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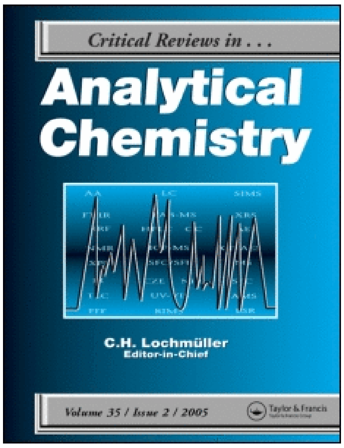

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Analytical Techniques Used in Monitoring of Atmospheric Air Pollutants

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The air pollution monitoring is one of the most pressing environmental problems today. The paper describes common air pollutants, their interaction and impact on the environment, and classifies the techniques and methods applied in air studies. Furthermore, the review characterizes the selected collection and sampling techniques used for gas sample analysis. Finally, the schematic diagrams of typical designs of systems applied in such studies are presented.

Keywords air pollution, analytical techniques, sample collection, sampling techniques

INTRODUCTION

In recent decades, air quality has become a very important concern as more studies have shown the great impact of atmospheric pollution on environment and health. Air quality is the result of a complex interaction between natural and anthropogenic environmental conditions (1, 2).

The clean air consists of gases, which were formed in a natural way. Of all gases, nearly 99% are oxygen and nitrogen molecules, and only 1% are other components, such as argon, carbon dioxide, water vapor, helium, and other trace substances. Air pollution is defined as the presence in the atmosphere of one or more contaminants (pollutants) in quantities and for durations that can injure human, plant, or animal life or property (materials) or that unreasonably interfere with the enjoyment of life or the conduct of business. Air pollutants, represent gases, solid particles, and aerosols that change the natural composition of atmospheric air.

Air pollution sources can be categorized according to the type of source, their number and spatial distribution, and the type of emissions. Categorization by type includes natural and human-made sources. Natural air pollutant sources include plant pollens, wind-blown dust, volcanic eruptions, and lightning-generated forest fires. Anthropogenic sources include transportation vehicles, industrial processes, power plants, municipal incinerators, and others.

Anthropogenic emissions dominate over industrial areas and over terrains with high population density. These emissions can be caused by accident disasters and uncontrolled discharges (casual emissions), but controlled emissions can also take place, accomplished according to determined rules and under close surveillance of trained personnel. Emissions originate from point, linear (communication route), or area (open container with volatile substance) sources.

Considering the character of the source, the pollutants can be divided into two main groups:

- biological pollutants, which include macroorganisms and microorganisms, such as viruses, bacteria and fungi, and products of their metabolism, their types and abundance differ from natural composition of air microflora; and
- physicochemical pollutants—gases and vapors of chemical compounds (oxides of carbon, sulphur and nitrogen, ammonia, fluorine, aliphatic and aromatic hydrocarbons, and their halogen derivatives, phenols) and solid inorganic and organic particles (particulate matter—such as fly ash, soot, dust from cement and metallurgical plants, compounds of lead, copper, chromium, cadmium, and other heavy metals).

Air pollutants can be divided into primary pollutants, which are present in air in a form released into the atmosphere, and secondary pollutants, products of physical and chemical reaction between components of atmosphere and their pollutants (products of these reactions can be more hazardous than the primary ones) and particles raised from the surface of Earth when the pollutants are dispersed in an atmosphere. The intensity of this process depends also on meteorological and local conditions.

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The main pollution sources are:

- combustion of fossil fuels (hard bituminous and brown coal, crude oil);
- forest and wasteland burning;
- combustion of fuels in engines;
- on-land waste disposal;
- using of fertilizers;
- animal husbandry; and
- using of different types of refrigerant agents.

The attention focused on air pollution is due to essential impact of the pollutants on a state of environment and human health. A protection against detrimental action of air pollutants with global range requires, first of all, reliable information on the level of occurrence and their physicochemical and/or microbiological properties, which can be obtained from analytical measurements. The conducted investigations should provide information about:

- qualitative and quantitative composition of pollutants;
- spatial and time fluctuations;
- sources and intensity of pollutant emissions;
- range of the emitters impact;
- transport processes and transformation of pollutants in the atmosphere;
- level of emission and intensity of pollutant deposition; and
- effectiveness of undertaken sozotechnical actions.

The broad spectrum of techniques and measuring devices, both for samples collection and final determination, depending on a particular kind of pollutant, the level of occurrence and required type of analytical information, are applied in analytical practice (3).

Characteristics of Air Pollution and Their Impact on Human Health

Although the air is not a matrix with a complex composition, its components fluctuate continually in space and time, can interact with each other, and have specific impact on nature and living organisms. The substances are present in air on different levels of concentrations and have specific color (nitrogen and sulphur oxides, benzene, toluene, xylenes) or as colorless and odorless gases (carbon mono- and dioxides). Air pollution can irritate the human respiratory system, causing inflammation of the lungs; reduce lung function, making it harder to breath for example. Manifold potential effects result from air pollution in an area. These effects are manifested in human, animals, plants, and materials or climatologically variations. The potential effects can be categorized in many ways:

- economics losses—resulting from air pollutants include soiling, damage to vegetation, damage to live stock, and deterioration of exposed materials (4, 5)
- visible and quantifiable effects—include tree injury and crop damage, with examples occurring nationwide (6)
- biodiversity—the fundamental influencing factors include the pollutant's environmental partitioning, exposure pattern, and toxicity and the sensitivity of the affect species. Biodiversity impacts occur on local, regional, and global scales. Local plume effects reduce vegetation cover, diversity, and ecosystem stability (7, 8).
- deterioration of exposed materials—includes the corrosion of metals, weathering of stone, darkening of lead-based white paint, accelerated cracking of rubber, and deterioration of various human-made fabrics (9–11)
- health effects—personal discomfort to actual health hazards. Personal discomfort is characterized by eye irritation and irritation to individuals with respiratory difficulties. Table 1 summarized the potential effects attributed to specific air pollutants and the sources of pollutants.

Air quality can be defined in terms of health because of the illnesses and deaths associated with those events. Air quality could be also defined as a function of visibility or some other pollutant-induced effect. Any definition of air quality should be, in whole or in part, based on its effects.

The success of pollution control efforts depends on the availability of good data on ambient concentrations of pollutants and emissions from individual sources and/or group of sources.

Air quality monitoring may be defined as a systematic, long-term assessment of pollutant levels in communities, less polluted rural areas, and for some pollutants the global atmosphere. Monitoring activities are intensively conducted by state/provincial and local agencies to determine the compliance status of air quality control regions relative to air quality standards.

INTERACTION RANGE OF AIR POLLUTANTS

Air quality is a major determinant of human health (23, 24). Atmosphere is a good carrier of pollutants, starting from gases, such as SO_2, NOx, VOC, aerosols, even to the particulate matter. Many of these compounds can be emitted from point or diffuse sources to the environment and may cause different diseases (25, 26). Depending on their interaction range, the pollutants may effect the atmosphere on a different scale (local, regional, or global). It is related not only to geographical and meteorological conditions but also to the stability characterized by their lifetime. Figure 1 shows the interaction range of typical air pollutants with their effects.

Recent estimates indicate that tens of thousands of premature deaths per year in Europe may be associated with exposure to particulate matter resulting from long-range transport (23, 27).

Because it is evident that clean air is an important requirement for human health, the World Health Organization (WHO) has been concerned with air pollution and its impact on human health for more than 40 years. The first WHO meeting on air pollution and public health was held in Milan in 1957. It was followed

TABLE 1
The potential effects attributed to specific air pollutants and the sources of pollutants

Toxic chemical	Sources	Environmental effects	Ref.
Nitrogen oxides (NO and NO_2)	• combustion of oil, coal, gas in both automobiles and industry • bacterial action in soil • forest fires • volcanic action • lightning	• decreased visibility due to yellowish color • causes visible leaf damage • irritates eyes and nose • suppress plant growth (even when not causing visible damage) • contributes to heart and lung problems • may encourage the spread of cancer • corrodes metals	(12)
Volatile organic compounds (VOCs)	• evaporation of solvents • evaporation of fuels • incomplete combustion of fossil fuels • naturally occurring compounds like terpenes from trees	• eye irritation • respiratory irritation • may be carcinogenic • decreased visibility due to blue-brown haze	(13)
Ozone (O_3)	• formed from photolysis of NO_2 • diffusion from stratosphere	• respiratory irritation, disturb lung function • irritate eyes, nose and throat • decreased crop yields • retards plant growth • discolors the upper surface of leaves of many crops, trees, and shrubs • damages and fades plastics and textiles • breaks down rubber • harsh odor	(14)
Peroxyacetyl nitrates (PAN)	• formed by the reaction of NO_2 with VOCs (can be formed naturally in some environments)	• irritates eyes • respiratory irritation, disturb lung function • high toxicity to plants • damaging to proteins • discolor the lower leaf surface	(15, 16)
Carbon monoxide (CO)	• incomplete combustion of fossil fuels • combustion of oil, coal, gas in both automobiles and industry	• causes headaches, dizziness, and nausea • absorbed into blood • reduces oxygen content • impairs mental processes	(17, 18)
Carbon dioxide (CO_2)	• combustion of oil, coal, gas in both automobiles and industry	• probably greenhouse effect	(19)
Sulphur dioxide (SO_2)	• incomplete combustion of fossil fuels • combustion of oil, coal, gas in both automobiles and industry • volcanic gases	• causes acute and chronic leaf injury • attacks a wide of variety of trees • irritates upper respiratory tracks • destroys paint pigments • erodes statuary • corrodes metals • ruins hosiery • harms textiles • disintegrates book pages and leather	(20, 21)
Particulates		• speed chemical reactions • obscures vision • corrodes metals • causes grime on belongings and buildings • aggravates lung illness	(22)

by many other activities resulted in international cooperation and harmonisation of environmental policies in European Region (23). Not only WHO but also other organisations—United Nations Environment Programme (UNEP) and Global Environment Monitoring System (GEMS)—operate worldwide networks to monitor both air and water quality under auspices of the WHO (28). In the USA, the Environmental Protection Agency (EPA) works with state, local, and tribal governments to reduce toxic air releases of 188 pollutants to the environment (29).

As everybody is conscious of the weight of environmental protection problems, the aim now is to solve them together, globally.

GENERAL CLASSIFICATION OF TECHNIQUES AND METHODS APPLIED IN AIR STUDIES

Generally, the choice of analytical method to study atmospheric air depends on numerous parameters:

- pollutant state (gaseous, liquid, aerosols, particulate matter),
- compound type and its concentration level,
- period of measurement (long- or short-term),
- manner of measuring (direct or with sample preconcentration)
- measurement site (in situ, in laboratory),
- automation level of measurements,
- aim of measurements (estimation of emission, short-term concentration, etc).

In Table 2 the classification of methods applied in air studies on the basis of different parameters is presented.

TABLE 2
Parameters used for classifications of techniques and instruments applied in atmospheric air studies

Parameter	Additional information
Pollutant state	Gaseous components Suspension matter components
Analyte type	Organic components Inorganic components
Aim of measurements	Estimation of: emission imission deposition
Type of desired information	Instantaneous concentration Short-term concentration Averaged weighted concentration Averaged weighted concentration for total measuring time
Manner of measurement	Direct After preconcentration step
Analyte concentration	Main components Minor components Trace components
Measurement site	In situ In laboratory
Type of used instruments	Stationary instruments Mobile instruments
Level of automation	Manual instruments Automatic instruments

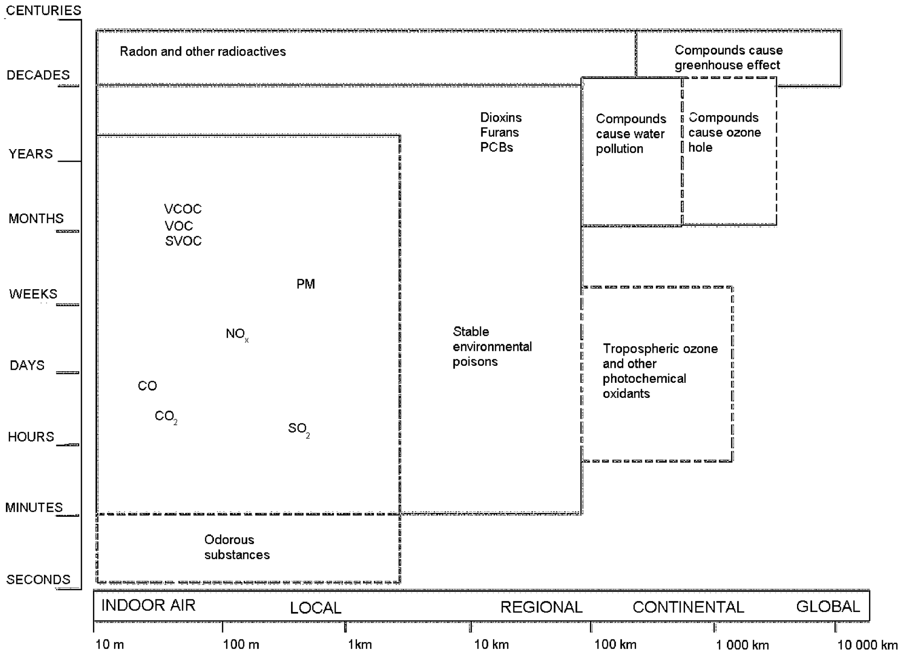

FIG. 1. Range of air pollutant actions.

The division based on the level of automation is important from a practical point of view. According to these criteria, two groups of methods are distinguished: manual and automatic. The manual methods, usually labor- and time-consuming, need the proper laboratory equipment. Furthermore, it is difficult to obtain good precision and the results are obtained after some hours or even days. Such measurements are applied mainly for immediate and periodic assessment of pollutants and air quality and also for calibration of measuring devices.

Automatic methods, demanding self-acting and usually expensive equipment, enable continuous recording of the concentration of measured substances delivering the results almost immediately. In such case the results obtained refer to real-time.

The information obtained concerns different types of concentrations of investigated pollutants, depending on applied sampling techniques and the measuring period. The results of measurements may be referred to real-time (instantaneous concentrations) or to a selected period of time (e.g., 30 days, 24 hours, month, year). Final measurements represent averaged concentrations.

Considering frequency, the sampling of discrete, periodic, and instantaneous measurements are distinguished. Taking into account space, parameter measurements are divided to a point, averaged along a defined part of space and averaged on the selected area. Final measurements enable determination of weighted average concentrations over the sampling period. Figure 2 presents schematically different forms of concentrations obtained in the function of sampling time.

GENERAL CHARACTERIZATION OF SELECTED COLLECTION AND SAMPLING TECHNIQUES USED FOR GAS SAMPLE ANALYSIS

It might seem that little sample preparation of gases should be needed as they can be analyzed directly by gas chromatography (GC). The whole sample is volatile and thus will leave no residue. However, the analytes of interest are often at low concentration, near or below the limit of detection. There has been considerable interest in concentrating, focusing, or trapping the analytes of interest to increase sensitivity and transportability.

Because of the vastness and dynamic nature of the atmosphere, it is not possible to determine the infinite number of values that are typical of pollutants in the atmosphere. Air is a very difficult matrix to handle; probably the most difficult environmental matrix to sample. In addition, the pollutants are present usually at very low concentrations; so their detection and quantification require a preconcentration step. A substance, such as carbon monoxide, exists only as a gas; an inorganic compound like iron oxide exists only as a particle. Many substances exist as either particles or vapors; however, substances that are gaseous can be attached (by some means) to particulate matter in the air. Many techniques can be used to sample air.

Concentrations are determined using sampling methods to collect pollutants in or on a sampling medium or bring them into the vicinity of a sensor. In methodologies where sampling and analysis are separated in time, a sufficient quantity of contaminant must be collected to meet the lower detection limit requirements of the analytical procedure used. The quality of collected pollutants will depend on the air concentrations and

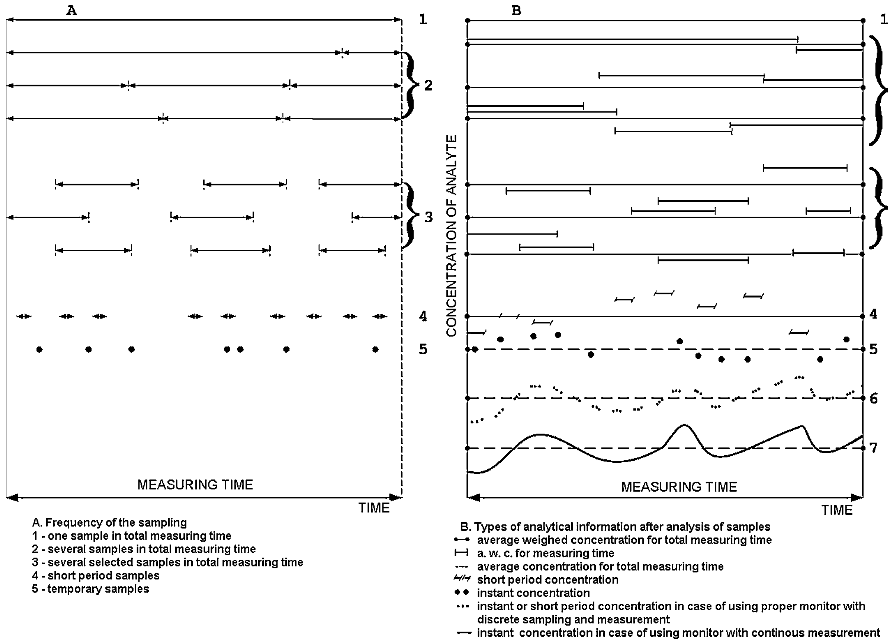

FIG. 2. Schematic diagram of different sampling techniques used for getting information on concentration of analytes in determined measuring time.

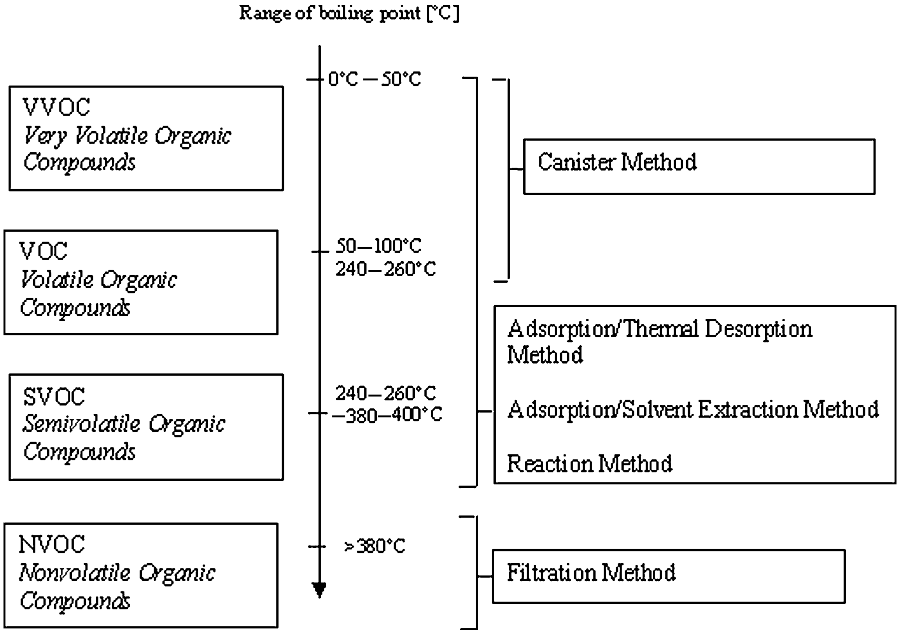

FIG. 3. Division of sampling techniques used for different types of organic compounds.

the size of sample. The sample size will be a direct function of the sampling rate and duration.

Collection and analytical limitations associated with intermittent sampling methodologies often require extending sampling durations that produce concentration values that are integrated or averaged over the sampling period. The averaging time used for pollutants concentrations is often determined by the duration required to collect sample. It is also determined by the intended use of the data collected. Averaging times for different pollutants are specified in ambient air quality standards (23).

The principal objective of sampling is to collect pollutants for subsequent analysis and/or provide a sensing environment for real-time measurements. Both require systems whereby gases or particles are drawn to the surface of a collecting medium into a sensing environment. These functions are accomplished by the sampling trains, which may also include vacuum pumps, flow regulators, and a collecting devices or sensing units.

Based on the type of information desired as well as collection and analytical limitations, sampling may be conducted by static, grab intermittent (whole-air sampling), or continuous procedures.

Organic compounds present in air matrix have different boiling points. In accordance with World Health Organisation (30) compounds normally present in the vapor phase at room temperature (vapor pressure greater than 0.0133 kPa at 25°C) are called volatile organic compounds (VOC). Compounds more volatile are known as very volatile organic compounds (VVOC). Compounds less volatile are known as semivolatile organic compounds (SVOC).

Next are nonvolatile organic compounds (NVOC)—particulate organic matter (POM) and aerosols, which have boiling points above 380°C. Figure 3 presents the detailed divisions of sampling techniques used for different types of organic compounds. Figure 4 presents general classification of methods and devices used for sampling and analysis of gaseous samples.

Whole-Air Sampling

In grab sampling, a small volume of air is collected in a matter of seconds or minutes. This is the simplest way to collect air samples. Samples can be collected by a variety of special containers and can be analyzed later primarily by GC techniques.

The most widely used sampling vessels are plastic bags and glass or stainless-steel containers.

Polymer bags are very simple to use. Materials suitable for use as sampling bags include Mylar, Saran, Scotchpak (a laminate of polyethylene, aluminum foil, and Teflon), and Tedlar (31–36). They can allow 10 to 100 L air to be sampled. However, filling the bags requires the air sample to be pumped in, which may be a potential source of contamination.

Another simple air sampling method uses glass (or stainless-steel) containers. Prior to their use, the canisters have to be carefully pretreated and conditioned, in order to avoid contamination or surface losses. The volume of containers is limited to a few liters, unless the sample is pressurized to allow larger amount of air to be collected (37). Whole air sampling may be used when we want to determine compounds whose analytes are in air matrix on a percent or a ppm level.

Reaction Method

Here, the air sample is passed through the tube packed with a sorbent on the surface of which reagent is coated. This reagent reacts with specific analytes to form a more stable or more

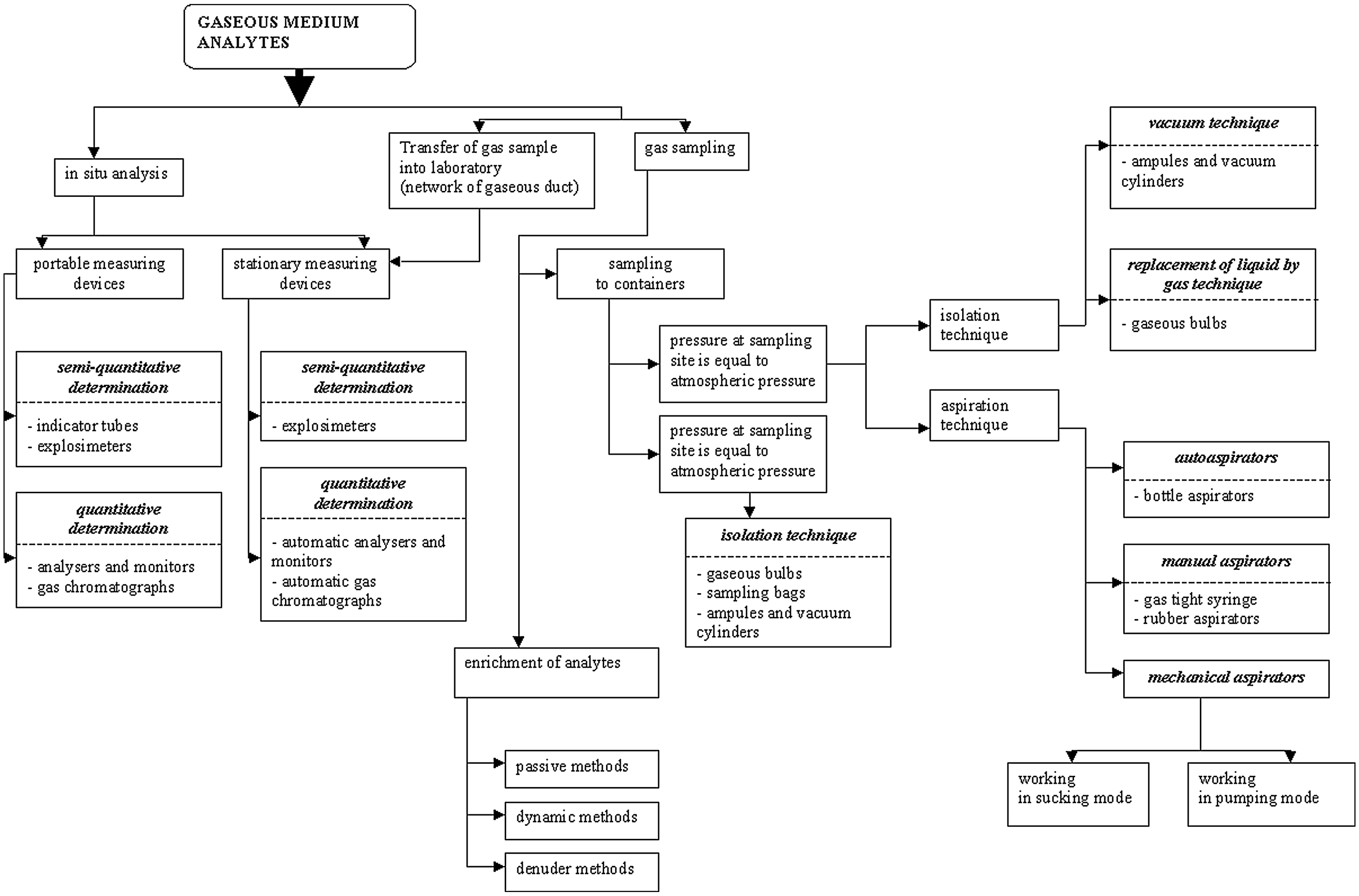

FIG. 4. General classification of methods and devices used for sampling and analysis of gas samples.

easily analyzed derivative (38, 39). The derivatizing agent or other reacting chemical may be impregnated on a filter; sorbents may also be used as supports for the color reactions used in detector tubes technologies. The most common method in use for trapping carbonyl compound in air is reaction with 2, 4-dinitrophenylhydrazine (40, 41).

Sorption Methods

Frequently, in analysis of air, due to low, and very low, concentrations of analytes, it is necessary to use analytical techniques combined with simultaneous preconcentration of analytes. Generally, three sampling techniques are used: dynamic techniques; passive techniques; and denudation techniques.

The detailed divisions of dynamic techniques, passive dosimeters, and denuders are presented in Figures 5, 6, and 7.

Collection in a Solvent

In absorption systems, polluted air is drawn through a liquid reagent. For collection in solvent, the sample is bubbled (using pumps) through a volume in a recipient where the analyte is dissolved. The contaminant is removed from the sampled air stream by being dissolved in absorbing reagent contained in a bubbler or impinger. The sampled gas enters the medium through a dispersion tube that is below the surface of the liquid. The gas forms bubbles and is dispersed in the liquid collection medium where it is absorbed. To enhance the liquid transfer of the solutes, the air bubbles have to be as small as possible.

This technique is very simple to perform and allows large volumes of air to be sampled. To avoid losses, the solvent needs to have a high boiling point. Besides, collection can be performed using two bubblers in series.

By adding a specific reagent to a collection medium, chemisorption takes place. This proved to be successful for direct detection of low-molecular-mass aldehydes (by reaction with 2,4-dinitrophenylhydrazine (2,4-DNPH) added to the solvent) in automobile exhaust gas (42). An aliquot of the solution is then injected into a liquid chromatograph (LC), most often, without any extraction or concentration step.

Collection on Solid Sorbents

Adsorption is a process that collects gaseous materials on a solid surface. In adsorption, gases are physically attracted to a solid, which has a large surface area, such as activated carbon, silica gel, molecular sieve, and others. The collected gases may

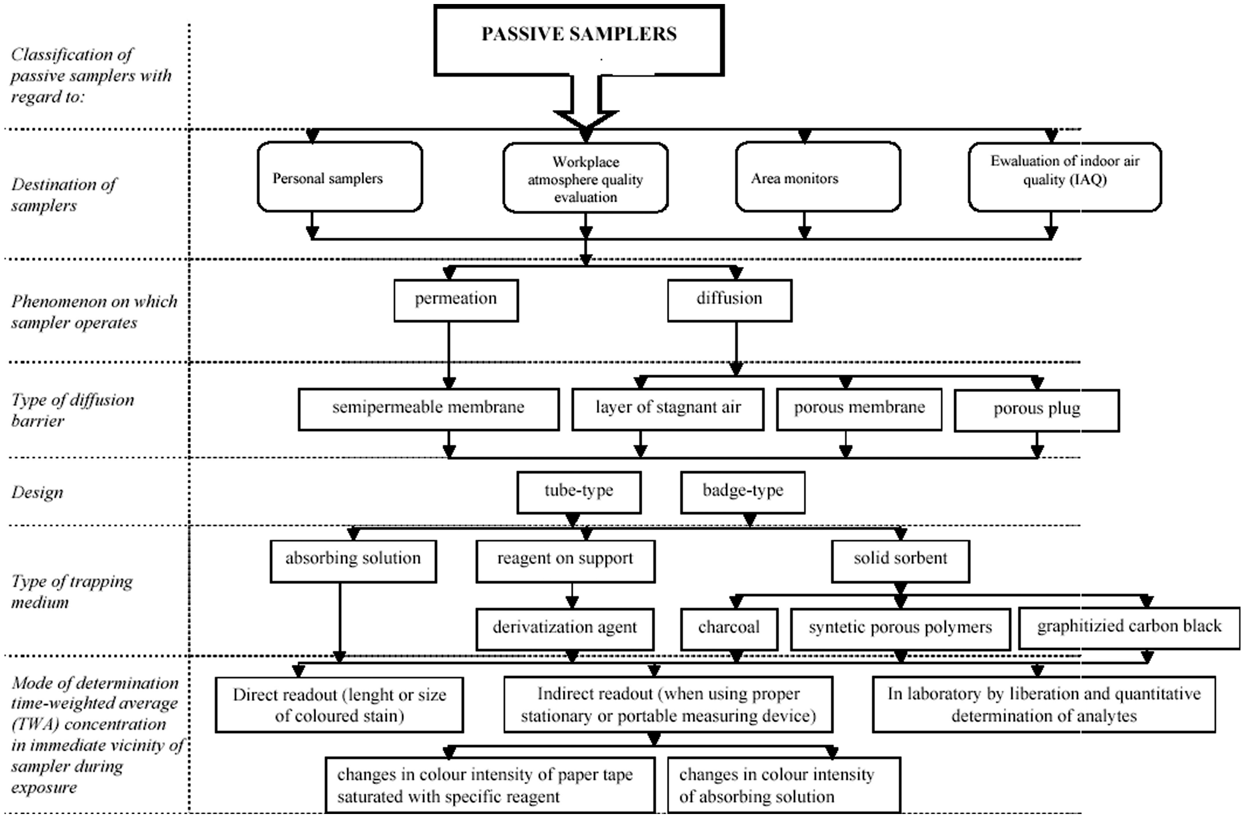

FIG. 5. Classification of air sampling techniques based on passive dosimetry.

be desorbed from the collecting medium and subsequently analyzed. Adsorption sampling is common for a variety of organic gases. Because adsorbents in general are not very specific, a mixture of gases is usually collected, making analysis more difficult. In addition, some collected gases may react with each other.

Two techniques of sampling analytes from air are commonly used in analytical practice (43):

- dynamic methods based on forced flow of analyte molecules from the sampled medium to a collecting medium; and
- passive methods based on free flow of analyte molecules.

In active sampling, a defined volume of air is pumped through the adsorbent at a specific controlled flow rate. In passive sampling, the tube (or badge-type sampler) containing sorbent is exposed to the atmosphere. Generally, there are two main types of passive samplers: diffusion and permeation type. The mass transfer process through the diffusion layer in diffusion samplers or permeation membrane in permeation samplers is described by Fick's first law of diffusion (44). This way of sampling is simpler and cheaper than active sampling, because there is no need for pumps or flowmeters (45). Whatever method, the concentrated analytes may be recovered with either thermal desorption or liquid extraction.

Thermal Desorption

Air samples are collected by passing through the tube packed with adsorbent such as porous polymer beads. The samples are introduced into the analytical instrument by heating the tube for the analysis. Table 3 presents sorbents using for air analysis-thermal desorption (using single or multibed sorbent layer).

Solvent Extraction Method

Air samples are collected by passing through the tube packed with adsorbent such as activated charcoal. After sampling, the samples are extracted with solvent for the determination, and analysis by GC or HPLC. The solvent must be capable of stripping the analytes from the sorbent with a high degree of efficiency and with high degree of reproducibility. For nonpolar compounds, a good solvent is carbon disulfide (45, 54, 55), for example. Polar compounds, such as alcohols, are poorly soluble in carbon disulfide, and in this case, polar solvents or two-phase desorbing solvents are useful.

Sorbents used with solvent desorption are silica gel, activated charcoal, Anasorb 747, Carboxens, or carbon molecular

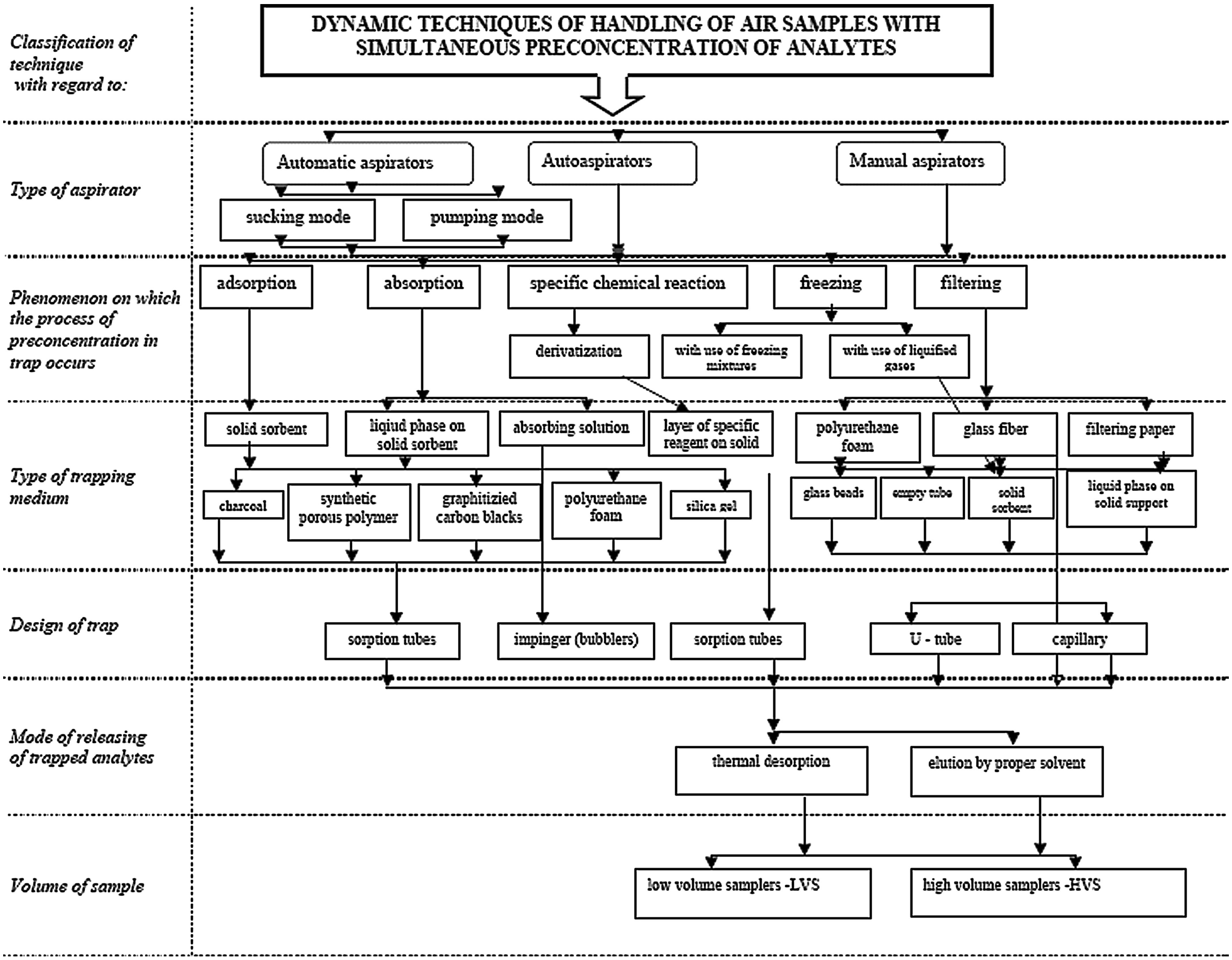

FIG. 6. Classification of air sampling techniques with simultaneous dynamic enrichment of analytes.

sieves. Silica gel has been used for the determination of very polar organic compounds (56) such as methanol, aminoethanol, amines and alkanoamines (57). Activated charcoal is the most commonly used sorbent.

SPME

Solid-phase microextraction (SPME) is a fast and solventless alternative to conventional preconcentration methods (with solvent or rather thermal desorption) for volatile organic compounds (VOC) in the air (58). This method uses a fiber coated with a stationary phase as the extraction medium and combines sampling and sample preparation. SPME is based on the partition equilibrium of target analytes between a polymeric stationary phase, which is a coated fused silica fiber, and the sample matrix. However, the volume of the fiber's polymer is so small that the target analyte is often not completely extracted and the extraction process from the representative sample should be compared with the model sample. After carrying out an extraction from a sample, the fiber can be placed in the injector port of a gas chromatograph so that the analytes are thermally desorbed directly into the carrier gas stream (59). Assay by HPLC can also be employed, but the sample is extracted directly into the eluent stream rather than thermally desorbed (60). The theory of SPME has been widely presented by Pawliszyn and coworkers (61–63).

A number of different fiber coatings are available, including the nonpolar (e.g., PDMS), semipolar (e.g., PDMS-DVB), and polar (e.g., PA, Car-DVB) liquid-like phases and solid polymeric phase (e.g., PDMS-Carboxen). They are available in increasing thickness from 7 to 100 μm, which increases the partitioning ratio and hence improves sensitivity but increases equilibration times (64, 65).

Skillfully used, SPME has many advantages. The main advantages of the system are that no solvent is required to elute the

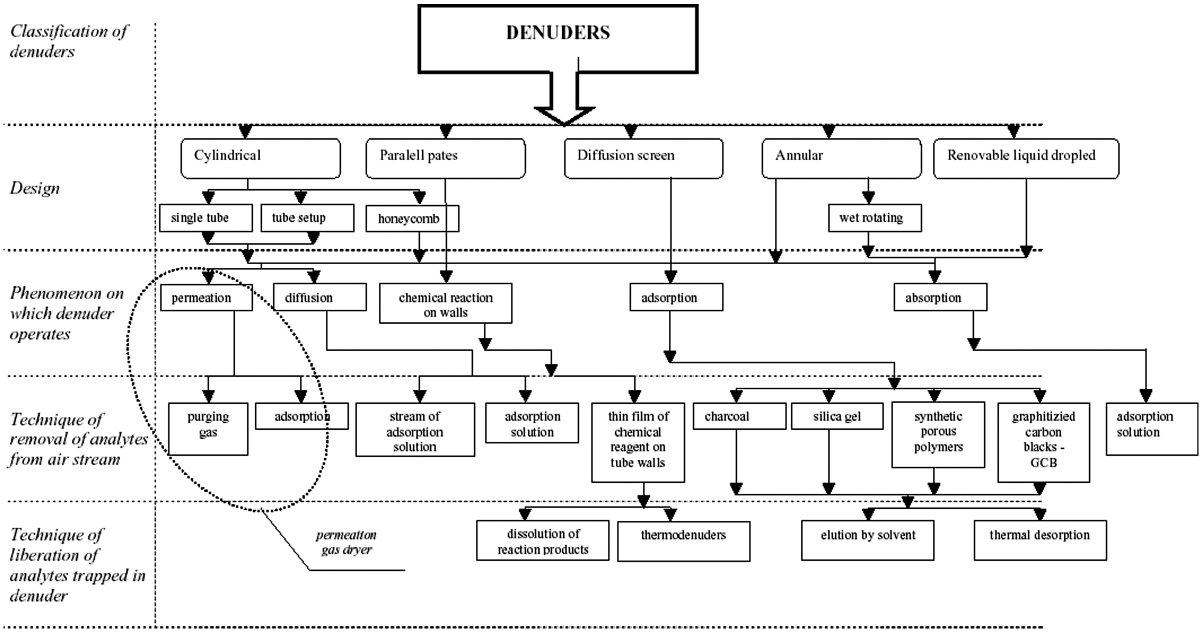

FIG. 7. Classification of denudation techniques of analyte sampling from an air stream.

analytes from the polymer (coating the fiber) and there is a direct transfer from sample preparation to the separation method. The extraction process can be relatively slow for nonvolatile and semivolatile analytes, but they are rarely investigated in air by this method. It seems to be competitive to conventional charcoal tube sampling/carbon disulfide extraction of volatile organic compounds (VOC) air. By combining sample collection and concentration in one step, the adsorbed/absorbed analytes can be easily thermally desorbed into an analytical instrument via the heated injector port, thus offering the benefits of minimal sample loss, maximum sample utilization since, there is no dilution involved (58, 66).

Unfortunately, there are same drawbacks of the SPME application to the air samples analysis (67). For example, it is

TABLE 3
Example of adsorbents used in adsorption/thermal desorption method

Category	Adsorbents	Pollutants	Ref.
Porous polymer beads	Tenax GR	Volatile organic compounds (C_5–C_{10})	(46)
	Tenax TA	Volatile organic compounds (C_5–C_{10})	(46)
		Volatile organic compounds (C_5–C_{10})	(47)
		Volatile organic compounds (C_5–C_{10})	(48)
		BTEX	(49)
		Aromatic compounds and linear alkanes	(50)
Graphite carbons	Carbotrap	Light volatile organic compounds (C_2–C_5)	(51)
		Volatile organic compounds (C_5–C_{10})	
		Volatile organic compounds (C_5–C_{10})	(46)
		Volatile organic compounds (C_5–C_{10})	(52)
		Volatile organic compounds (C_5–C_{10})	(52)
	Carbotrap B	Semivolatile organic compounds	(53)
	Carbotrap C	Light volatile organic compounds (C_2–C_5)	(51)
		Volatile organic compounds (C_5–C_{10})	
		Volatile organic compounds (C_5–C_{10})	(46)
Carbon molecular sieves	Carbosieve S-III	Volatile organic compounds (C_5–C_{10})	(46)
		Volatile organic compounds (C_5–C_{10})	(52)
	Carboxen 569	Light volatile organic compounds (C_2–C_5)	(51)

difficult to prepare standards for the gas sampling in the range of concentration for the calibration process. Also, calibration and sampling have to be done at the same temperature to obtain the reproducible results (68). Of course, these problems are quite easily solved. A method has been developed for determining organic pollutants from gaseous matrices by preparing gaseous standard mixtures with the use of apparatus for their dynamic generation (69).

The standard sample preparation is not necessary to quantify analytes when partition coefficients are determined. Martos and his coworkers (70) proposed a method for estimating these coefficients by using a linear temperature-programmed index. The dependence of the amount extracted on the temperature was determined by calculating the theoretical expression that describes the partition coefficients at any temperature for each fiber-analyte pair (71). This method has been used to determine formaldehyde (72), iso-paraffins (70), and aromatic hydrocarbons such as styrene (70).

In spite of many problems, a lot of new inventions enable convenient air pollutant analysis. For example, new SPME fibers with high surface areas, such as Carboxen-PDMS, allowed small volatile analytes to be extracted from air samples as gases (73). Using SPME device as diffusive sampler with on-fiber derivatization allows the determination of ethylene oxide in the air (74).

Biomonitoring

In the general meaning, biomonitoring is the use of a biological entity, as a detector, and its response, as a measure to determine environmental conditions. Here, the relevant information is commonly deducted from the changes in the behavior of the monitor organism or from the concentrations of specific substances in the monitor tissues (75).

Various monitor materials have been applied in air pollution monitoring programs, such as plants (e.g., lichens, mosses, ferns, grass), parts of plants (e.g., tree bark, tree rings, and pain needles), animals and human biological fluids (e.g., blood, urine, saliva) (76–77).

Bioaccumulation monitoring methods can be divided into two groups: passive and active. Active monitoring includes the exposure of well-defined species under controlled conditions, whereas passive monitoring refers to the observation or chemical analysis of indigenous plants (76).

Biomonitoring of air trace element analysis, unfortunately has a lot of disadvantages. First of all, there are same problems with calibration and quantitative analysis, probably because of differences in metal uptake and upkeep. Differences in concentration between lichens and mosses could be statistically significant for many elements (e.g., Al, B, Fe, Hg, Pb, Sb, Zn) (76, 79).

In spite of some drawbacks, biomonitoring is widely used in air pollution monitoring not only for trace element analysis but also for other contaminants. For example: SO_2, NO_2, O_3 (from urban origin) content in air was estimated, using mung bean, palak, wheat, and mustard as bioindicators (80). The other example uses bioindicators for documenting the presence of hydrogen fluoride and sulphur dioxide exposure that are classically associated with point source emissions (81), or ambient ozone effects on forest trees (82).

The relative ease of sampling, the absence of any need for complicated and expensive technical equipment, and the accumulative and time-integrative behavior of the monitor organisms that make biomonitoring of atmospheric pollutants possible could be continued for the foreseeable future, especially in large-scaled surveys. The necessary quantitative assessment of elemental ability asks for well-defined dose-response relationships, and knowledge on disturbances by impacts on the plant parameters on accumulation, retention, and release processes (77).

Remote Monitoring Techniques

Remote monitoring of air pollutants has many advantages over instruments generally used for in situ measurements. It allows the determination of air pollutants just after their release into the atmosphere, eliminating any preparatory steps inside a plant. Remote sensing is recommended for the detection of diffuse emissions, which are hard to qualify with typical ground-point measurements. Contrary to some other remote-sensing techniques, LIDAR (light detection and ranging) provides data on air pollutant concentrations at high spatial resolution (83). The lidar instrument transmits light out to a target. The transmitted light interacts with and is changed by the target. Some of this light is reflected/scattered back to the instrument where it is analyzed. The change in the properties of the light enables some property of the target to be determined. The time for the light to travel out to the target and back to the lidar is used to determine the range to the target.

There are three basic generic types of lidar: Range finders, DIAL, and Doppler lidars.

Range-finder lidars are the simplest lidars. They are used to measure the distance from the lidar instrument to a solid or hard target.

Differential Absorption Lidar (DIAL) is used to measure chemical concentrations (such as ozone, water vapor, pollutants) in the atmosphere. A DIAL lidar uses two different laser wavelengths that are selected so that one of the wavelengths is absorbed by the molecule of interest while the other wavelength is not. The difference in intensity of the two return signals can be used to value the concentration of the molecule being investigated.

Doppler lidar is used to measure the velocity of a target. When the light transmitted from the lidar hits a target moving toward or away from the lidar, the wavelength of the light reflected/scattered off the target will be changed slightly. This is known as a Doppler shift, hence Doppler Lidar. If the target is moving away from the lidar, the return light will have a longer wavelength (sometimes referred to as a red shift), if moving towards the lidar the return light will be at a shorter wavelength (blue shifted). The target can be either a hard target

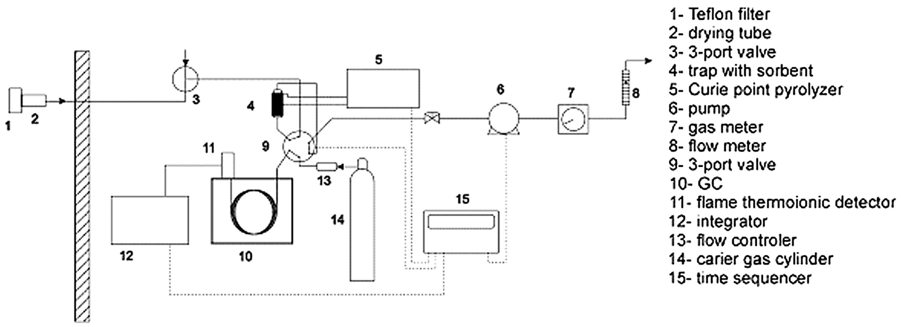

FIG. 8. Schematic diagram of the system for preconcentration of atmospheric ammonia with gas chromatography equipped with a flame thermionic detector (86).

or an atmospheric target; the atmosphere contains many microscopic dust and aerosol particles that are carried by the wind. These are the targets of interest to us, as they are small and light enough to move at the true wind velocity and thus enable a remote measurement of the wind velocity to be made (84).

The other type of device for remote monitoring is sodar (Sound Detection and Ranging). It can be used for detecting wind speed and wind direction at different heights above ground level. The Doppler sodar sends out sound pulses of several frequencies in slightly different directions. The acoustic signals are backscattered by inhomogeneities in the atmosphere. Meteorological parameters are derived from frequency shifts of the signals, and the run time of the signals leads to the location of height levels of backscattering (85).

Other Methods

Gases may also be collected by condensation or freezing. In such sampling, air is drawn through a collection vessel maintained at subambient temperatures. The low temperatures cause some vapors to condense or freeze and be retained in the collecting vessel. The sample must be removed and an analysis subsequently performed. Such cryogenic or freeze-out sampling has been used to condense and isolate various organic gases. It is the most difficult to use of the gas sampling techniques available.

EXAMPLES OF EQUIPMENT USED FOR SAMPLING AND ANALYSIS OF GAS SAMPLES

Scientific literature describes a great number of analytical methods and instruments that can be applied for determination of different pollutants in atmospheric air. In this chapter some examples of typical systems are presented. They are based on preconcentration of analyte before the final determination. Two approaches are the most frequently used for these purposes: adsorptive and/or cryogenic preconcentration.

The system presented in Figure 8 enables continuous, automatic determination of ambient atmospheric levels of ammonia (86).

The combination of an adsorbent (Porasil B) and analysis with extremely sensitive gas chromatograph using flame thermionic detector allows the determination of ammonia concentrations as low as 0.1 ppbv with a resolution of 15 or 30 minutes. The obtaining of good precision (relative standard deviation was better than 5% in the range of 2–106 ppbv of ammonia) was possible due to using a Curie-point thermal desorption device.

The system for measurements of methyl halides in the marine atmosphere (Figure 9) is based on canister sampling and capillary GC/MS. A 500 ml of air sample in a canister is drawn through two traps. The first, filled with glass beads and cooled at −150°C, collects CH_3Cl and less volatile compounds (87).

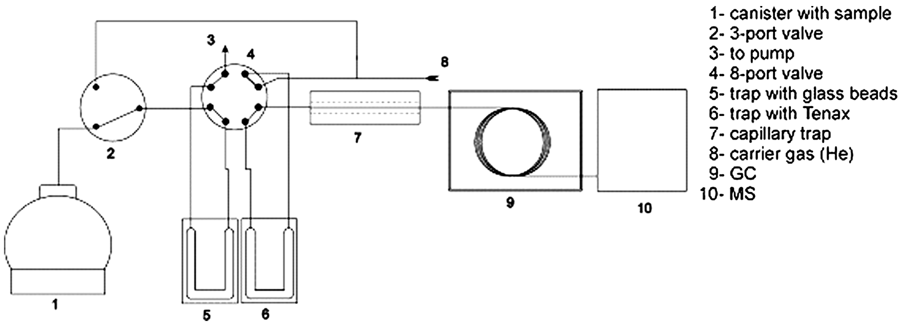

FIG. 9. Schematic diagram of the system for preconcentration of methyl halides and the GC/MS unit for air samples collected in canisters (87).

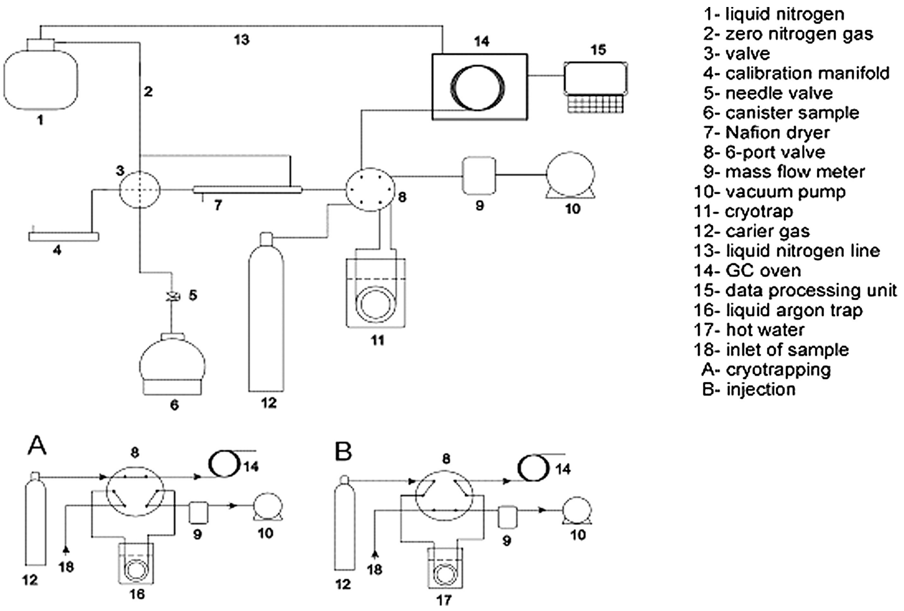

FIG. 10. Flow diagram of the system for preconcentration of C_2–C_{10} hydrocarbons from air samples (88).

The analytes are desorbed at 20°C (low enough to prevent water vapour desorption but high enough to desorb target compounds) and transferred to the second trap with Tenax TA, which is kept at −20°C (high enough to prevent CO_2 trapping but low enough to collect target compouds). The compounds after desorption from the second trap at 180°C are transferred to the capillary trap cooled at −180°C for cryofocusing. GC/MS analysis is started when the capillary trap reaches 100°C. Stability tests of samples collected in two types of canisters (electrochemical buffing and fused-silica lined) with smooth surfaces showed that both could hold methyl halides for long periods (even up to 6 weeks) without significant change in gas concentration.

Preconcentration using cryogen (liquid nitrogen or argon) is technically more complicated but generally is more versatile. It can be applied for collecting compounds with a broad range of boiling points and especially for volatile analytes. Futhermore, it enables cryofocusing of chromatographic zones, which makes separation easier.

The arrangement presented in Figure 10 (88) permits measurement of C_2–C_{10} hydrocarbons at the sub-ppb level. Air samples of 400 ml collected in canisters were preconcentrated in an open nickel tube (80 cm × 0.5 mm) cooled with liquid argon. The moisture in air samples was removed using a Nafion dryer inserted between the sample inlet and cryotrap. The transfer line (70 cm × 0.16 cm), between the valve and column, is kept at 60°C. The FID was calibrated using standard reference material, propane in air at 3 ppm. The standard was diluted to ppbC levels using a dynamic dilution system. The trapped analytes were

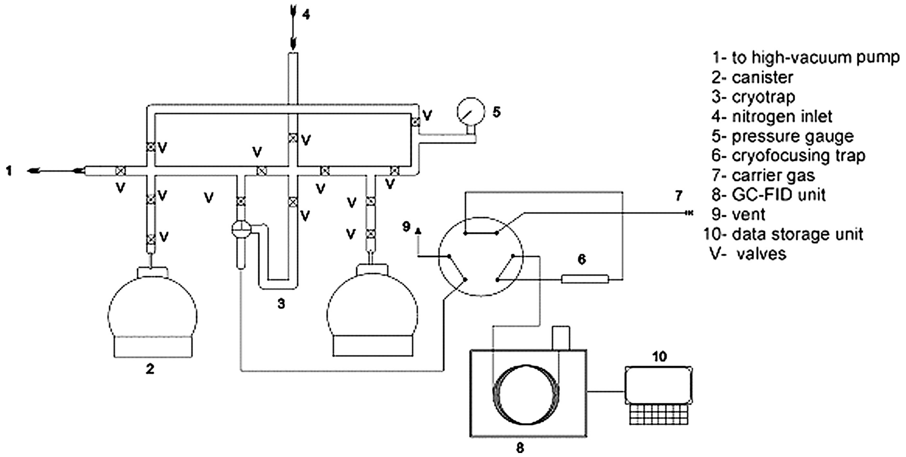

FIG. 11. Schematic diagram for preconcentration and cryofocusing trap for determination of C_2–C_8 hydrocarbons in background air samples (89).

desorbed by heating with 90°C hot water and determined chromatographically. More than 50 ambient hydrocarbons, including C_2–C_{10} alkanes, C_2–C_6 alkenes, some alkylated aromatics, and isoprene were determined with an estimated accuracy of $\pm 20\%$.

The second system uses 2-liter canisters with electropolished internal surfaces (Figure 11) (5). The canisters before using were cleaned under high-vacuum conditions and tested by connecting them to a high-vacuum pump system (10^{-9} Torr). Air samples (100–2000 ml) were passed through a cryotrap U-tube cooled by liquid nitrogen to preconcentrate nonmethane hydrocarbons (NMHCs). Next, the cryotrap was heated with an electric heater and analytes were transferred to a cryofocusing unit (-175°C). After liberation analytes were analysed using the gas chromatography with an Al_2O_3/KCl PLOT column. A total of 52 of NMHCs were found. The detection limits were typically in the 10 pptv range and the reproducibility was 5–7% precision at the 1–10 ppb level.

Sampling of air containing semivolatile compounds (pure compounds vapour pressure in the range 10^{-8}–10^{-2} Torr), e.g., polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), should take into account the fact that these compounds may be present to a significant degree in two phases—in the gas phase and as sorbates on the suspended particles. In such cases filter/sorbent samplers are used. The particles are collected on filters and analytes from the gas phase are adsorbed on properly chosen adsorbent.

Two high-volume filter/sorbent samplers used for simultaneous collection of particulate matter and gaseous species are presented in Figure 12 (90).

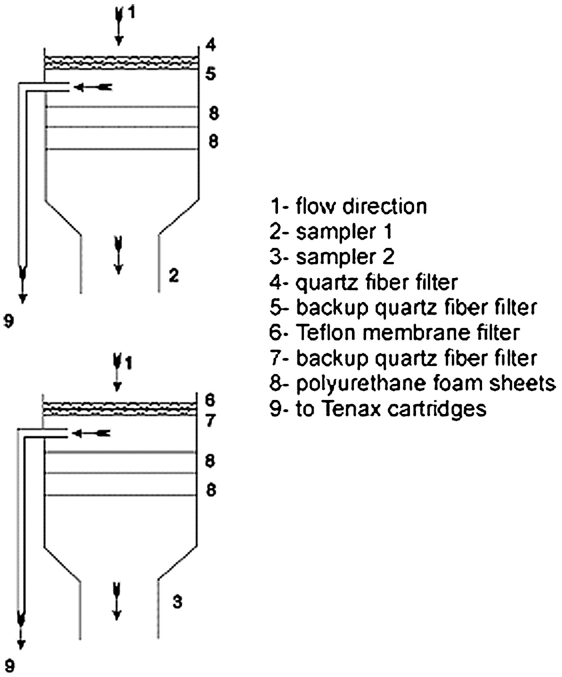

FIG. 12. Schematic diagrams of samplers for particle and gas sampling (90).

In the first sampler, the main (front) and backup filters are made of quartz fibers. In the second filter, the main filter is in form of a Teflon membrane. The backup filter providing two estimates of the amounts of gas phase adsorption to the front quartz filter in the first sampler allows corrections for gas adsorption to that quartz fiber filter. The losses from the filter due to volatilization during a sampling can be minimized by shortening the sampling time and maintaining constant temperature of the filter. The main stream of air (1.4 m^3/min) passes trough both filters and two 1.27-cm-thick polyurethane foam (PUF) sheets. The more volatile compounds are sorbed on PUFs and volatile compounds from the stream of 600 cm^3/min are sorbed on Tenax-TA. Both samplers were used for determination of PAHs in air giving the similar results.

SUMMARY

The large number of analytes and the broad range of concentrations in which they can be present means that there is no universal method for air sampling. The different aims of analysis and the necessity of getting the desired information require the application of specific sampling techniques and methods for final determination (91). Analysis of the atmosphere is conducted using a wide variety of analytical approaches and techniques among which gas chromatographic one of the most commonly used. Important applications includes the chromatographic analysis of hydrocarbons (for example VOCs, CFCs, DMS) by GC and carbonyls after derivatization by LC (92–94). These analytical techniques are undergoing a steady evolution, resulting in continuous improvements in areas such as sensitivity, accuracy, precision, and ease of operation, as well as by using proper sample preparation techniques (95).

This can be confirmed by literature concerning the analysis of air in which many different systems for air sampling and analysis are presented. In this paper some exemplary solutions have been presented. Many review papers have dealt with these problems (95–101).

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