

Preparation of Environmental Samples for the Determination of Trace Constituents

J. Namieśnik, T. Górecki*

Department of Analytical Chemistry, Chemical Faculty, Technical University of Gdańsk, Gdańsk, Poland *
Department of Chemistry, University of Waterloo, Waterloo (Ontario), Canada

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Abstract

The paper presents basic information on the preparation of environmental samples for trace analysis. Sample preparation is of utmost importance for the quality of analytical results and their usefulness for decision making in the area of environmental protection and management. The type and number of operations required for a given procedure is determined by the available information about the sample and the goal of the analytical determination (speciation analysis, determination of total parameters or elemental composition, etc.)

Keywords: environmental samples, preparation, QA/QC

Introduction

Information available in literature invariably points out that analytical chemists face two major challenges:

- Development and adoption of new methods and devices for sample preparation for trace and (particularly) ultratrace analysis. For example: more than 25 lists of substances are regulated under various EPA programs. The number of substances on these lists range from as few as 5 to as many as 750. These lists do not include the more than 5,000 substances reported to the EPA's Office of Prevention Pesticides and Toxic Substances [1]. This stage of the analytical procedure is difficult; even more complex (or inhomogeneous) is the sample matrix, and the less-so is the concentration level of the analytes [2];
- Assurance of proper quality of the results and estimation of their uncertainty. The final result of any analysis is affected by all the stages of the analytical procedure, which itself is a chain of interrelated operations and decisions. Thus, a holistic approach to this problem is required [3].

Reliability of measurement results is usually achieved by [4]:

- Proving that the supplier has the necessary technical competence in the field concerned;
- Demonstrating traceability of the measurements in question to recognized references, thus allowing a complete uncertainty statement to be made.

There is a general consensus among experts that sampling and sample preparation are the weakest links in the chain, therefore much more attention should be paid to these stages. Unfortunately, many analysts are truly fascinated with the developments in modern instrumentation, which leads them to a false belief that application of modern, complex instrumentation is a solution to all problems encountered in trace analysis. The instruments are often treated as black boxes capable of solving any and all analytical tasks. What is frequently forgotten is the fact that the results can only be as good as the sample itself. If the sample is not representative, even the most modern and complex instruments produce misinformation rather than information, which in turn may lead to poor decisions, often bearing serious, long-term consequences. In any case, looking for the source of misinformation once it is identified as such is a laborious and time-consuming task. The entire analytical procedure has

Table 1. Main types of environmental samples and major groups of analytes determined in such samples.

No.	Type of environmental sample	Source	Major analytes
1.	Gaseous samples	Stack gases (emission measurements)	Gases and vapours: – inorganic gases; – organic gases and vapours, including: – VVOC – Very Volatile Organic Compounds; – VOC – Volatile Organic Compounds – SVOC – Semivolatile Organic Compounds Dust, aerosols: – POM – Particulate Organic Matter – surface-adsorbed organic substances – cations, anions – heavy metals – dioxins
2.		Atmospheric air (emission measurements)	
3.		Upper layers of the atmosphere	
4.		Indoor air	
5.		Workplace atmospheres	
6.		Exhaust gases from vehicles (mobile emission sources)	
7.		Landfill gas	
8.		Industrial gases from open and closed installations	
9.		Special atmospheres (caissons, submarines, emergency capsules)	
10.		Exhaled breath	
11.		Biogenic emissions	
12.		Emissions from dangerous and/or hardly accessible sources (e.g. volcanic eruptions)	
13.		Leaks from industrial installations	
14.	Liquid samples	Potable water	Dissolved Inorganic gases Dissolved organic substances: – THM – Trihalomethanes – VOC – Volatile Organic Compounds – petroleum hydrocarbons – pesticides – organometallic compounds (e.g. organotin compounds) – dioxins. Dissolved inorganic substances: – nutrients (biogens) Suspended matter: – organic compounds adsorbed on the surface; – heavy metals, cations and anions
15.		Power plant water	
16.		Surface water	
17.		Groundwater	
18.		Water from the unsaturated zone	
19.		Rainwater	
20.		Run-off water	
21.		Sea water	
22.		Industrial wastes	
23.		Toxic wastes	
24.		Sewage	
25.		Surface films (oil and petroleum products spills)	
26.		Body fluids (urine, sweat, blood)	
27.	Solid samples	Ice and snow	Inorganic compounds: – anions and cations – heavy metals. Organic compounds. Surface-adsorbed organic compounds: – dioxins – petroleum hydrocarbons – organometallic compounds – pesticides
28.		Soil	
29.		Sewage sludge, bottom sediments	
30.		Street dust	
31.		Vacuuming dust and TV dust	
32.		Dust from electrofilters	
33.		Fly ash from solid waste incinerators	
34.		Plant material	
35.		Tissue and organs of living organisms	
36.		Forest floor	
37.		Dangerous waste	
38.		Industrial waste	
39.		Municipal waste	
40.		Ashes	

to be repeated, beginning from collection of new samples, their proper transport and storage, through sample preparation and final determination.

The wide variety of the types of environmental samples and the broad spectrum of analytes that can be of interest in such samples can be daunting. Table 1 illustrates the difficulties involved in trace environmental analysis by listing basic types of samples and main groups of analytes of interest.

Applications of Analytics and Monitoring in Environmental Studies

According to an increasingly common opinion, analytics and monitoring of environmental pollutants constitute the two pillars on which the entire field of environmental science is based. Consequently, one can share the opinion of some specialists that there already exists a separate field of chemical analytics named *ecoanalytics*. However, we should be aware of the fact that neither analytics nor monitoring as such solves any problem concerning pollution or degradation of specific elements of the environment. They are only powerful tools which can provide information required for reliable evaluation of the state of the environment and changes taking place in it, and for making correct decisions for sozotechnical actions [5].

The significance of chemical analytics in the modern world is tied to the development of instrumentation. Rapid advances in this area have resulted in widespread use of a variety of instruments. They are typically highly integrated. Increased automation and robotic technologies combined with artificial intelligence, made possible by microprocessor control, make them more and more autonomous. Figure 1 presents classifications of analytical methods used in environmental studies.

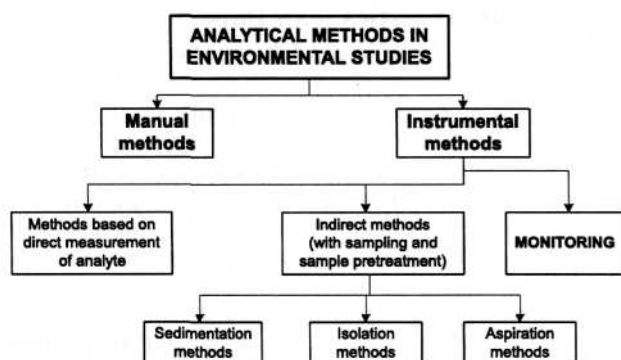


Fig. 1. Classification of the main types of analytical tools used in environmental studies.

In general, manual methods are based on sampling of a given environmental compartment directly by a human, or by an instrument controlled by a human. Sampling time is pre-set. The sample is analyzed in a laboratory using manual or instrumental techniques. When manual

techniques are used, the time span between sampling and obtaining the final result can be very substantial. This is sometimes referred to as information delay of the analytical result.

When fully automated devices are used, a sample is collected automatically at predetermined time intervals, and the remaining stages of the analytical procedure are also carried out without human intervention. The final result is obtained not by chemical analysis, but indirectly through the measurement of a physical or (less frequently) chemical characteristic related to the concentration (amount) of the analyte in a given sample (e.g. absorption of UV, VIS or IR radiation; heat or electrical conductivity; viscosity, density, or other parameters). The instrument is supervised by a human; however, human intervention is limited to periodical maintenance and calibration, necessary repairs and the addition of reagents (if required). Automated instruments make it possible for the final result to be obtained in near real time, right after the sampling step. Instruments of this kind (analyzers, monitors) can be relatively easily coupled to devices that average the results, or to recorders. The latter enable the analyst to do the averaging himself. Comparative studies indicate that both manual and automated methods are capable of producing results of similar accuracy and precision. The only significant difference is the effort and time required to get the final result.

All analytical methods and techniques used in environmental monitoring can be divided into two groups with respect to the method of analyte determination [6]:

Direct methods - when analytes can be determined directly in the sample. This approach is applicable only when the matrix is relatively simple (no interfering substances), and analyte concentration is higher than the detection limit of the method or instrument. Because of this, direct methods find only limited applications in environmental analysis and monitoring. Examples of methods which do not require sample preparation include:

- Potentiometric techniques (ion selective electrodes used in the analysis of surface waters),
- Graphite furnace atomic absorption spectrophotometry (GFAAS),
- Atomic emission using inductively coupled plasma (ICP),
- Proton-induced X-ray fluorescence (PIXE),
- Neutron activation analysis,
- Surface analysis techniques (SEM, AES, XPS, SIMS, ISS, ESCA).

Other techniques usually combine sample preparation and analyte separation with various methods of detection.

Indirect methods - when analytes present at trace and ultratrace levels are detected not directly in the original matrix, but in a matrix resulting from sample preparation, analyte isolation and/or preconcentration. These additional operations, included in the vast majority of analytical methods used in environmental analysis, make it possible to:

- Increase analyte concentration in the final sample to a level higher than the detection limit of the instrument used,

- Simplify the matrix and remove interferences by replacing the original matrix with a recipient matrix (a suitable solvent or gas),
- Average the sample composition,
- Store the sample for prolonged periods of time (the concentrate is usually much more stable than the original sample).

Precipitation methods - when the analyte is separated from the original matrix by precipitation on the surface of a suitable device.

Examples:

1. Contact method of SO₂ determination in air,
2. Determination of dust precipitation.

Isolation methods - an environmental sample (air, water, soil, etc.) is isolated in a vessel of known volume. Analyte amount or concentration in the sample is determined either directly by analysing an aliquot of the sample, or following additional stages of isolation and/or preconcentration.

Examples:

1. Collecting gas (air) samples in gas pipettes, bags or other similar containers.
 2. Collecting water samples in suitable vessels.
- In both cases, the process can be carried out manually or automatically using an autosampler.

Aspiration methods. Sample or analyte isolation is carried out by forcing the flow of the sample through a suitable trap. When the trap is equipped with a suitable (selective) filter, analytes are preconcentrated during sampling.

Examples:

1. Determination of dust concentration in atmospheric air.
2. Determination of suspended particulate matter in water.
3. Trapping of analytes from a liquid or gaseous streams on a solid sorbent, in an absorbing solution, on the surface of a chemical reagent or in a cryogenic trap.

In general, the role and tasks of analytics and environmental monitoring can be summarized as follows:

- Standard quality assessment of the individual compartments of the environment (conformity to standards and regulations),
- Identification of pollution sources and determination of emissions, as well as estimation of the extent of their influence on the environment,
- Evaluation of phenomena and processes taking place in the atmosphere, in water, and in soil (transport and deposition of pollutants; chemical, biochemical and photochemical conversion of the pollutants in the individual compartments of the environment),
- Elucidation of the ways of pollutant transfer.
- Examination of the effect of the pollutants on climatic changes,
- Determination of the effect of pollutants on the environment and on human health (monitoring combined with, e.g., epidemiological or ecotoxicological studies),
- Investigation of the background and long-term trends,
- Evaluation of the effectiveness of sozotechnical facilities.

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

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

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

Next, monitoring imposes several requirements concerning:

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

A number of different analytical methods and techniques are used in environmental analytics and monitoring for:

- Determination of elemental composition of the pollutants,
- Determination of so-called total parameters of environmental pollution, usually determined by examining the total content of a given element in all the pollutants (or a given group of pollutants) present in a given sample,
- Speciation analysis.

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 changes of species must be elucidated.

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

Generally, speciation analytics plays a very important role in:

- Studies of geochemical cycles of elements and chemical compounds,

- Determination of toxicity and ecotoxicity of selected compounds,
- Quality control of food products,
- Research on the impact of technological installations on the environment,
- Examination of occupational exposure,
- Control of medicines and pharmaceutical products,
- Clinical analysis.

Literature search allows one to distinguish several types of speciation analytics [7]:

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, complexed forms, etc.

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 known for especially high environmental toxicity;

group speciation determination of the concentration level of a specific group of compounds, or elements existing in different compounds at a specific oxidation level, and their physical forms;

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 the most difficult type of speciation analytics, involving the broadest range of analytical work. Its task is to separate, detect, determine and identify all species of an element in a sample.

Chromatographic techniques, and especially so-called hyphenated methods, have become ideal tools for speciation analytics due to their ability to separate even very complex mixtures into individual components.

Stages in Environmental Sample Preparation

The wide variety of environmental samples, related to their different states of aggregation, sampling location, matrix composition, as well as analyte type and concentration level, make it extremely difficult to present even the most basic information on sample preparation in a single article. A large number of operations can be performed during the sample preparation step. They can be performed *in situ* during sampling, or after the sample is delivered to the laboratory [8-11]. Quite obviously, the

manner in which a sample is processed depends on the final determination method. Independent of the type of sample and the analyte(s) determined, the analysts have to deal with specific problems of trace analysis. Each stage of sample preparation carries a risk of analyte loss or sample contamination. Thus, special measures must be taken to prevent these unwanted phenomena.

Apart from random errors, the potential for systematic errors is increased in trace analysis. The most common sources of systematic errors are related to:

- Differences in volatilities of sample components,
- Adsorption and desorption of sample components onto/from the walls of containers and instruments (memory effects),
- Sample contamination caused by contact with laboratory air,
- Change in sample composition caused by addition of chemical reagents,
- Human factor.

Table 2 lists basic operations and activities carried out during preparation of environmental samples for analysis.

Even a cursory review of literature indicates that chromatographic techniques overwhelmingly prevail at the component separation and quantitation stage. Table 3 lists the specific requirements of chromatographic techniques with respect to sample preparation.

Figure 2 presents the general procedure for environmental sample handling.

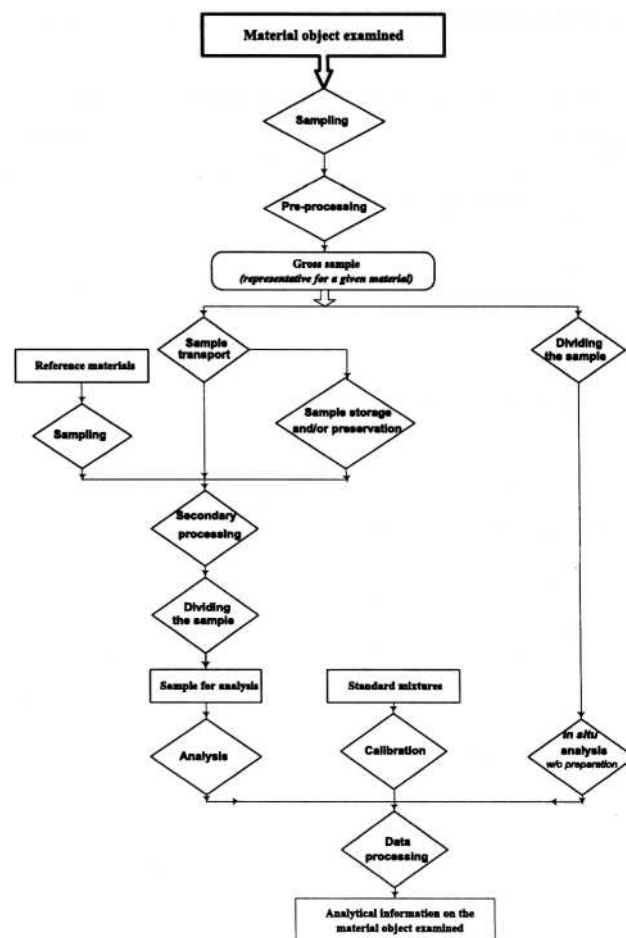


Fig. 2. General procedure for environmental sample handling.

Table 2. Sample preparation stages:

Operations and activities	Sample type		
	Gaseous samples	Liquid samples	Solid samples
1. Carried out <i>in situ</i>			
- Dust removal	+		
- Drying	+		
- Removal of interferences (e.g. deoxygenation)	+		
- Suspended particulate matter (SPM) removal		+	
- Preservation (chemical)		+	
- Derivatization		+	
- Isolation and/or preconcentration	+	+	+
- Transport	+	+	+
2. Carried out in the laboratory			
- Drying		+	+
- Grinding			+
- Homogenization and mixing	+	+	+
- Preservation (thermal and/or chemical)		+	+
- Sieve analysis			+
- Mineralization		+	+
- Isolation and/or preconcentration	+	+	+
- Derivatization	+	+	+
- Purification and removal of interferences	+	+	+
- Sample fractionation and partitioning	+	+	+
- Calibration and verification of the instruments and methods	+	+	+
- Sample introduction to the instrument	+	+	+

Table 3. Sample preparation for chromatographic analysis.

No.	Goal	Operations
1.	Assuring sample stability and homogeneity during sample transport and storage	<ul style="list-style-type: none"> - Grinding - Homogenization - Sieve analysis - Drying - Freeze drying - Chemical preservation - Thermal preservation
2.	Removal of interferences	<ul style="list-style-type: none"> - Dust removal from gaseous samples - Drying of gaseous samples - Oxygen removal from gases - SPM removal from water
3.	Analyte conversion into a form suitable for: Isolation and concentration Separation Determination	<ul style="list-style-type: none"> - <i>In-situ</i> derivatization - On-column derivatization - Post-column derivatization
4.	Matrix exchange into one compatible with the instrument	<ul style="list-style-type: none"> - Analyte extraction using: <ul style="list-style-type: none"> - carrier gas stream - supercritical fluid - Application of membrane processes - Application of thermal desorption for analyte transfer from a solid sorbent bed to the chromatographic column
5.	Bringing analyte concentration in the sample fed to the instrument to a level enabling quantitative analysis	Use of isolation and preconcentration techniques increasing analyte concentration (or amount) with respect to matrix components (effectiveness of this stage is characterized by so-called concentration factors)
6.	Reducing solvent consumption	Use of solventless sample preparation techniques

It follows from the above diagram that two types of sample processing can be distinguished:

- Pre-processing, aimed at bringing the sample to a form which can be transported to the laboratory (adjusting sample temperature and pressure, stabilizing the composition),
- Secondary processing, aiming at bringing the sample to a form compatible with the requirements of the analytical instrument.

Quality Assurance/Quality Control

Quality assurance (QA), quality control (QC) and associated good laboratory practice (GLP) should be essential components of all activities in the field of environmental analytics and monitoring [12]. The need for good QA/QC in the chemical analysis of environmental samples has been well recognized and has been tested in a number of international QA exercises.

By definition, QA refers to all of the actions, procedures, checks and decisions undertaken to ensure the representativeness and integrity of samples and accuracy and reliability of analytical results. QC comprises those actions that monitor and measure the effectiveness of QA procedures with respect to defined objectives. This might include checking of equipment cleanliness, duplicate sampling, measurement of field and laboratory blanks, and the analysis of replicates and reference materials.

QC is therefore an essential component of a QA program and both are usually jointly recognized by referring the implementation of good QA/QC as an essential part of good laboratory practice.

To assure proper quality of analytical results, it is necessary to verify the reliability of the instruments and the applicability of the analytical procedures. Consequently, analytical procedures usually include the following two steps:

1. Periodical checking of the reliability of the analytical instruments using standard mixtures. So-called zero mixtures' are just a special case of standard mixtures, used for:

- Zeroing the instrument
- Dilution of so-called primary standards, in which the analyte(s) are present in well-known, but relatively high concentrations.

2. Verifying the reliability of the entire analytical procedure. This can be accomplished by:

- Addition of standard to real samples analyzed,
- Analysis of certified reference materials.

In both cases, the procedure used normally for real samples must be followed.

Three types of reference materials can be generally distinguished [13]:

- Chemical reference materials,
- Physical reference materials
- Reference materials for special technical properties.

Only the first type of reference materials is normally used in an analytical laboratory. These materials should meet the following criteria:

- homogeneity,

- long-term stability of chemical composition,
- certified content of a possibly large number of analytes.

Certified chemical reference materials are used increasingly often in analytical practice. Their applications include:

- determination of analytical characteristics and validation of methods (at the method development stage),
- checking the skill level of laboratory personnel,
- verifying the skill level of analytical laboratories and their accreditation,
- routine control of analytical laboratories.

Interlaboratory studies play a particularly significant role in this area. Literature in general, and International Organization for Standardization (ISO) in particular, distinguish the following types of interlaboratory studies:

- collaboration analytical studies,
- interlaboratory tests,
- round robin tests.

Studies of this type are also carried out during certification of proposed new reference materials. The biggest advantage of reference materials is their ability to transfer measured or assigned values from one location to another.

Analytical chemistry lacks an organized measurement system analogous to that used in metrology, based on standard and calibration laboratories, as well as easily accessible standards. Traceability of the entire analytical procedure, defined as the ability to show an unbroken chain of relationships between a measurement and a calibration, is the biggest problem. Links to standards are broken every time the sample is physically or chemically modified during preparation, for example when it is dissolved or treated in a similar fashion. This has to be taken into account when estimating the overall uncertainty of the result. When establishing the chain of relationships for this part of the analytical procedure, the relationship between the initial sample and the solution obtained from it must be examined. A number of questions must be answered, the most important of which are:

- was the sample completely dissolved?
- how great were analyte losses?
- was the sample contaminated in the process?
- has the analyte changed during dissolution?

For organic compounds, extraction efficiency is the critical source of difficulties.

If the resultant sample solution is further processed (concentration, solvent evaporation, precipitation, etc.), each additional step makes traceability more difficult and increases the potential for analyte losses and sample contamination. Thus, each additional step should be carefully examined in this context.

Summary

Even this general and rather cursory review of issues related to preparation of environmental samples for trace analysis clearly indicates the difficulty of the challenge faced by analytical chemists involved in the development of new analytical procedures or applying accepted procedures in everyday practice. In any case, it is the characteristics of the sample itself and the goal of the analysis

(analyte speciation, determination of total parameters, determination of elemental composition of the analytes, etc.) that determine which operations should be included in sample preparation to make the sample amenable for final determination using the chosen (or available) analytical technique.

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