Polish Journal of Environmental Studies Vol. 11, No. 3 (2002), 211-218

Review

Monitoring and Analytics of Atmospheric Air Pollution

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Received: 10 September, 2001
Accepted: 8 October, 2001

Abstract

This paper presents the tasks, procedures and instrumental trends in analytics and monitoring of air pollution. The classification of methods and analytical techniques used for atmospheric air studies are also discussed.

Keywords: air pollution, monitoring, environmental analytics, monitors, sampling techniques

Introduction

The quality of atmospheric air, connected essentially with the level of pollutants due to transmission and deposition phenomena and secondary pollutant formation as a result of primary pollutant conversion, can affect the state of other environmental areas, mainly surface waters and soil.

Therefore, it is necessary to obtain and collect versatile information on the type and quantity of pollutants that are present in air or are introduced to it from different emission sources.

A great number of methods and analytical techniques are used to study atmospheric air. Generally, they can be classified according to the following parameters:

- compound type (analyte) and its concentration level,
- measurement mode (continuous or periodical),
- period of investigation (long- or short-term measure ments),
- automation level of measurements,
- measurement sites *(in situ,* in laboratory),
- manner of measuring (directly in sample or in second ary matrix),
- sampling mode,
- type of appliances used for sampling.

On the basis of literature research, it can be concluded that analytics and monitoring of atmospheric air are those areas of environmental studies that are expanding most rapidly [1-8].

Aims and Tasks of Atmospheric Air Analytics and Monitoring

The use of appriopriate methods and analytical techniques in practise for air studies provides information necessary for: 1. assessment of pollutant emission, particularly:

- identification of emission sources,
- assessment of the interaction range of particular emit ters,

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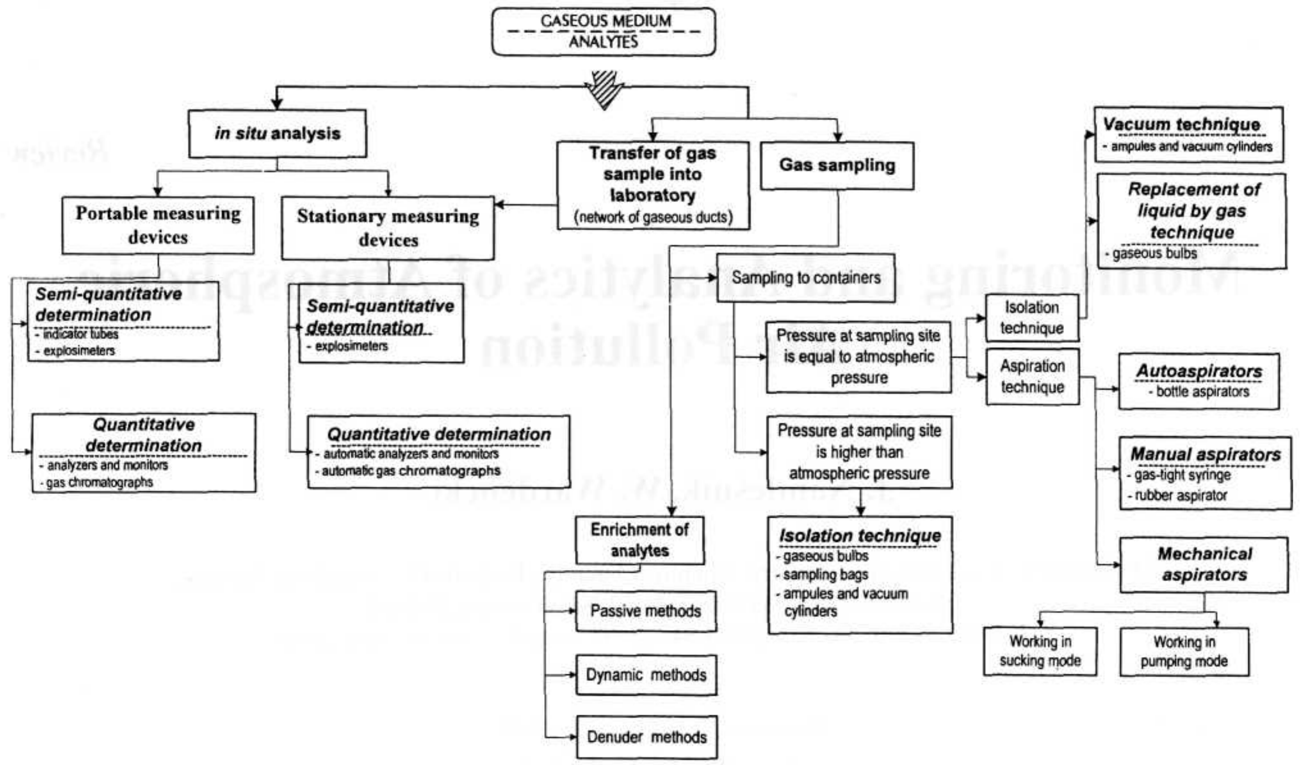

Fig. 1. Classification of methods and devices used for sampling and analysis of gas samples.

- estimation of technical effectiveness of protective measures,
2. determination of ambient air pollutants and investigation of long-term trends in concentration changes,
3. studies of processes in the atmosphere, i.e.:
- transport and deposition of pollutants,
- chemical, photochemical and biochemical conversion of pollutants,
4. estimation of exposure rate and accumulation of pollutants by living organisms.

Such a wide spectrum of tasks for analysts dealing with air quality studies is possible due to the availability of various procedures and analytical techniques [9].

Monitors - Specific Analytical Instruments

Considering the analytical characteristics of instruments used in air studies two types of devices can be distinguished:
- analysers, instruments used both for *in situ* measurements (portable) and for the equipment of mobile analytical laboratories,
- monitors, automatic devices belonging to this group should possess specific characteristics and fullfil several methological and technical demands.

The classification of devices used for sampling and determination of analytes in atmospheric air is presented in Figure 1.

Methodological demands:
- high sensitivity of measurements,
- providing analytical information in continuous mode in real time or with only a slight time delay,
- high resolution of results (characterised by short response time),
- long independent working time.

Technical demands:
- automatic instrument zeroing and calibration,
- safe guarding system against sudden breaks in power supply,
- equipment of instrument in
  (i) independent power supply
  (ii) calibration module
  (iii) system for filling and suplementing the working solution and reagents (electronic monitors)
  (iv) device protecting flame extinguishing (monitors based on FID and FPD)
- possibility of automatic regeneration or exchange of waste filters.

Trends in Monitoring and Analytics of Atmospheric Air

Vast information on new solutions appears each year in scientific literature that can be used in air studies. Examination of the available literature data enables us to distinguish a number of trends, both procedural and instrumental (caused mainly by new achievements in instrumentation) [10]. The most important trends include:

Procedural trends in environmental analytics and monitoring
- widespread use of speciation analytics [11],
- application of total (summarical) parameters to the evaluation of the pollution degree [12, 13],
- search for determination of increasingly lower concentrations of analytes in samples with very complex matrices [14, 15],
- search for new methods for determining of many analytes using one sample and in one analytical cycle [16,17],
- growing importance of bioanalytics and biomonitoring [18, 19],
- the use of simple tests for initial evaluation of the pollution degree of atmospheric air [20].

Instrumental trends
- new design of sensors and detectors [21, 22],
- introduction of multidimensional techniques to practice, [23, 24],
- automation, robotization and computerization of measuring instruments [25, 26],
- the use of expert systems [27, 28],
- miniaturization of analytical instuments (introduction of electronic nose to analytical practice) [29],
- design of passive devices for *in situ* measurements including direct readings of analyte amount (concentration) [30, 31],
- development of remote sensing techniques for evaluation of the pollution degree of the atmosphere [32],
- the use of film techniques, photographical documentation and geographical information system (GIS) technology for evaluating air quality [3, 34].

The trends that are particulary important for scientific research are discussed in more detail below.

New Sampling Techniques for Atmospheric Samples

In analysis of air, due to low and frequently very low concentrations of analytes it is necessary to use special techniques combined with the simultaneous preconcentration of analytes. Generally, three sampling techniques are used [35]:
- dynamic techniques,
- passive techniques [36],
- denudation techniques [37].

The operating principles of particular sampling devices belonging to each group are schematically presented in Figure 2.

A thorough examination of scientific literature leads to the conclusion that there is a vast procedural and instrumental design connected with the above-mentioned sampling techniques. The designs described may be classified on the basis of parameters decisive on the

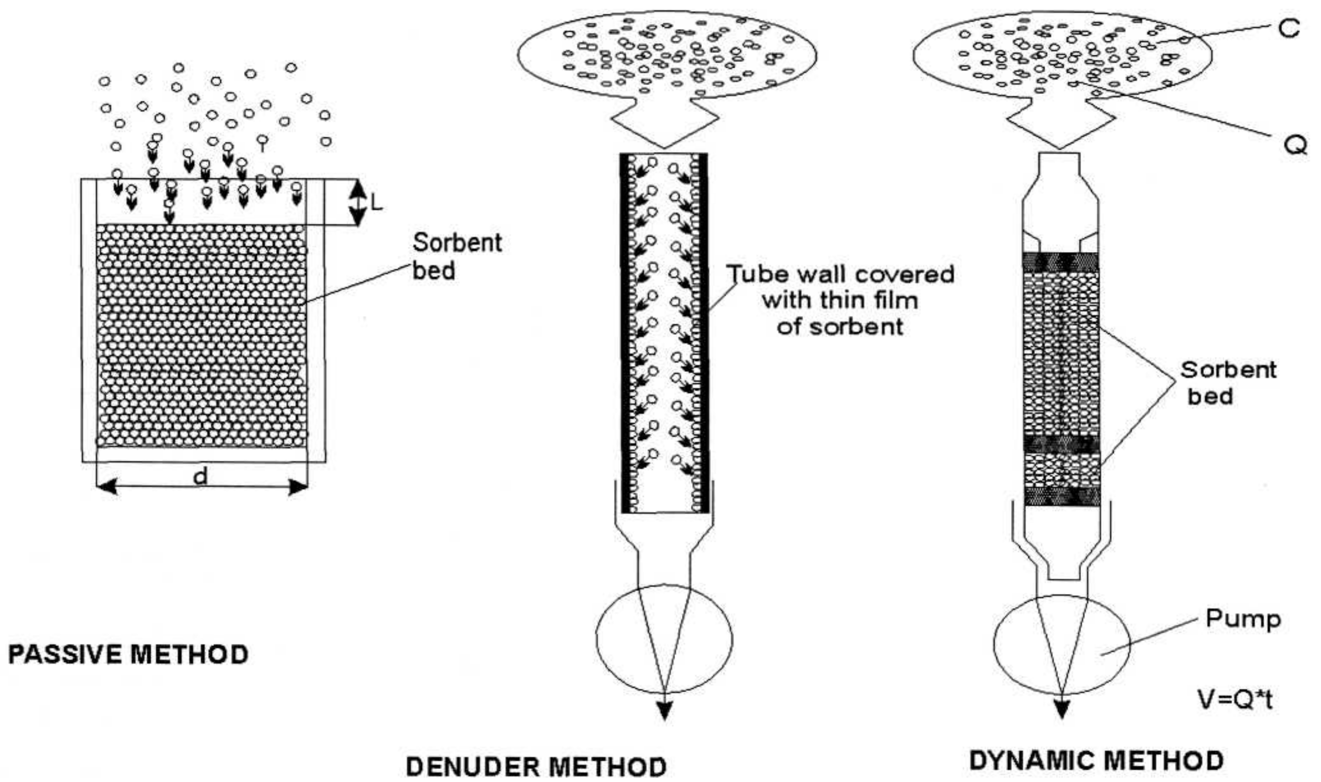

Fig. 2. Schematic representation principle of operation of sampling devices using passive, dynamic and denuder techniques C - concentration of pollutant, Q - flow rate of sample, t - sampling time, d - tube diameter, L - height of stagnant air

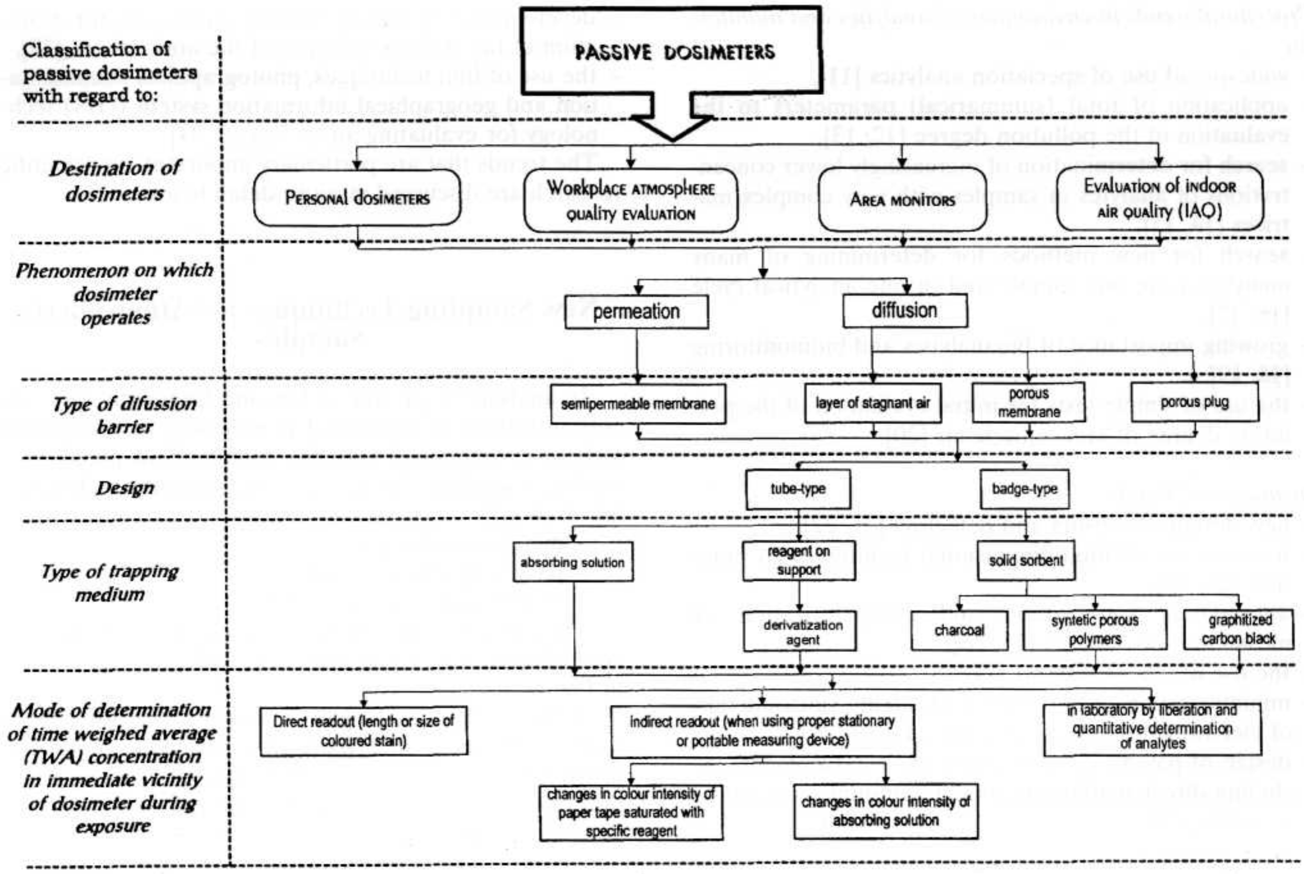

Fig. 3. Classification of air sampling techniques based on passive dosimetry.

Table 1. Brief description of bioindicators and biomonitors.

Parameter	Name of bioindicator/biomonitor	Description of bioindicator/biomonitor
Mode of action	Accumulation indicators/monitors (accumulative indicators)	Organisms that accumulate one or more elements and/or compounds from their environment
	Effect or impact indicators/biomonitors	Organisms that demonstrate specific or unspecific effects in response to exposure to a certain element or compound or a number of substances. Such effects may include changes in their morphological, histological or cellular structure, their metabolic-biochemical processes, their behaviour or their population structures
Origin of organisms	Active bioindicators/biomonitors	Organisms bred in laboratories that are examined for accumulation of elements or compounds and for specific or unspecific effects after exposure for a define period in the area studied
	Passive bioindicators/biomonitors	Organisms that are taken from their natural biotope and analyzed for accumulation of elements or compounds and for a specific or unspecific effects

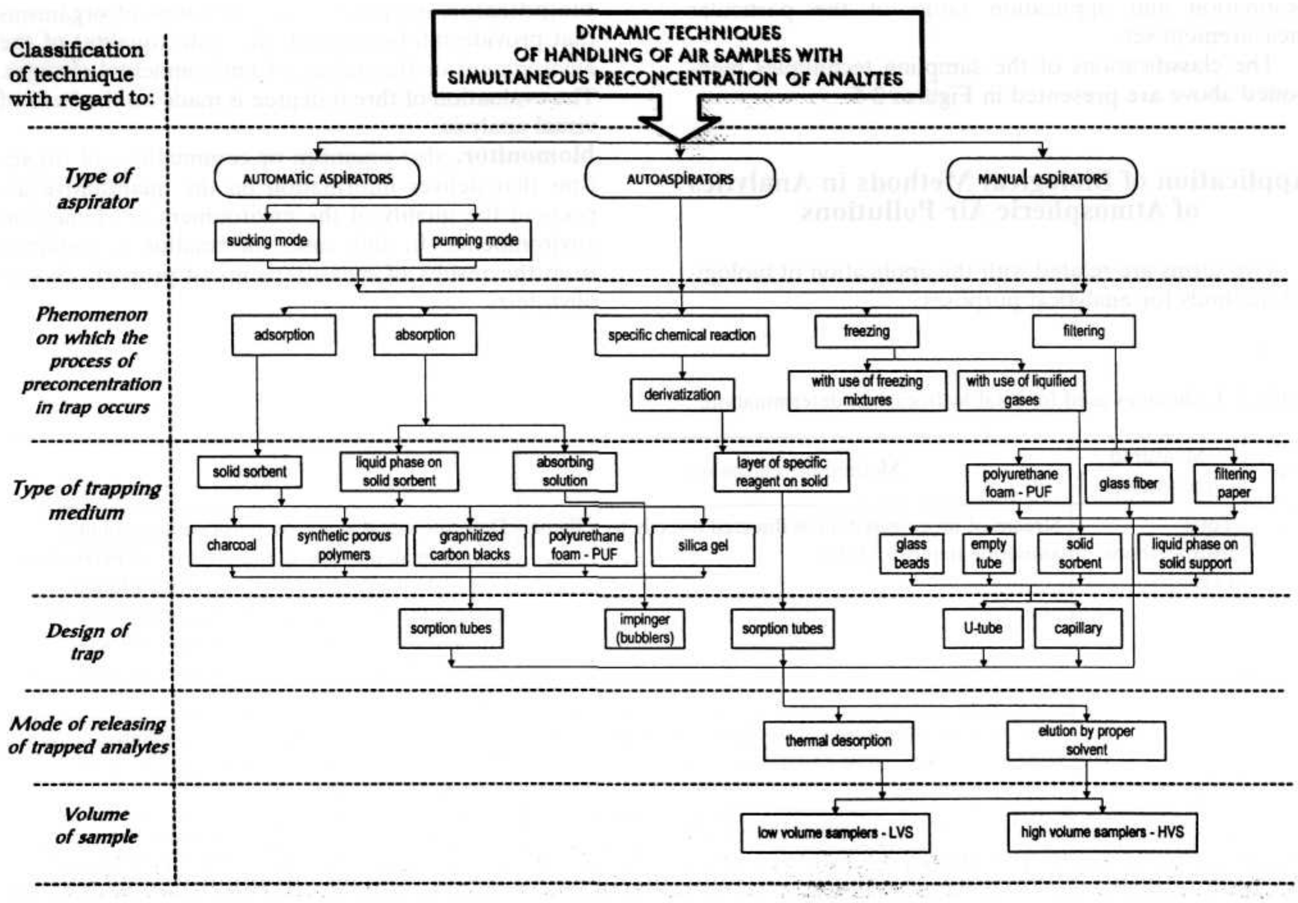

Fig. 4. Classification of air sampling techniques with simultaneous dynamic enrichment of analytes.

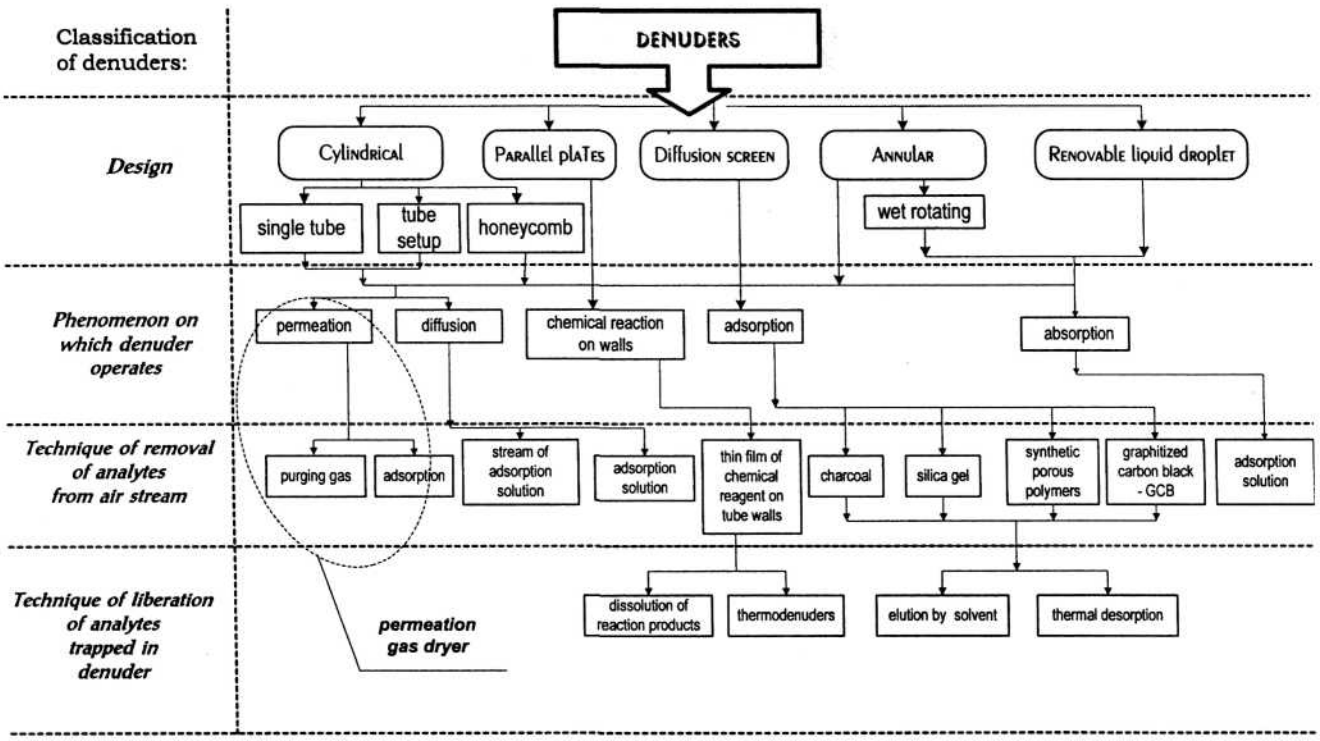

Fig. 5. Classification of denudation techniques of analytes sampling from air stream.

destination and application range of the particular measurement set.

The classifications of the sampling techniques mentioned above are presented in Figures 3-5.

Application of Biological Methods in Analytics of Atmospheric Air Pollutions

Two terms are related with the application of biological methods for analytical purposes:

- **bioindicator,** organism or communities of organisms that provide information on the state (quality) of the **environment** or the nature of environmental changes. The evaluation of threat degree is made on the basis of **visual** analysis.
- biomonitor, also organism or communities of organ isms that deliver information on the quantitative as pects of the quality of the environment or changes in environments. In this case, information is obtained **from the** results of measurements of properly chosen phytotests.

Table 2. Techniques used for total hydrocarbon determination.

No	Measured parameters	Method of realization	Notes
1	Total hydrocarbons (TH)	Stream of investigated air is directed directly to a flame ionisation detector (FID)	Detector signal is not proportional to a number of carbon atoms (due to the presence of heteroatoms in analyte molecules). Methane concentration is many times higher than total concentration of remaining compounds, it is difficult to observe the changes in the level of total amount of other compounds
		Stream of air, after removal of CO and CO_2, is directed through a bed of catalyst to a near infra red absorption detector	Detector signal is proportional to a number of carbon atoms. The disadvantage of the method is low sensitivity of NDIR
		Stream of air, after removal of CO and CO_2, is directed to flame ionisation detector through: – bed of catalyst (to oxidize organic compounds) – bed of catalyst (metallic nickel on support) heated to 400°C to convert CO_2 to CH_4 (in presence of H_2)	Very high sensitivity of TH determination
2	Total non methane hydrocarbons (TNMHC)	Stream of air is directed to flame ionisation detector (FID) through a bed of catalyst (where non methane hydrocarbons are selectivily mineralized). The determination of CH_4 and TNMCH is possible as a result of alternately directed air stream (through catalyst or beyond catalyst)	Choosing of the proper catalyst and temperature of work, in which all organic compouds are quantitatively oxidated, except of methane, are the most important problem
		Air sample is injected into chromatographic column, where CO, CO_2 and CH_4 are separated from organic compounds. Analytes leave a column through metanizer and are directed to flame ionization detector (FID). Compounds retained at the head of chromatographic column, after changing the direction of carier gas stream, are eluted from column (as one peak) and directed to detector	It represents periodical determination of TNMHC amount by chromatography
		Stream of air is drawn through cryogenic trap, where organic compounds, except methane, are retained. In next step the trap is extensively heated and analytes are eluted to detector in the stream of air	Water vapour, retained in trap in the form of ice, creates a problem
		Stream of air is drawn sequentionally through – reactor for a catalytic oxidation of CO; – absorber for a selective retaining of CO_2; – reactor for selective catalytic oxidation of organic compounds (in the presence of CH_4 to CO_2); The remaining CO_2 (equivalent to carbon in the oxidized organic compounds) is retained on the layer of molecular sieve. Determination of CO_2 can be performed with using different techniques after a thermal desorption	The procedure is very complicated and many steps of the technique may be source of errors.

Organisms (or communities of organisms) can also be classified on the basis of their "mode of action" and their "origin". The characteristics of both types of indicators are given in Table 1.

The application of bioindicators and biomonitors for evaluation of air pollution degree and its effects on the environment have presently become very popular. The criteria useful for selection of appropriate organisms as bioindicators for evaluating the pollution degree or pollutant influence on the environment were defined over twenty years ago [39] and are still actual:

- relatively resident character of organisms (to fulfil rep resentative demands in relation to studied ecosystem),
- wide distribution all over the examined area
- facility to identify and to collect samples,
- possibility of collecting an appropriate amount of ma terial for studies,
- relatively good organism tolerance in relation to inves tigated pollutants (heavy metals, organic compounds, etc.),
- facility to transplant of organisms to another place and also to transport to laboratories,
- population stability of chosen organism to assure multiple sampling in longer periods of time (to assess the trends),
- existence of reasonable correlation between the degree of pollution of particular element of environment (air, water, sediments, food) and concentration of analyte in tissue (s) of selected organisms,
- the same value of bioaccumulation factor of pollutants (biomagnification of analyte concentration in organism in relation to investigated environment) in different sites (this is not always possible because of different variables affecting the taking up of pollutants by a given organism).

Application of Total (Summarical) Parameters to Studies of Atmospheric Air

Considering the great variety of chemical compounds that can be atmospheric air pollutants, their separation and determination (speciation analysis) can be a very difficult and expensive task.

The application of total parameters (giving total amount of a particular element - most frequently carbon - in all pollutants or a certain group of pollutants) en ables in many cases a limitation of the number of necess ary steps of analysis and faster evaluation of degree of pollution.

It should be noted that both approaches to pollution degree evaluation, i.e. tendency to measure all species (chemical forms) or their physical forms (speciation analysis) and determination of total parametrs are fully complementary [44].

Two parameters are the most frequently used in analytics of air pollution: total hydrocarbons (TH) and total non-methane hydrocarbons (TNMTH). The contents of these compounds are expressed as a sum calculated as carbon concentration (e.g. ppm of C).

Short description of techniques used for measuring total hydrocarbons present in air samples is shown in Table 2.

Concluding Remarks

More detailed description of basic trends in monitoring of atmospheric air may be found in recently published reviews. It should be realized that such papers are to a large extent very subjective and depend both on degree of knowledge of literature data and personal experience.

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