new solventless techniques is a good example of activities in this field. The following direct analytical techniques (a preparation step is not necessary) may be treated as typical examples of procedures that are friendlier to the environment:

- X-ray fluorescence,
- a surface acoustic wave (SAW) used during determination of volatile organic compounds (VOCs),
- immunoassay.

In addition, the other techniques in which the amount of reagents and solvents is limited (calculated per one analytical cycle) are part of environmentally benign procedures, *eg*:

- solid phase extraction (SPE),
- accelerated solvent extraction (ASE),
- solid phase microextraction (SPME),
- liquid-liquid microextraction (MLLE), and other microextraction techniques, ultrasonic extraction,
- supercritical fluid extraction (SFE),
- extraction in automated Soxhlet apparatus,
- vacuum distillation of volatile organic compounds,
- mass spectrometry with membrane interface (MIMS).

The extraction of pesticides from soil samples using accelerated solvent extraction is a good example of an analytical procedure fulfilling the rules of green chemistry. This procedure is characterized by many advantages in comparison with classical extraction techniques used for extraction of analytes from complex matrices.

The main advantages considering green chemistry are as follows:

- reduction of used solvents (up to 95%),
- shortening of analysis time (from 16 hours to 10 minutes),
- energy savings (the heating of the extraction cell of an ASE instrument to 100°C in 10 minutes in comparison with 16 hours heating of a plate in a Soxhlet apparatus), decreasing exposure to solvents due to shortening of extraction time and the smaller amounts of applied solvents,
- similar analytical characteristics (precise and analyte recoveries) for smaller samples (ASE).

This procedure can be treated as an alternative to commonly used extraction in a Soxhlet apparatus.

Table 25 compares various solvent extraction techniques, with regards to the duration and the amount of the solvent used (per 1 sample).

Table 25

Comparison of solvent extraction techniques

Extraction technique	Amount of solvent used [cm^3]	Mean duration of the extraction process
Soxhlet extraction	200÷500	4÷48 h
Automated Soxhlet extraction	50÷100	1÷4 h
Ultrasound enhanced solvent extraction	100÷300	30 min÷1 h
Microwave enhanced solvent extraction	25÷50	30 min÷1 h
Accelerated solvent extraction	15÷40	12÷18 min
Supercritical fluid extraction	8÷50	30 min÷2 h

Figure 18 presents basic information on main groups of solvent-free techniques concerning sample preparation for analysis.

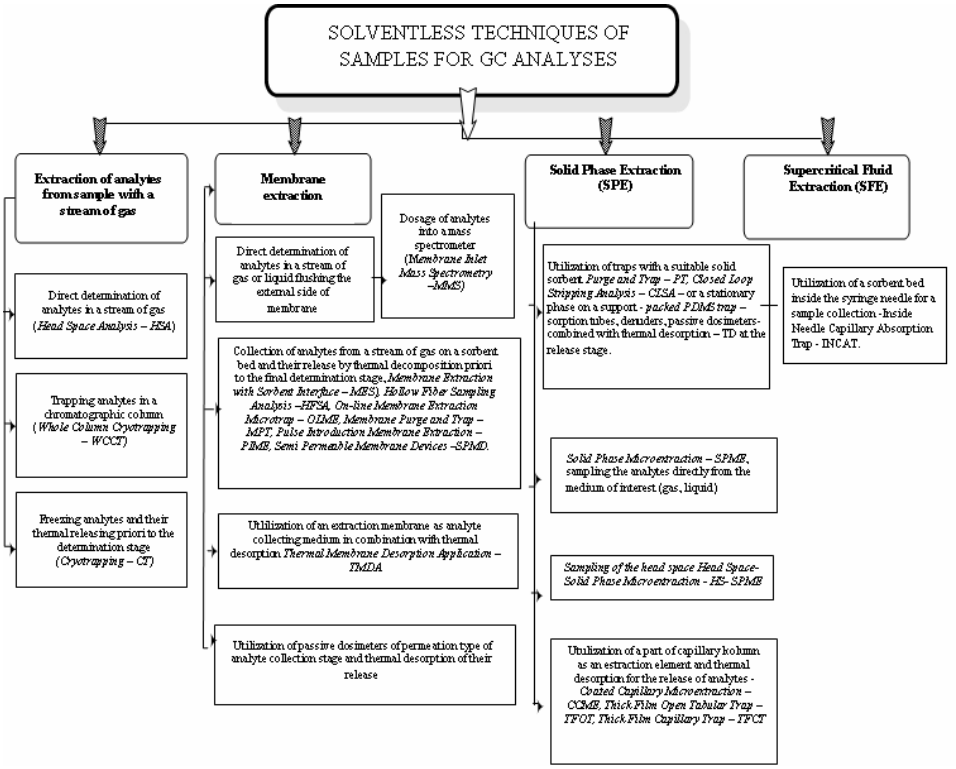


Fig. 18. Classification of solvent-free techniques concerning sample preparation for analysis

Using thermal desorption enables the exchange of solvent into a more environment-friendly stream of gas in the stage of releasing analytes into an adequate trap (sorption tube, denuder, passive dosimeter).

Figure 19 presents the basic mechanisms of the thermal desorber.

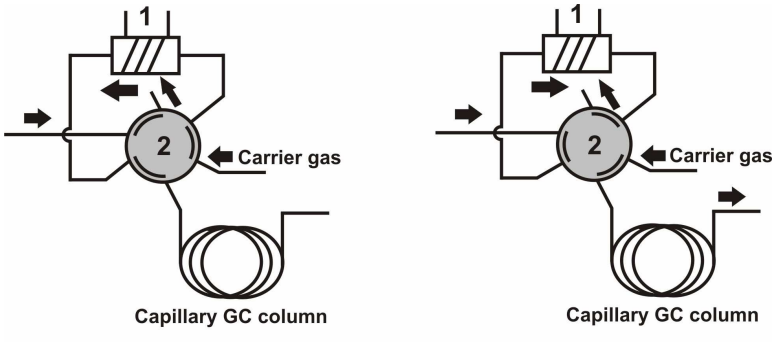


Fig. 19. Thermal desorber diagram

The ability to rapidly assess or monitor the disposition of environmental contaminants at purported or existing hazardous waste sites is an essential component of green chemistry. Soil samples have to be collected from surface to ground water and then shipped off-site for analysis, with waiting periods in excess of several months. Soil samples, which represent approximately half the total number, are extracted with solvents, then further separated using additional solvent to produce chemical-specific fractions. Each fraction is then analyzed using an appropriate method. A proposed technology by Professor Albert Robbat from Tufts University, Massachusetts, USA is aimed at reducing or eliminating solvent usage during the sample collection and sample analysis processes by collecting and detecting organic pollutants in depth without bringing the actual soil sample to the surface. A thermal extraction cone penetrometry probe coupled to an ultra-fast gas chromatography/mass spectrometer (TECP-TDGC/MS) has been developed to collect and analyze subsurface organic contaminants *in situ*. The TECP is capable of heating the soil to 300°C, which is sufficient to collect volatile and semi-volatile organics bound to the soil, in the presence of a soil-water content as high as 30%. Rather than using solvents to extract organics from soil, the TECP uses heat, then traps the hot vapour in a Peltier-cooled thermal desorption GC sample inlet for on-line analysis. In addition, the proposed technology reduces solvent usage when decontaminating sample collection probes and utensils used to homogenize samples. No other technology exists that is capable of thermally extracting organics as diverse as PCBs, explosives, or PAHs under these conditions. When combined with the ION Fingerprint Detection TM software, ultra-fast TDGC/MS is capable of analyzing complex environmental samples in less than 5 minutes.

The next important challenge of green analytical chemistry is in-process monitoring. Developing and using the in-line or on-line analyzers allow us to determine analytes in real time, in turn enabling us to detect disturbances in the course of a process in the initial steps. Such means of analysis gives rapid information and a chance for proper reaction - stopping the technological process or changing the operational parameters - and improves overall efficiency.

The application of green chemistry rules in designing greener analytical methods is key to diminishing the negative effects of analytical chemistry on the environment. The same ingeniousness and novelty applied earlier to obtain excellent sensitivity, precision and accuracy is now used to abate or eliminate the application of hazardous substances in environmental analytics.

15. Quality control and quality assurance (QC/QA) of analytical results

The final effect of the chemical analyst's work should be authoritative information on the chemical composition of the examined material. The source of this information is the analysis of samples obtained and prepared in an adequate fashion to determine the selected analytes. Incorrect action at any stage of the analytical procedure may cause misinformation. Thus it is necessary to apply different types of actions aimed at [1]:

- assuring the representativeness of obtained samples with relation to the examined material,
- assuring the stability of the sample composition from the moment of obtaining it until final determinations,
- checking analytical characteristics, or validating the individual stages and the entirety of the analytical procedure,
- determining the uncertainty budget.

The first two tasks are part of good laboratory practice, and the remaining two are connected with the monitoring and quality of analytical measurements.

For a considerable period of time, a suitable QC/QA system has been a significant part of analytical activities [300-305].

Results of analytical measurement can be the source of reliable and authoritative information only when they are obtained with an implemented QC/QA system. According to many opinions [306], such a system differentiates chemical analysis from modern chemical analytics.

CHEMICAL ANALYSIS	+	**QC/ QA SYSTEM**	=	**CHEMICAL ANALYTICS**

Quality Control (QC) in analytical chemistry consists in utilizing specific means of conduct in order to assure precision and accuracy in every stage of an analytical procedure, and in turn to obtain high quality results.

Quality Assurance (QA) is a detailed description of conduct - from the moment of taking samples until the processing of obtained results - concerning the monitoring of activities assuring high quality of the analytical results. A program of such activities should be introduced in written form.

Figure 20 presents a diagram with quality system components.

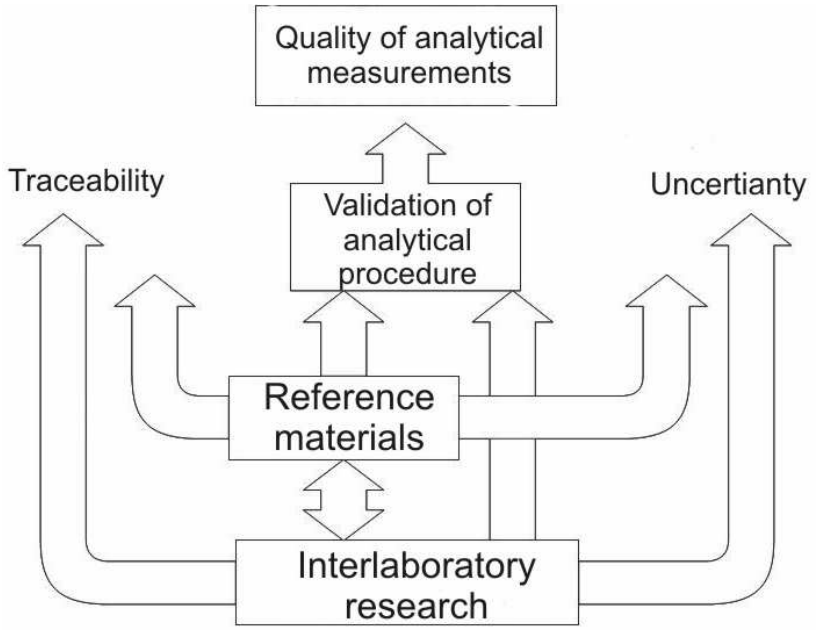


Fig. 20. Quality system components

Below, we will elaborate on basic problems connected with the diagram above [1].

Traceability

In the search for adequate quality of analytical results, greater and greater attention is paid to the traceability of results. Traceability is a feature of a measurement result or a standard value which provides a possibility of referring this value to national or international standards using an uninterrupted chain of comparisons, given that the uncertainty values, connected with all the known sources of errors, are known.

Moreover, it is assumed that:

- all indispensable actions to diminish error sources and the size of measurement errors have been taken,
- wherever possible, corrections were made in calculation of the final results.

This definition refers to all types of measurements, including analytical measurements.

The following are applied to achieve traceability:

- calibration of basic measurement instruments by specialists from a suitable metrological center,
- application of patterns and reference materials to check the methods and analytical techniques used.

Traceability of a specific measurement methodology is assured when one complies to the code of conduct presented in Figure 21.

An important part at this stage is played by reference materials, and by using them one can assure conformation to standards, traceability, and consequently a worldwide agreement of measurements.

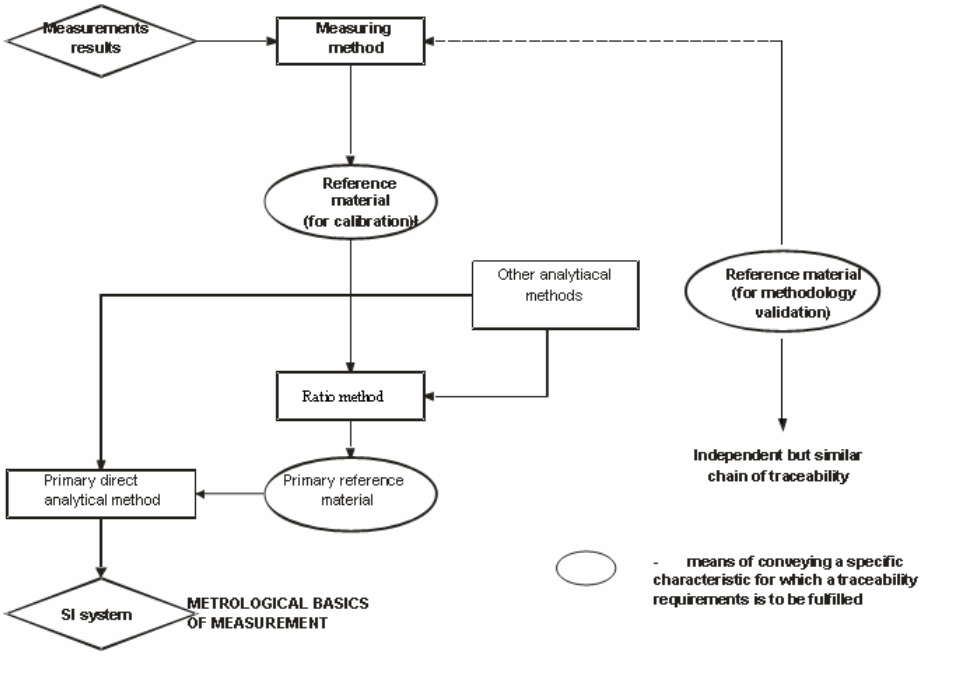


Fig. 21. General scheme of analytical conduct for assuring traceability

The Figure 22 presents three basic types of traceability tools for assuring quality.

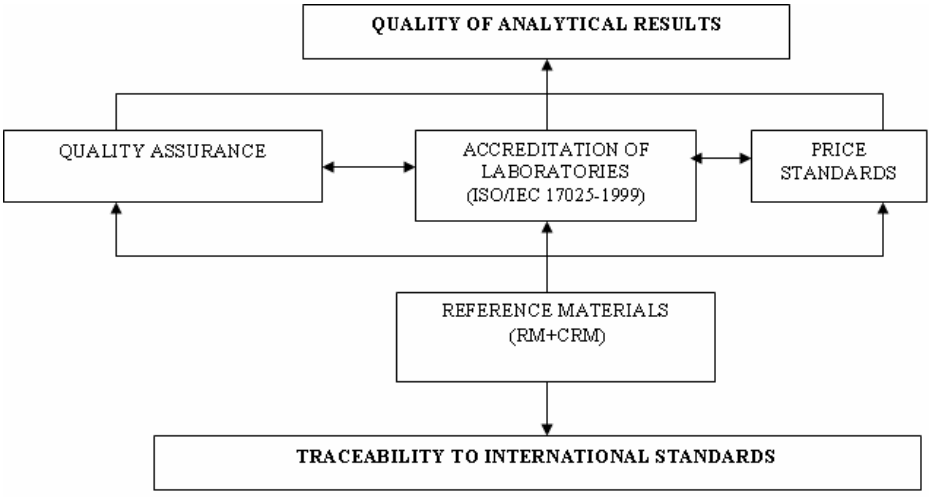


Fig. 22. Schematic presentation of relationships between the quality of analytical results and the traceability to international standards

Reference values should originate from specialized laboratories with international reputation in a given field.

In the case of trace analysis, traceability for a typical analytical procedure requires application of a matrix and certified reference materials. The principles of traceability realization are presented in Figure 23.

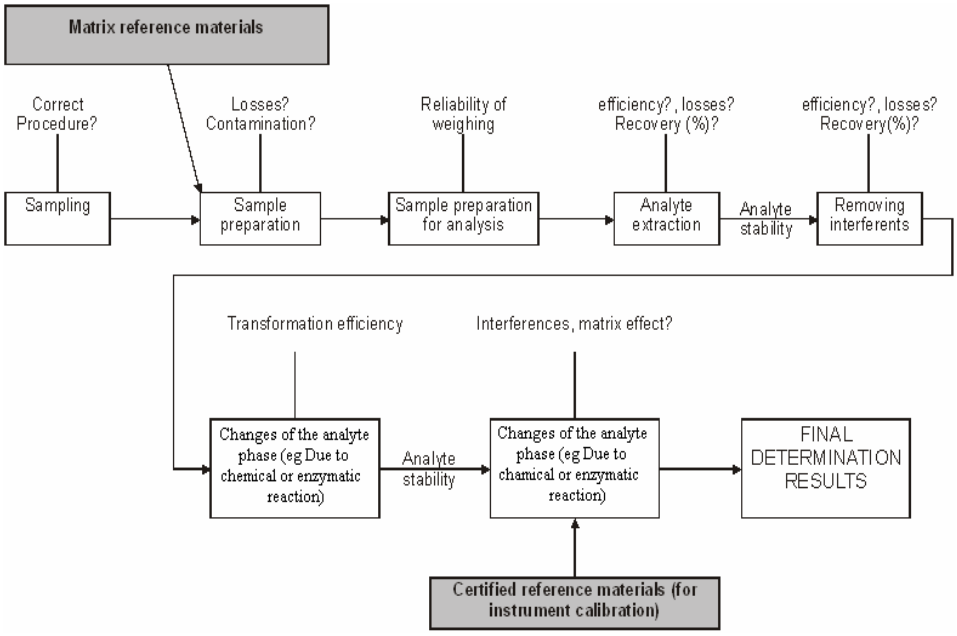


Fig. 23. Scheme of traceability requirements for a typical analytical procedure with regards to trace analysis

Validation

In order for a laboratory to be able to deliver reliable and repeatable results, it is necessary to perform systematic calibration of analytical instruments and validation of all the analytical procedures. The term validation has firmly entrenched itself in analytical nomenclature. Analysts 'owe' its introduction to accreditation and certification managers, and it means the determination of a methodology's characteristics, entirely covering the previous notion of 'methodology applicability' (specificity, selectivity, correctness, accuracy, precision, repeatability, limit of detection, measuring range, linearity range, etc.). In order to monitor the quality of a laboratory, reference material samples are subject to the same processing and determinations as real samples. A comparison of the obtained results with the real content of the analyte in a reference material sample determines the reliability of the analytical works in a given laboratory. Figure 24 presents the components concerning the quality of an analytical process, and Figure 25 shows a general scheme of a system assuring the quality of analytical results.

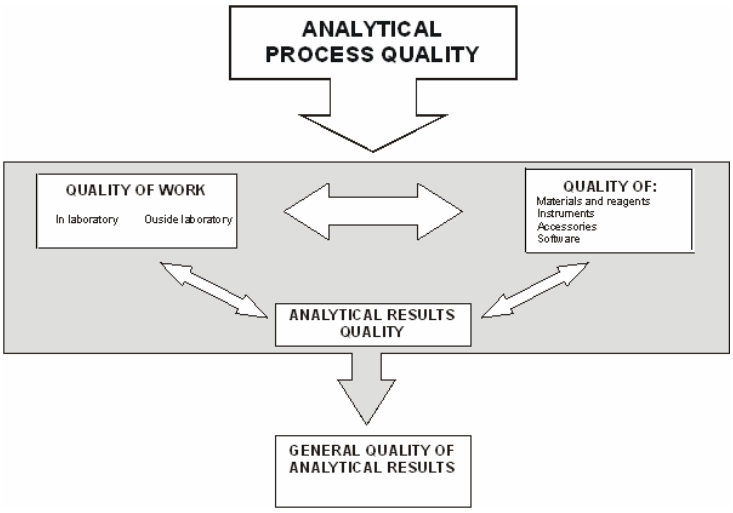


Fig. 24. Components concerning the quality of the analytical process

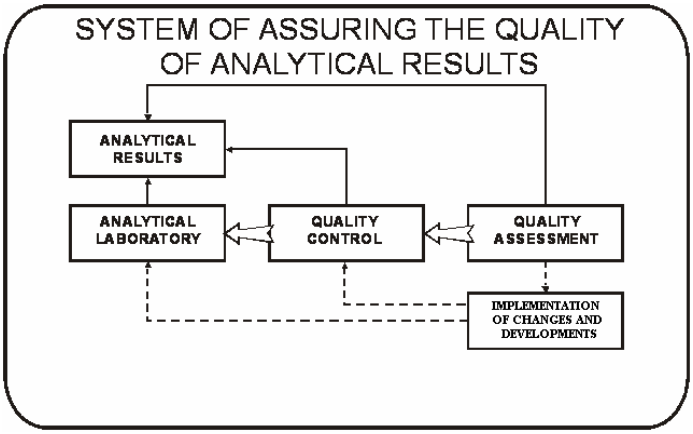


Fig. 25. General scheme of the system assuring the quality of analytical results

Reading the literature on the subject may lead to a false conviction that “validation” serves to determine new tasks which must be realized so that a given analytical procedure can be applied in practice. It is quite to the contrary however - this term was introduced to describe actions that were previously called “evaluation of an analytical procedure”.

Validation is most frequently performed when:

- a new analytical procedure is prepared,
- an attempt is made to increase the applicability of a well-known analytical procedure, *eg* determination of a given analyte, but in a different matrix,
- the quality inspection of an applied procedure shows variability of its parameters over time,

- an analytical procedure is to be used in another laboratory (different from a laboratory where it has already been validated) or with different instruments, or determinations are to be performed by a different analyst,
- a new analytical procedure is compared with another, well-known method of reference.

Reference materials

The range of parameters, the determination of which should underlie the validation process for a given analytical procedure, depends on the following:

- the character of the analytical research to be carried out using a given analytical procedure (qualitative or quantitative analysis, single sample analysis or a routine analytical investigation),
- requirements for a given analytical procedure,
- time and costs, which can be spent during the validation of an analytical procedure.

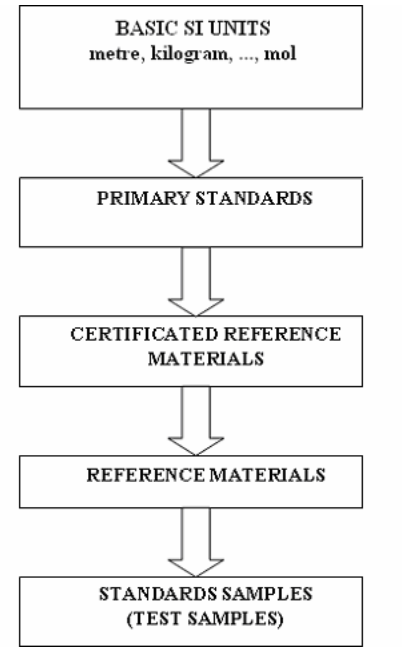


Fig. 26. Hierarchy of different types of reference materials

The more parameters involved in the validation of an analytical procedure, the more time is needed for its completion. Additionally, the more restrictive the assumptions for limiting (expected) values for respective parameters, the more frequent should calibrations, controls and even revisions of the analytical procedure occur. It is not always necessary to perform the entire validation process for an analytical procedure. One should determine which parameter should be included in this process.

Table 26 compares parameters which, in compliance with recommendations by the International Conference on Harmonisation and The United States Pharmacopeia, should be engaged in the validation process.

Table 26

Parameters of an analytical procedure that are subject to validation according to recommendations by the International Conference on Harmonisation and The United States Pharmacopoeia

Parameters	*ICH*	*USP*
Precision - repeatability	+	+
- indirect precision	+	
- reproducibility	+	
Accuracy	+	+
Limit of detection	+	+
Limit of determination	+	+
Specificity/selectivity	+	+
Linearity	+	+
Measuring range	+	+
Resistance		+
Elasticity		+

Standards and reference materials are important tools for maintaining suitable quality of analytical measurement results. Figure 26 presents hierarchically different types of standards and reference materials.

Figure 27 presents the hierarchy of reference elements in chemical analytics [307] with special regard to the reference materials.

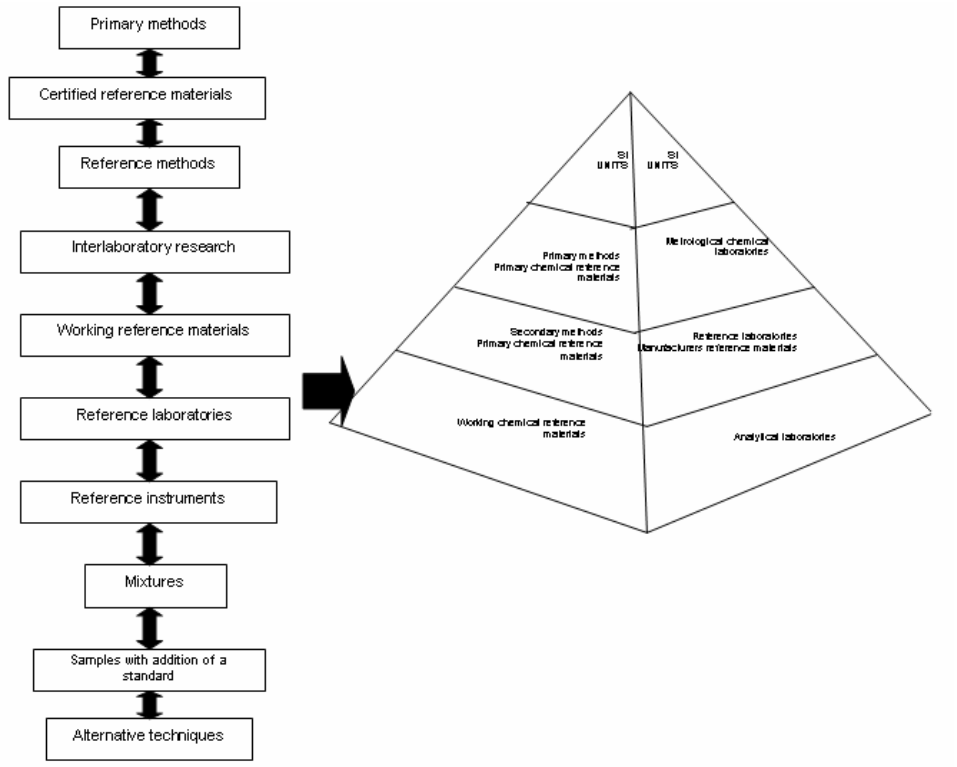


Fig. 27. Hierarchy of some elements of reference in chemical analytics

In order for the substance to be treated as a first-class standard, it must fulfill the following requirements:

- accessibility in trade,
- high chemical purity (100 ± 0.02%),
- high stability,
- homogeneity,
- non-hygroscopicity and resistance to erosion,
- dissolubility,
- high molecular mass or low analytical coefficient (to minimize weight errors),
- quantitative and stoichiometric plot of reaction during titration.

Uncertainty

In many fields, not only scientific ones, an immense number of decisions are based on analytical findings. Obviously, their quality is becoming increasingly important. The uncertainty of measurement is a component of uncertainty for all individual stages of an analytical procedure. Hence the need to determine the sources and types of uncertainty for each individual stage of an analytical procedure.

Uncertainty is a basic property of every measurement. It always occurs and in every stage of every measurement procedure. Therefore, it should not produce additional difficulties in the measurement process.

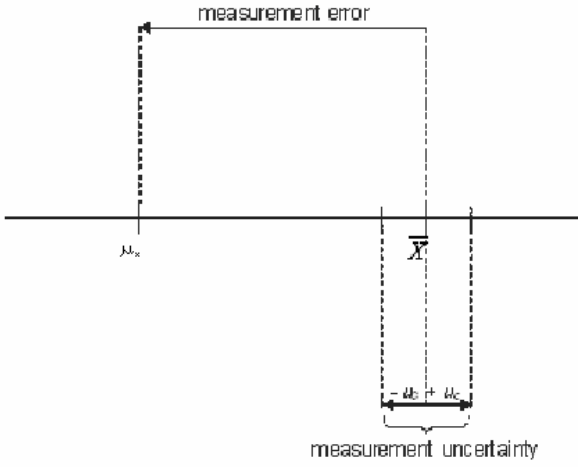
Basic sources of uncertainty in sample analysis using a suitable analytical procedure are:

- incorrectly or imprecisely determined parameters,
- unfulfilled requirements of representativeness for the taken sample,
- incorrectly applied determination methodology,
- human errors in readings of analog signals,
- ignorance of the influence of external conditions on the results of analytical measurements,
- uncertainty connected with the calibration of the applied control and measuring instrument,
- resolution of the applied instrument,
- uncertainties connected with applied standards and/or reference materials,
- uncertainties of parameters determined in separate measurements and applied in calculations of the final result, determinations such as physico-chemical constants,
- approximations and assumptions associated with the use of a given instrument applied during the measurement,
- oscillations in repeated measurements under seemingly identical external conditions.

The difference between measurement error and uncertainty should be pointed out here. An error is a difference between the determined and expected values, while an uncertainty is a range in which the expected value can be found with some probability. Thus, the level of uncertainty cannot serve to correct the obtained measurement result.

The difference between an error and uncertainty is presented in Figure 28.

The influence of individual parameters on the value of the combined uncertainty for a measurement result is usually presented on a fish-bone diagram, also called an Ishikawa diagram (after the Japanese chemist and statistician) (Fig. 29).



μ_x - expected value,
$\overline{X}$ - measurement result value (arithmetical mean),
u_c - the combined uncertainty of a measurement result;

Fig. 28. Schematic presentation of a difference between calculated error values and the combined uncertainty of a measurement result

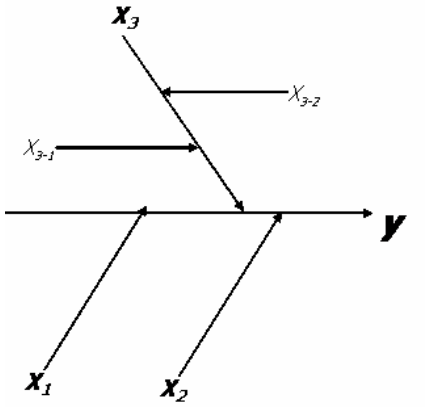


Fig. 29. An Ishikawa diagram representing the influence of individual parameters of an analytical process on the combined uncertainty of analyte content determination (y) in an investigated sample

A QC/QA system is associated with all stages of suitable analytical procedures carried out both *in situ* and in a laboratory [72].

QC/QA comprises the following elements:

- monitoring and estimation of analytical result precision through performing periodic examination of control samples,
- estimation of analytical result accuracy through,
- analysis of certified samples of reference materials,

- comparison of results obtained with a reference method,
- analysis of samples augmented with a standard,
- inter-laboratory research,
- control cards,
- audits.

Figure 30 can help to understand [308] the most important aspects of the quality assurance system for analytical measurements performed on representative samples obtained from an examined material object.

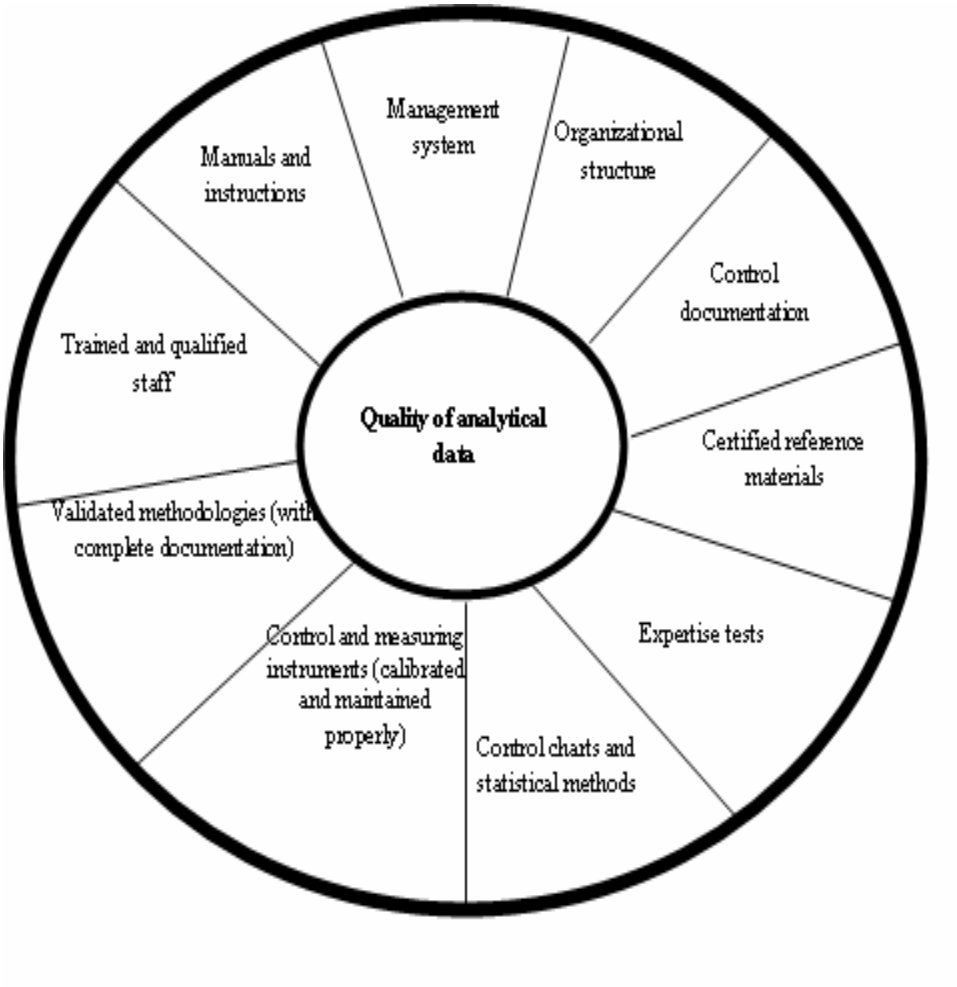


Fig. 30. The most important aspects of quality assurance for analytical measurement results

Figure 31 presents the location of individual QC/QA system elements, necessary for the quality of analytical results in general analytical conduct [73].

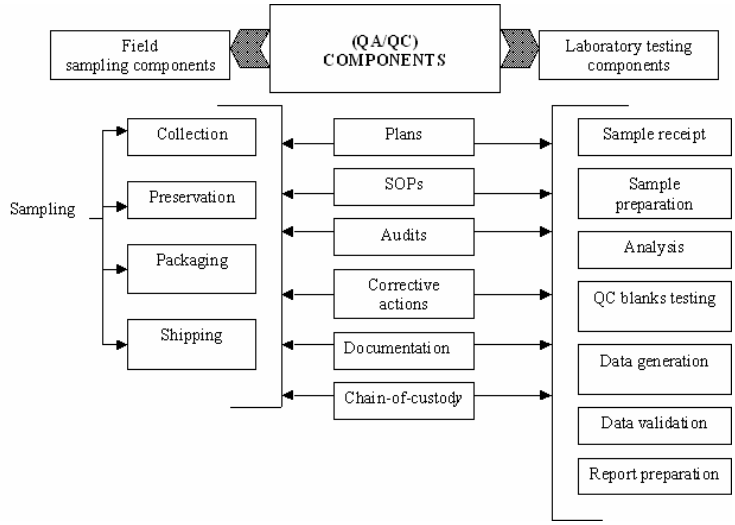


Fig. 31. Estimation of the background level is one of the significant elements of quality control for analytical measurement results [73]

Table 27

General characteristics of suitable control samples for the purpose of quality control of analytical measurement results

Short description of background and manner of preparation	**Stage of the procedure**	**Application of the obtained analytical information**
Background of operations performed in the field (field blank). A sample is prepared on the standard-matrix basis without addition of any analyte. Such samples are included into the sequence of samples obtained in the field.	Sampling in the field	Determination of contamination associated with the sampling technique, an analytical procedure, field conditions, sample containers, preservatives, transport and storage of samples, sample preparation techniques and measurement of analytes.
Transport background (trip blank). Samples are prepared in the field or a laboratory, and are transported together with the 'real' samples.	Sampling in the field	Determination of contamination associated with the sampling, preservatives, and the techniques of sample preparation and analyte determination.
Method background (method blank). Samples are prepared using a standard matrix without an analyte. Used to determine contaminants from the laboratory.	Sample preparation for analysis and analyte determination	Determination of contamination associated with sample preparation and analyte determination.
Reagent background (reagent blank). Determination of analyte levels in reagents used in sample preparation and analyte determination.	Sample preparation for analysis and analyte determination	Determination of contamination associated with specific reagents used in sample preparation and analyte determination
Instrument background (instrument blank). Determination of analytes in a sample, using a standard matrix without analytes.	Analyte determination	Determination of contamination associated with the measuring instruments.

16. Final conclusion

Analytical research is usually labor- and time-consuming as well as expensive, and thus its result should provide authoritative and reliable information. Because of this, the following conditions must be fulfilled:

- a sample must be representative with regards to the examined object material,
- a sample must be properly prepared for analysis,
- a sample analysis should be carried out with suitable control and measurement instruments which cannot be treated as a black.

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PRZYGOTOWANIE PRÓBEK DO ANALIZY - DROGA DO SUKCESU

Streszczenie: Przedstawiono i dokonano krytycznego omówienia informacji literaturowych na temat poszczególnych etapów przygotowania próbek środowiskowych do etapu oznaczeń końcowych analitów występujących w tych próbkach na niskich poziomach zawartości.
Szczególną uwagę zwrócono na:
- ✓ wyzwania związane z analityką specjacyjną,
- ✓ nowoczesne techniki ekstrakcji i wzbogacania analitów,
- ✓ możliwość zastosowania ultradźwięków oraz promieniowania mikrofalowego na poszczególnych etapach procedur analitycznych,
- ✓ wprowadzenie zasad związanych z koncepcją zrównoważonego rozwoju do pracy laboratoriów analitycznych.

Słowa kluczowe: przygotowanie próbek do analizy, konserwacja próbek, ekstrakcja i/lub wzbogacanie analitów, wykorzystanie ultradźwięków i promieniowania mikrofalowego w laboratorium analitycznym, analityka specjacyjna, zielona chemia analityczna