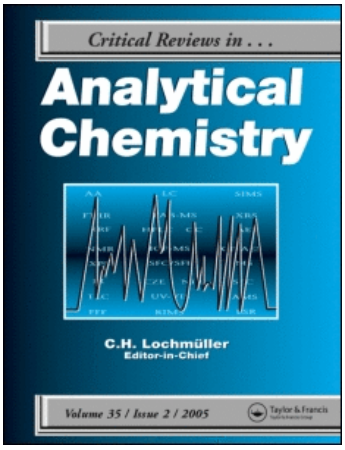

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Development of Techniques of Generation of Gaseous Standard Mixtures

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Various reference materials are increasingly used in analytical work. This is directly related to the assessment and quality control of results of measurements in order to make them a reliable source of analytical information. Reference materials are an indispensable tool in the development and validation of new analytical procedures. They also are often used in interlaboratory studies. The use of reference materials allows maintaining traceability. More and more reference materials containing analytes in solid and liquid matrices are becoming available. However, gaseous reference materials are much less available. This is because of the lack of stability with this type of reference materials. Consequently, not all techniques of the generation of gaseous standard mixtures can be used to prepare appropriate matrix-free gaseous reference materials.

This article discusses the following topics: (1) classification of known techniques of generation of gaseous standard mixtures; and (2) review of most commonly used techniques, including schematic diagrams of the apparatus. The article also includes the information on a new approach to the problem of generation of gaseous standard mixtures whereby the analyte is generated in the process of thermal decomposition of suitable immobilized compounds formed by chemical modification of an appropriate solid support.

Keywords gaseous standard mixtures, matrix-free reference materials, reference materials, thermal decomposition of immobilized compounds, supports for immobilized compounds

INTRODUCTION—REFERENCE MATERIALS

Recently, reference materials have been increasingly used in analytical laboratories. Undoubtedly, the reason for this is the need for traceable and thus comparable results of measurements. The use of reference materials is necessary in all analytical laboratories and especially in those which examine environmental samples characterized by:

- low or very low concentration levels of analytes,
- complex matrices,
- temporal and spatial variability of samples, and
- possibility of interferences.

The first institutions that developed appropriate techniques of preparation of reference materials were: the U.S. National Bureau of Standards, presently US-NIST (National Institute of Standards and Technology), established in 1901 and BAM (*Die Bundesanstalt für Materialforschung und -prüfung*) established in 1904 in Berlin (1). At that time, one of the most important analytical problems was the precise determination of carbon in steel; hence, the first reference materials were matrices used for the determination of metals in alloys and steels. Over the years, the list of reference materials was extended to include the materials with a certified content of organic compounds, such as analytes belonging to polycyclic aromatic hydrocarbons, polychlorinated biphenyls, dioxins, or pesticides, as well as microbiological reference materials. It is evident that the growing demand for a variety of reference materials has resulted in an increasing

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TABLE 1
Institutions supplying reference materials (2, 3)

No.	Name of institution	Area of applicability	Country
1	Behring Institute (BI)	Biology	Germany
2	Bureau Communautaire de Reference (BCR) (at present—Standards, Measurements and Testing Programme—European Community)	Biomedicine, agriculture, food industry, industry, environment	European Commission (Brussels)
3	Canadian Certified Reference Materials Project (CCRMP)	Geology, environment	Canada
4	Ferroetalon Vaskut (FV)	Industry	Hungary
5	Geological Survey of Japan (GSJ)	Geology	Japan
6	Geological Survey of the United States (GS)	Geology	USA
7	International Atomic Energy Agency (IAEA)	Biology, environment, nuclear power	Austria
8	Instytut Chemii i Techniki Jdrowej (IChTJ) (Institute of Nuclear Chemistry and Technology)	Environment	Poland
9	Institute of Environmental Sciences (TNO)	Environment	The Netherlands
10	Institute of Geological Sciences (IGS)	Geology	Great Britain
11	Institute of Radioecology and Applied Nuclear Techniques (IRANT)	Environment	Czech Republic
12	Institute for Reference Materials and Measurements (IRMM), formerly Central Bureau for Nuclear Measurement (CBNM)	Biology, environment	Belgium
13	Japan Society for Analytical Chemistry (JAC)	Environment	Japan
14	Kaulson Laboratory (KL)	Biology, environment	USA
15	Laboratory of the Government Chemist (LGC)	Biology, environment, agriculture, food industry	Great Britain
16	National Institute for Environmental Studies (NIES)	Biology, environment	Japan
17	National Institute of Standards and Technology (NIST), formerly National Bureau of Standards (NBS)	Biology, environment, food industry, industry	USA
18	National Research Centre (NRC)	Environment	China
19	National Research Center for Certified Reference Materials (NRCCRM)	Biology, environment, agriculture, food, industry	China
20	National Research Council of Canada (NRCC)	Biology, environment	Canada
21	South African Bureau of Standards (SABS)	Environment	Republic of South Africa

supply of available materials as well as an increasing number of suppliers. Table 1 compiles a list of suppliers of reference materials (2, 3).

There are many types of reference materials used in everyday laboratory practice whose application depends on the nature of analytical work being carried out (4). Classification of reference materials can be found in original papers (5–8) as well as in a chapter of the book recently published by the Centre of Excellence in Environmental Analysis and Monitoring (CEEAM) (9).

GASEOUS STANDARD MIXTURES

Intensive development of analytical techniques used for the measurement of components of gaseous media (outdoor air, indoor air, workplace air) has been observed for many years. This trend is closely associated with the need to obtain results of high quality, which necessitates the use of matrix-free (gaseous standard mixtures) as well as matrix reference materials (10, 11). The use of reference materials having matrix composition and analyte concentrations close to those of real samples results in more reliable measurement results.

In order for a gas mixture to be called "standard," it has to meet a number of specific requirements, the most important of which are (12, 13):

- constant concentration of the analyte;
- knowledge of concentration of the analyte in a mixture with an accuracy greater by a factor of 2.5–3 than the accuracy of a device being calibrated;
- ready availability because of a large number of determination during the device calibration step; and
- knowledge of all sources of error (13, 14).

Gaseous standard mixtures consist of (1, 15): a specific amount of an analyte, playing the role of an analytical standard; and diluent gas.

With respect to the composition of a mixture, gaseous mixtures fall into two categories: single component and multicomponent (16, 17). In the former case, the mixture contains a single analyte, whereas in the latter case it has more than one analyte. A third type of gaseous mixture that can be distinguished is the one void of an analyte and containing solely the diluent gas. This is so-called "zero gas." It deserves special attention because of its wide applicability, including matrix of generated mixtures, carrier gas for gas chromatographs and measuring devices, and gas used for setting zero point of analytical instruments (18–19).

A special case of zero gas is zero air prepared by mixing electrolytically generated oxygen and nitrogen in a proper ratio or by purifying air from an air tank or atmospheric air (10).

Gaseous standard mixtures also can be classified as *primary mixtures*, in which the concentration of analyte is calculated from the measurement of basic quantities (mass, volume, pressure); and *secondary mixtures*, which are obtained, for example, by way of additional dilution of primary mixtures (20).

Gaseous standard mixtures find use primarily in the calibration step, which is an integral part of every analytical procedure. The purpose of calibration is minimization of measurement errors, such as quality assessment/quality control (QA/QC; 5, 9, 20–25). Gaseous standard mixtures, in addition to their main applications, which is calibration and testing reliability of measurements of measuring devices (sensors, detectors, analyzers and monitors), are also used for (26–31):

- calibration and determining characteristics and applicability of analytical procedures;
- checking qualifications of laboratory personnel (analytical, forensic, medical);
- interlaboratory studies, intercalibration;
- model investigations when developing new analytical procedures;
- model investigations of the course of chemical reactions (oxidation, reduction) and physical processes (adsorption, desorption) taking place in the gaseous phase;
- investigation of the effectiveness of various catalysts (used, for example, in the process of catalytic purification of flue gases).

Besides gaseous standard mixtures as typical examples of standard solutions (15), in special cases they can be treated as matrix-free reference materials (10), with their main application being the validation of analytical procedures. An example is gaseous standard mixtures with certified content, playing the role of reference materials for specific volatile organic compounds (10). Among currently available, scarce reference materials for volatile compounds in gaseous media, four kinds can be distinguished, which is shown in Figure 1 (9).

In spite of existence of a variety of reference materials, the availability of reference materials for volatile organic compounds is still very limited. The main manufacturers of certified gaseous standard mixtures of this type are US-NIST and BCR. These institutions also offer certified gas mixtures of selected organic compounds prepared in ultrapure nitrogen. Such a method of preparation of gas mixtures used in the monitoring of degree of air pollution extends considerably their stability. Mixtures of more stable analytes are also prepared in air. The most popular reference materials of this type manufactured by the US-NIST are compiled in Table 2.

As a result of limited availability of reference materials for volatile compounds and that the magnitude of error (and hence precision and accuracy) of the final results of analyses of gas, samples strongly depend on the stability and reliability of the composition of gaseous standard mixtures, there is a continuing search for new procedures of their generation.

The development of techniques of preparation of gaseous standard mixtures having a wide, adjustable, and controlled range of concentration levels of the analyte allows lowering

TABLE 2
Gaseous reference materials offered by US-NIST (32)

Type of reference material	Analytes	Certified component	Concentration of analyte in mixture
2651	Propane and oxygen in nitrogen	C_3H_8	100 μmol/mol
		O_2	50 mmol/mol
2652	Propane and oxygen in nitrogen	C_3H_8	100 μmol/mol
		O_2	100 mmol/mol
Set of 8 mixtures	Propane in nitrogen	C_3H_8	100 μmol/mol–20 mmol/mol
Set of 6 mixtures	Propane in air	C_3H_8	0.25–500 μmol/mol
Set of 4 mixtures	Methane in air	CH_4	1–100 μmol/mol
Set of 15 mixtures	Carbon monoxide in nitrogen	CO	10 μmol/mol–130 mmol/mol
Set of 3 mixtures	Carbon monoxide in air	CO	10–45 μmol/mol
Set of 11 mixtures	Carbon dioxide in nitrogen	CO_2	5–160 mmol/mol

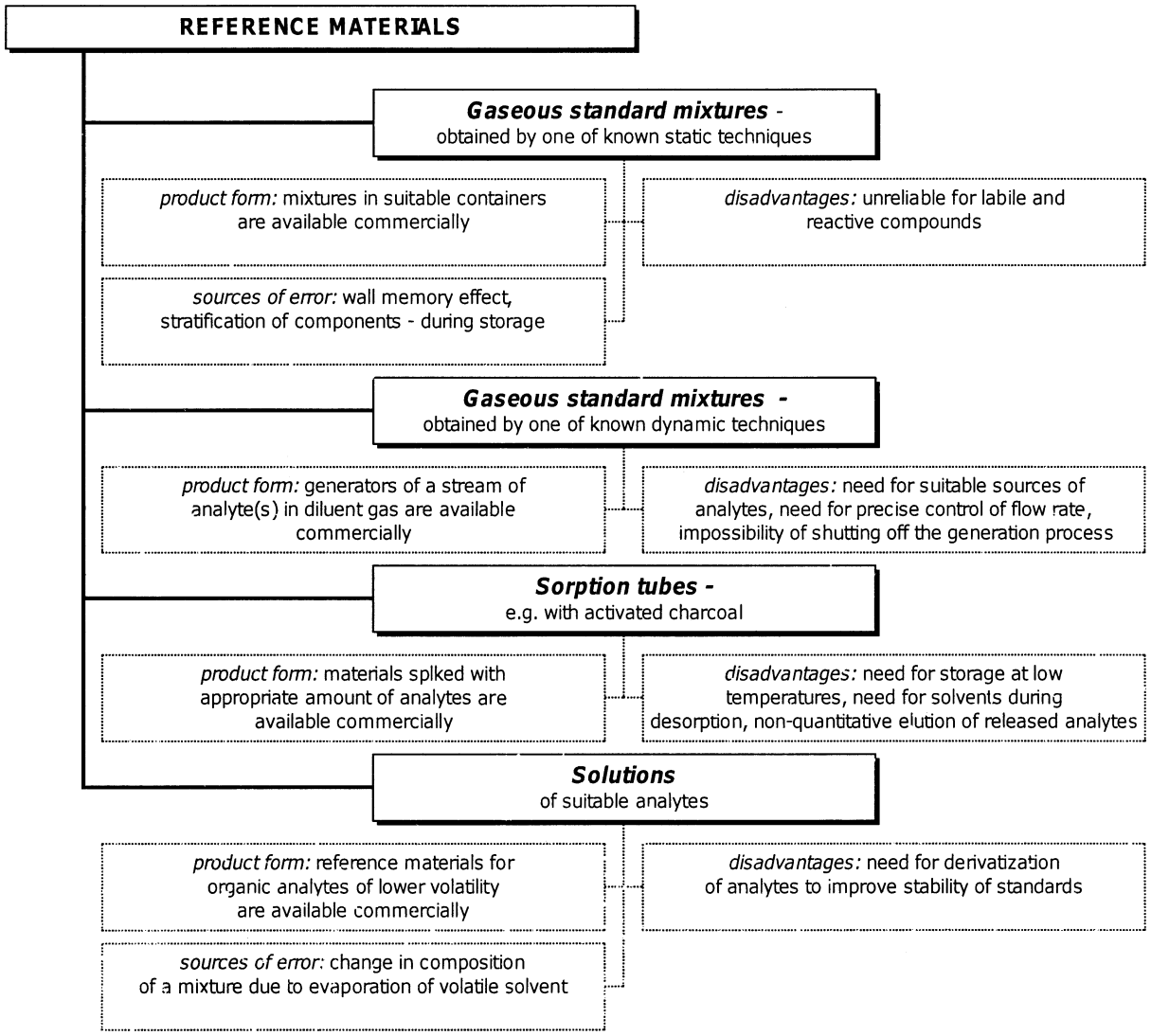


FIG. 1. Available types of reference materials for volatile organic compounds used in the investigation of gaseous media (9).

time and labor consumption of the calibration step of measuring devices.

A number of different techniques of preparation of gaseous standard mixtures are available and the selection of an appropriated technique (i.e., the one that would ensure obtaining a gaseous standard mixture with the desired operational parameters) depends on the nature of analytes and diluent gas as well as upon the required amount of the analyte in the mixture. Other essential parameters affecting the choice of the method of generation of gaseous standard mixtures include the desired volume of the mixture and the expected concentration level of analytes in the mixture.

All available techniques of preparation of gaseous standard mixtures fall into three basic groups, schematically presented in Figure 2:

1. Static techniques
2. Dynamic techniques
3. Miscellaneous techniques (combination of static and dynamic techniques).

Static techniques involves the introduction of a specific amount of analyte into a known volume of the diluent gas under defined conditions (35). When using these techniques, the precision of determination of analyte concentration in a mixture depends upon the selection of the equation describing the state of the gas (under real conditions) (36).

Dynamic techniques make use of the continuous introduction of a stream of analytes into a stream of the diluent gas. When the standards to be prepared contain reactive components, dynamic techniques are definitely preferable to static techniques, because their use enables generation and introduction of analytes into the diluent gas just prior to the application of the mixture in the analytical process.

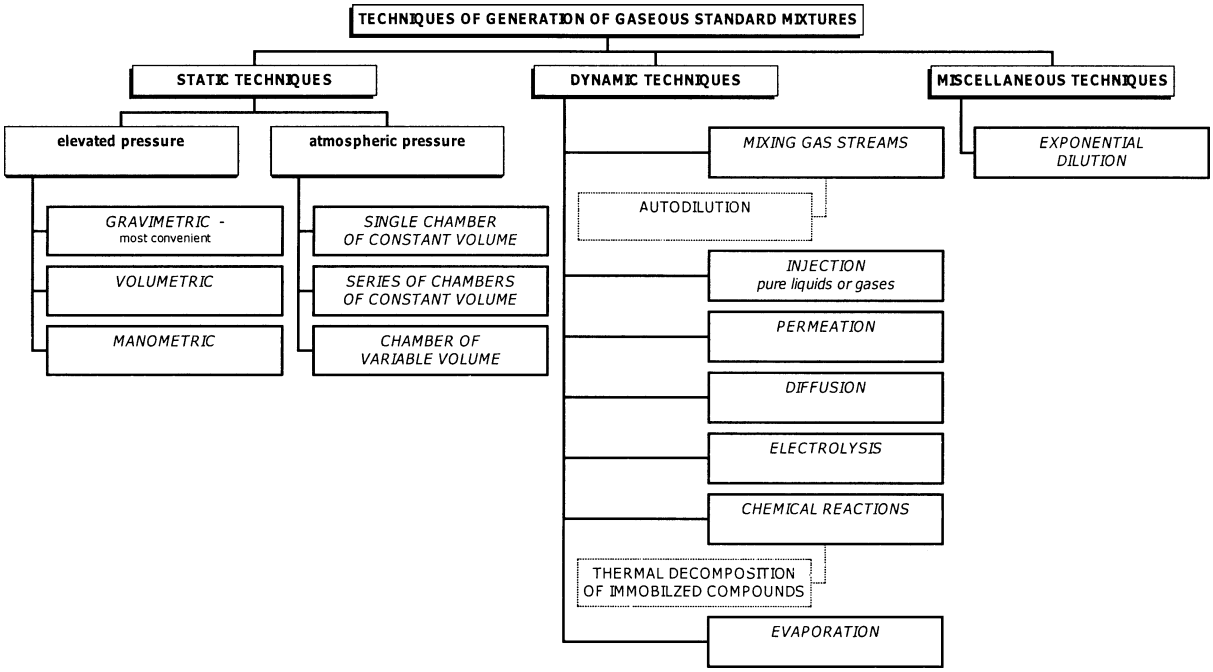


FIG. 2. Classification of techniques of preparation of gaseous standard mixtures (1, 13, 33, 34).

Advantages and shortcomings of the two techniques of preparation of gaseous standard mixtures are compiled in Table 3.

DIFFICULTIES AND INCONVENIENCES ASSOCIATED WITH PREPARATION OF GASEOUS STANDARD MIXTURES

The process of preparation of gaseous standard mixtures is much more complicated compared to the preparation of liquid or solid standards. The degree of difficulty increases with the decrease of concentration level of analytes in the gaseous standard mixture being prepared.

All the techniques of preparation of gaseous standard mixtures (shown in Figure 3) have a number of shortcomings despite their numerous advantages. Furthermore, generation of standard mixtures containing trace concentrations of analytes is associated with numerous technical and procedural problems. The most serious problems include (35, 37, 38):

- adsorption and desorption of analytes on/from the walls of containers and connections
- change in composition of mixtures due to the presence of contaminants from the containers (so-called "wall memory")
- problems related to obtaining and maintaining complete homogeneity of the mixture and thus the danger of stratification of the gas mixture
- presence of disturbances resulting from the measuring technique itself (instrumental noise)
- need to determine the analyte in a gaseous standard mixture with the precision higher by at least an order of magnitude than that for the analyte in real gas samples
- problems associated with ensuring a uniform way of transport of the real sample and the gaseous standard mixture to the detector
- need to prepare a standard mixture having the composition as close as possible to that of the analyzed real samples
- occurrence of so-called "ghost peaks," representing noise generated by the detector during chromatographic analysis of samples of gas mixtures

The selection of a specific, most suitable technique depends on the applicability and the required detailed characteristics of a gaseous standard mixture. Static and dynamic techniques of generation of gaseous standard mixtures are characterized in Table 4. The most: common dynamic techniques of generation of multicomponent mixtures are permeation and diffusion. The principle of these techniques along with designs of devices for the generation of a stream of analytes(s) or of a standard mixture is shown in Figures 3 and 4 (63, 73, 92).

The use of chemical reactions to generate reactive and labile components was a significant achievement in the area of preparation of gaseous standard mixtures. Examples of chemical reactions used to generate selected analytes in gas mixtures are shown in Table 5.

Probably the most advantageous approach to the preparation of gaseous standard mixtures containing "troublesome" gaseous components in terms of their physical and chemical properties is to use the techniques allowing generation of the analyte combined with its simultaneous introduction into a stream of the diluent gas just prior to the calibration step. This results in a

TABLE 3
Comparison of static and dynamic techniques of preparation of gaseous standard mixtures

Technique	Shortcomings	Advantages	Remarks
Static techniques	– Danger of adsorption, desorption and condensation – Possibility of errors related to introduction of small amounts of analytes into diluent gas – Impossibility of long-term storage of mixtures due to potential losses of analytes (adsorption, diffusion) – Possibility of preparation of only single-analyte mixtures when using a single chamber of constant volume – No possibility of generation of mixtures over a wide range of concentrations – Preparation of only a limited volume of mixtures – Danger of stratification of mixture components, resulting in impossibility of preparation of mixtures with analytes of different densities	– High precision of introducing analytes into diluent gas – Simple, inexpensive techniques not requiring complex apparatus – Possibility of generation of multicomponent mixtures	These techniques are usually employed for the preparation of small volumes of mixtures used for calibration of GC detectors Mixtures of this type are prepared in metal cylinders, glass bottles and plastic containers The process of preparation of standard gaseous mixtures involves several steps (13) 1. ensuring that the internal surface of a container and valves is chemically inert 2. evacuation or purging the container with an inert gas (with simultaneous heating) 3. introduction of individual components of a mixture 4. homogenization of the mixture 5. analysis of a sample of the prepared mixture In order to obtain a mixture of known composition, the amounts of individual components have to be carefully measured by determining their volume or pressure or their mass
Dynamic techniques	– Need for special techniques – Need for specialized, expensive equipment for each device (e.g., permeation or diffusion tubes) – Impossibility of turning off the generator even after completion of work due to continuous emission of the analyte – Relatively long start-up period (e.g., permeation or diffusion tubes) – Need for devices capable of a very accurate measurement of flow rate of the diluent gas (accuracy of flowmeters affects the accuracy of determination of analyte concentration in the mixture)	– Possibility of generation of gas mixtures over a wide range of concentrations due to variation of flow rate of gas streams – Capability of generation of multicomponent mixtures – Lack of or small “wall memory effect” and lack of problems related to adsorption (smaller area of contact and a shorter time of contact between the gas and the wall of container) – Lack of stratification; the mixtures prepared are not prone to loss of homogeneity	These techniques are used for the generation of mixtures containing reactive or labile analytes, which cannot be practically stored The most widely used techniques make use of diffusion or permeation Schematic representation of permeation and diffusion techniques is depicted in Figure 3 and 4, respectively

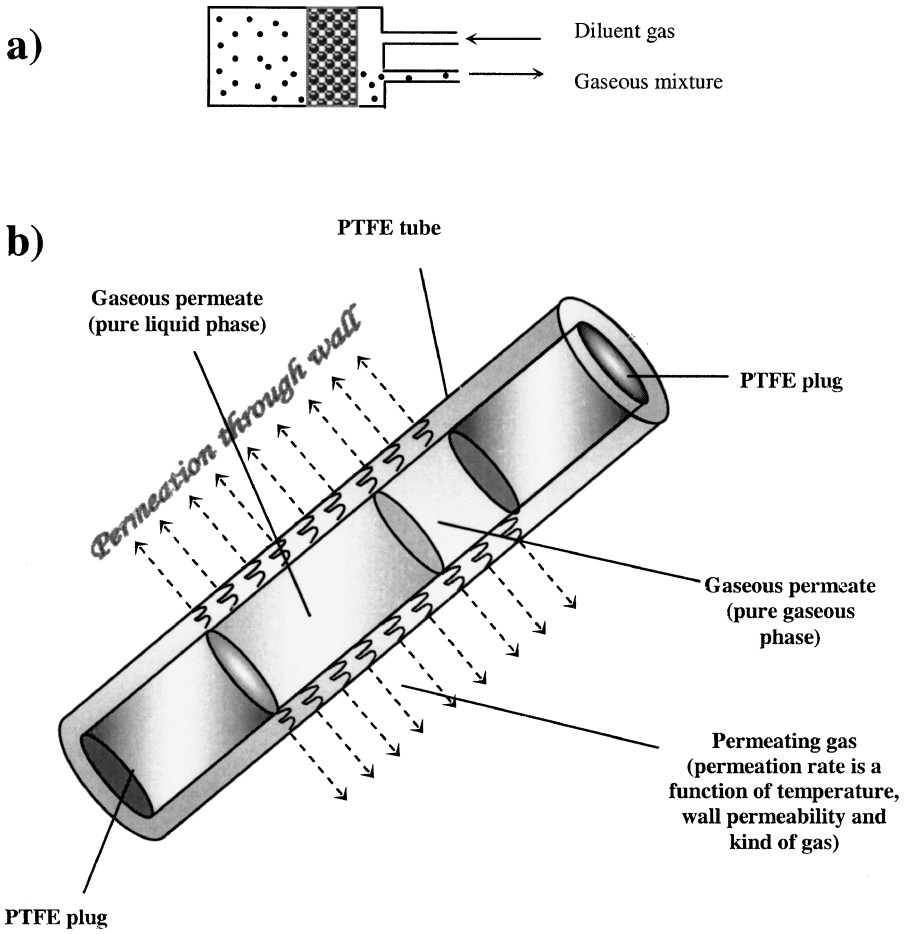


FIG. 3. (a) Diagram of introduction of analytes into a stream of diluent gas using permeation; (b) design of a permeation tube.

stream of standard mixture that is directly passed to the sensor of a measuring device. Examples of reactions of generation of specific analytes of gaseous standard mixtures just prior to the calibration step are listed in Table 6.

The first three examples shown in Table 6 illustrate the case when nontoxic and noncarcinogenic reactants yield by way of various chemical reactions toxic and carcinogenic gaseous products which are passed in a stream of carrier gas directly onto the GC column. The reaction of thermal decomposition of dithiocarbamates is initiated by a high temperature, therefore, there is no need for additional reagents. Thermal decomposition of dithiocarbamates takes place in the injection chamber of a gas chromatograph heated to 250°C. As a result of this process a mixture of thiols is formed, containing carrier gas as the diluent gas and thiols as the analytes whose concentrations depend on the temperature of the injection chamber and the flow rate of the carrier gas.

An original methodical approach to the preparation of gaseous standard mixtures of toxic, reactive, and malodorous substances is the generation of specific amounts of analytes by thermal decomposition of immobilized compounds. The approach is based on utilization of immobilized compounds, chemically bonded to the surface of a support (silica gel, porous glass, glass rods coated with silica gel, and glass fibers), which, under specific temperature conditions, undergo thermal decomposition or rearrangement releasing specific amounts of volatile analytes. The released analytes are purged from the reaction chamber (GC injector, thermal desorber) by a stream of diluent gas, yielding a stream of gaseous standard mixture. A general scheme of chemical modification of the support surface and generation of a specific volatile analyte in the process of thermal decomposition of immobilized compound is illustrated in Figure 5 (93).

The support of immobilized compound plays an important role in the generation of gaseous standard mixtures through thermal decomposition (pyrolysis) of immobilized compounds. Its selection directly determines the amount of liberated analyte. An ideal support for immobilized compounds should be characterized by (24):

- uniform and/or spherical shape of particles with a narrow range of particle sizes;

TABLE 4
Characteristics of techniques of preparation of standard gaseous mixtures

Technique	Principle	Shortcomings	Advantages	Remarks
Static Techniques				
Elevated Pressure				
Gravimetric (40, 41)	Analyte and diluent gas are introduced into a cylinder one by one. The mass of the cylinder can be determined in a vacuum chamber or under atmospheric pressure.	• The need to weigh the cylinder (with content) prior to and after the introduction of each analyte using special purpose balances characterized by high capacity and high sensitivity; • Danger of adsorption, desorption and condensation.	• High precision of determination of the amount (concentration) of analyte in a mixture based on weighing using special purpose balances; • Simple technique for preparation of multicomponent standards.	Concentration of a given component can be calculated from the following equation [13]: $C_i = \frac{\frac{m_i}{M_i}}{\sum_{i=1}^{n} \frac{m_i}{M_i}} \cdot 10^6$ [3] where: C_i - concentration of a given component (ppm); m_i - mass of component i with a molar mass M_i.
Volumetric	Container of a known volume V is filled with gaseous components of known volume at atmospheric pressure and temperature T.	• Danger of adsorption, desorption and condensation. • Errors associated with introduction of small amounts of analytes into diluent gas; • Possibility of change in composition of mixtures due to the presence of contaminants from the containers.	• Simple, inexpensive technique for the preparation of multicomponent standards, not requiring sophisticated apparatus.	Concentration of a given component can be calculated from the following equation [13]: $C_i = \frac{n_i}{n_g} = \frac{(P - P_s) V M_g}{zRTm_g} \cdot 10^6$ [1] where: C_i - concentration of a given component (ppm); n_i, n_g - number of moles of analyte and diluent gas, respectively; P - total pressure; P_s - equalizing pressure; V - volume of a measured component; z - compressibility factor; R - gas constant; T - temperature; M_g, m_g - molar mass and mass of diluent gas, respectively.
Manometric	Analyte(s) and diluent gas are introduced one by one into a high pressure cylinder, and the pressure inside the cylinder is measured every time a new gas is introduced into the cylinder.	• Danger of adsorption, desorption and condensation. • Need to maintain constant temperature inside the cylinder.	• Possibility of preparation of large volumes of gaseous standard mixtures. • Simple, inexpensive technique for the preparation of multicomponent standards, not requiring sophisticated apparatus.	Concentration of a given component can be calculated from the following equation [13, 39]: $C_i = \frac{znRT}{VP} \cdot 10^6$ [2] where: C_i - concentration of a given component (ppm); P - total pressure; V - volume of a measured component; n - number of moles of measured component; z - compressibility factor; R - gas constant; T - temperature.

Atmospheric Pressure				
Single chamber of constant volume	Measured amounts of a gas or liquid are introduced into a single chamber of constant volume.	• Possibility of removal from the chamber at most 10% of the mixture (to avoid taking into account the drop in concentration of the analyte); • Only single-component mixtures can be prepared; • Lack of possibility of long-term storage of mixtures due to analyte losses (adsorption, diffusion).	• Simple, inexpensive technique for the preparation of multicomponent standards, not requiring sophisticated apparatus.	• Chamber should be heated (to evaporate liquids) and equipped with a stirrer; • Air is most commonly used as diluent gas.
Series of chambers of constant volume	Measured volumes of gases or liquids are introduced into a defined number of chambers of same volume connected in series. When the mixture from the last chamber is removed, the mixture from the chamber next to it takes place of the air.	• Lack of possibility of long-term storage of mixtures due to analyte losses (adsorption, diffusion); • Possibility of change in composition of mixtures due to the presence of contaminants from the containers.	• Possibility of preparation of multicomponent mixtures. • Simple, inexpensive technique for the preparation of multicomponent standards, not requiring sophisticated apparatus.	This technique enables preparation of multicomponent mixtures with the number of analytes depending on the number of chambers connected in series.
Chamber of variable volume	Measured amounts of a gas or liquid are introduced into a single chamber of variable volume.	• Lack of possibility of long-term storage of mixtures due to analyte losses (adsorption, diffusion); • Possibility of change in composition of mixtures due to the presence of contaminants from the containers.	• Chamber volume can be up to 14 m^3 (possibility of preparation of large volumes of gaseous standard mixtures); • Possibility of dilution of the prepared mixture → preparation of mixtures with varying concentration of the analyte.	• Elastic chamber can be made of plastic, e.g., PTFE, metallized plastic or composites (of sandwich type); • The technique is sometimes combined with preliminary dilution of the mixture.

(Continued on next page)

TABLE 4
Characteristics of techniques of preparation of standard gaseous mixtures *(Continued)*

Technique	Principle	Shortcomings	Advantages	Remarks
Dynamic Techniques				
Mixing gas streams (so-called gas stream dilution technique) [43–48]:	Mixing two or more gas streams whose rates are known and controlled by flow meters. Dilution can be done in a single step or in several steps. The device for multiple dilution consists of a specific number of identical elements equal to the number of dilution steps.	• Danger of adsorption, desorption and condensation → containers should be made of glass or PTFE; • Danger of stratification of the mixed components, which can be prevented by using a mixing chamber of proper design.	• Possibility of generation of gaseous mixtures over a wide range of concentrations due to adjustment of flow rates of gas streams and temperature of a saturator placed in a thermostat; • Possibility of designing portable devices; • Possibility of rapid change in composition of a mixture; • Possibility of generation of multicomponent gaseous standard mixtures.	Analyte concentration in case of mixing two gas streams can be calculated from the following equation [13]: $C_2 = C_1 \cdot \frac{Q_1}{Q_1 + Q_2}$ [4] where: C_1 - concentration of analyte in the gas stream with flow rate Q_1; Q_2 - flow rate of diluent gas. Accuracy of composition of the prepared mixture depends upon the accuracy of measuring flow rates of the streams being mixed and especially upon the content of analytes in the stream.
Autodilution (48–51)	Division of the stream of a primary gas mixture containing high concentration of the analyte into two substreams of controlled ratio of flow rates. In one of the substreams the analyte is quantitatively removed by way of adsorption, absorption or oxidation, resulting in the formation of the zero gas. By subsequent combination of the substreams a secondary standard gas mixture is generated, in which the analyte concentration is determined by the ratio of flow rates of the two substreams.	• Lack of control of the ratio of concentrations of individual analytes in the generated multicomponent gaseous standard mixtures.	• Possibility of generation of the analyte concentrations over a wide range, from zero up to the concentration of analyte in the primary gas mixture, using only one tank containing a standard gaseous mixture; • Ease of generation of zero gas; • Possibility of improving yield and accuracy of preparation of a standard mixture; • Making calibration more efficient by generating a series of standard mixtures by dilution of one primary standard mixture having a relatively high concentration of the analyte; • Possibility of carrying out multi-step Autodilution by connecting several modules in series, resulting in a decrease in time and labor of multi-step calibration.	• Final concentration of the analyte in the resulting mixture can be calculated from the following equation [51]: $c_2 = \frac{Q_1}{Q_1 + Q_2} \cdot c_1$ [5] where: Q_1 - gas flow rate in the stream bypassing the trap; Q_2 - gas flow rate in the stream flowing through the trap; c_1 - concentration of analyte in the primary mixture; c_2 - concentration of analyte in the generated secondary mixture. • In order to generate very low analyte concentrations, the use of several modules connected in series is recommended. • An autodilution module can be connected directly (*on-line*) to the measuring device. • This technique can also be used to reduce the analyte concentration in standard mixtures obtained by other dynamic techniques, e.g., permeation.

Injection (13, 52, 53)	Injection of pure liquid or gaseous substances into a stream of diluent gas flowing through a mixing chamber by means of: • syringe • microsyringe • electrically driven syringe • injection pump • syringe equipped with a paddle wheel driven by a stream of air.	• Danger of adsorption, desorption and/or condensation of analytes on the walls of the mixing chamber.	• Simple, inexpensive technique for the preparation of single-component standards, not requiring sophisticated apparatus; • Possibility of controlling the analyte concentration in the generated standard mixture; • Generation of gas mixtures containing very reactive, labile and toxic analytes.	• The technique is used to prepare gas standards containing analytes that are liquid or of diverse volatility; • The injection technique is essential—it determines the accuracy and constancy of composition of the mixture; • In order to speed up the mixture preparation process, the following approaches are used: ○ Special atomizers ○ Heating of the device ○ Injection of a liquid into a small stream of inert gas. The resulting mixture is diluted to the desired concentration.
Permeation (54–70)	All permeation techniques are based on the Fick's law, according to which the rate of diffusion (R) of any gas through a membrane (silicone, polyethylene or PTFE) can be described by the following equation [13]: $R = DS(p_1 - p_2)\frac{A}{L}$ [6] where: R - permeation rate; D - diffusion coefficient; S - solubility constant; L - membrane thickness; A - membrane surface area p_1 and p_2 - partial pressures on both sides of the membrane. All permeation systems can be classified into three categories:	• Relatively long start up procedure for permeation tubes; • Too low analyte concentrations in mixtures, when high flow rates of the diluent gas are required; • Impossibility of shutting off the generator after completion of work due to continuous emission of the analyte; • Relatively high cost associated with the need to use special equipment for each permeation tube.	• Wide applicability; • Ease of automation; • Ease of use; • Numerous analytes can be used; • Flexibility of composition of the generated mixtures (generation of individual analytes takes place from separate permeation tubes) • Generation of a wide range of concentrations by varying parameters such as: ○ Flow rate of gas stream, ○ Oven temperature, ○ Length of permeation tubes, ○ Wall thickness of permeation tubes, ○ Material from which permeation tubes are made.	Final concentration can be calculated from the following equation [54–56]: $C = \frac{22.45R}{MQ}$ [7] where: R - permeation rate; Q - flow rate of the diluent gas; M - molar mass. • Standard mixture prepared by permeation technique find particular use for the calibration of thermal desorption—GC (TD-GC) systems. • In case of low permeation rates resulting from extremely low concentrations of analytes, when calibration of permeation tubes is very time-consuming, thermogravimetric technique can be used. The use of thermogravimetric (TG) device for continuous monitoring of weight loss has a number of advantages, such as:

(Continued on next page)

TABLE 4
Characteristics of techniques of preparation of standard gaseous mixtures *(Continued)*

Technique	Principle	Shortcomings	Advantages	Remarks
	1) Two-phase system—liquid and its vapor or liquefied gas and its vapor; 2) Two-phase system—solids (polymers: paraformaldehyde and polyoxymethylene) and formaldehyde vapor at elevated temperature; 3) One-phase system – standard gas or its mixture with diluent gas at atmospheric or elevated pressure. Analytes are generated by way of permeation from permeation tubes or vials filled with suitable liquid analytes, placed in a generator chamber. A stream of diluent gas is flowing through the generator, carrying molecules of compounds permeating through the membranes.	• Possible problems related to fluctuations of permeation rate of a gas.	• Lower calibration costs compared to calibration using gas tanks; • Low weight, small dimensions of the apparatus; • Possibility of obtaining labile analytes just prior to calibration; • Preparation of multicomponent mixtures containing over forty analytes; • Capability of continuous generation of gas standards.	• Ease of visualization of stabilization period; • Ease of estimation of permeation rate over a relatively short measurement period; • Possibility of modification of both gas temperature and flow rate with minimum perturbation of measuring conditions; • Possibility of direct connection of the generator to a gas analyzer to provide *on-line* calibration. • The technique is widely used to prepare standard mixtures containing halogenated hydrocarbons, sulfur compounds, and volatile fatty acids (VFAs), such as acetic, propionic, isobutyric, butyric, isovaleric, valeric and hexanoic acid. • The technique is not recommended for the generation of gaseous standard mixtures of organic compounds (C_5–C_{12}).
Diffusion (71–75)	Dilution of vapor of liquids diffusing from a container through a capillary or directly from a capillary to the space purged by the diluent gas. The fundamental equation is given by [71, 73]: $$R = 2.21 \cdot 10^6 \cdot \frac{DMPA}{TL} \cdot \log\left(\frac{P}{P-p}\right) \quad [8]$$ where: R - diffusion rate; D - diffusion coefficient; M - molar mass of diffusing component; p - vapor pressure of analyte at temperature T; P - total pressure; A - cross-section area of diffusion part of the device; L - length of diffusion device.	• Impossibility of preparation of a multicomponent gaseous standard mixture in one vessel → to accomplish this, several diffusion tubes filled with pure components have to be used; • Relatively high cost associated with the need to use special equipment for each diffusion tube.	• Ease of change in diffusion rate of the analyte at a constant temperature and thus the possibility of adjustment in concentration of the analyte in diluent gas over a wide range by adjusting quickly, easily and reproducibly the level of the liquid in the capillary; • Wide applicability; • Ease of automation; • Ease of use; • Many analytes can be used.	Concentration of a diffusing substance in a mixture can be calculated from the following equation [13]: $$C = \frac{R}{dQ} \quad [9]$$ where: R - diffusion rate; d - vapor density of diffusing component; Q - flow rate of a stream of diluent gas. Diffusion can be combined with other techniques. It is possible to include an additional gas stream or to use chemical reactions. The combination of a diffusion device with a dynamic dilution system allows preparation of standard gaseous mixtures of volatile organic compounds with concentrations ranging from several pptv to several ppbv. Such a system is very useful for the generation of mixtures of components having a wide range of boiling points. It is also recommended for the calibration of GC-FID and GC-ECD systems.

Electrolysis (13, 76)

Electrolytic decomposition of chemical compounds.

There are two approaches: direct and indirect.

Direct approach – primary electrolysis product is the desired component of a gaseous standard mixture.

Indirect approach – the desired product is obtained only after chemical conversion of the primary electrolysis product.

Examples of direct approach:

- Anodic generation of CO_2 from the saturated aqueous solution of oxalic acid;
- Anodic generation of O_2 and cathodic generation of H_2 from an acidic or basic aqueous;
- Cathodic generation of NO during electrolysis nitrosylsulfuric acid solution.

Examples of indirect approach:

- Generation of nitrogen dioxide after electrolytic oxidation of nitric oxide with oxygen;
- Generation of water by catalytic oxidation of electrolytically formed hydrogen in the presence of excess hydrogen or stoichiometric amount of electrolytic oxygen;
- Formation of methane through catalytic reduction of electrolytically generated carbon dioxide.

- Limited applicability;
- Need to use special techniques;
- Possibility of deviations from Faraday's law due to evaporation of water or depletion of electrolyte.

- Possibility of generation of solely the analyte;
- Variation of analyte concentrations in the mixture simply by varying electrolysis current;
- Portable devices can be designed;
- The device can be built as a calibration module;
- Ease of automation;
- Possibility of shutting off the device at any time;
- Possibility of solving the problem of generation of gaseous standard mixtures containing reactive, labile, toxic, malodorous, flammable or corrosive components;
- Generation of the analyte just prior to the calibration step.

The amount of gaseous component generated at the electrode can be calculated from the following equation [13]:

$$Q_{A(K)} = \frac{Vi}{F_n} \quad [10]$$

where:

$Q_{A(K)}$ - flow rate of the stream of gaseous component generated at the electrode;

F - Faraday constant;

V - experimental molar volume of the generated gaseous component;

n - number of electrons exchanged in the electrolysis process;

i - electrolysis current.

When the flow rates of the diluent gas and the gases generated in the electrolytic process are constant, the analyte concentration in the mixture is expressed by the following equation [13]:

$$C_{A(C)} = \frac{Q_{A(C)}}{Q_A + Q_C + Q} \cdot 10^6 \quad [11]$$

where:

$Q_{A,} Q_C$ - flow rates of the streams of components generated at the two electrodes;

Q - flow rate of the diluent gas;

Assuming that $C_{A(C)} < 1000$ ppm and $Q_A + Q_C$ are much smaller than Q, the simplified equation is as follows [13]:

$$C_{A(K)} = \frac{Vi}{FQn} \cdot 10^6 \quad [12]$$

(Continued on next page)

TABLE 4
Characteristics of techniques of preparation of standard gaseous mixtures *(Continued)*

Technique	Principle	Shortcomings	Advantages	Remarks
Chemical reactions (13, 76–83)	Due to a variety of chemical reactions, the reagents in the reactor can be solid, adsorbed on a support or liquid (in the form of a solution). Air is passed through the reactor along with a gas or vapor reagent (so-called precursor). In cases when oxygen present in the air would undergo chemical reactions with the reagents, e.g., oxidize the reacting compounds or the product formed, an inert gas is used as the carrier gas.		• Solution to the problem of preparation of gaseous standard mixtures containing as the analytes compounds that are reactive, labile, toxic, malodorous, flammable or corrosive; • Possibility of introduction of the analyte to the stream of diluent gas just prior to the calibration step. This results from combining generation of the analyte with the step of its introduction into the diluent gas, thus yielding the stream of a standard mixture which is passed directly to the sensor of a measuring device.	• Examples of *chemical reactions* used for the generation of analytes of gaseous standard mixtures: hydrolysis (77), dehydration (78), oxidation (79), photochemical (80) and thermal (81) or electrolytic (82) decomposition of appropriate reactants. • The technique can be applied for the generation of a wide range of gaseous analytes, such as ammonia, carbon monoxide, carbon dioxide, ethene, methane or acetylene. Examples of chemical reactions employed for the preparation of a variety of analytes in gaseous mixtures are listed in Tables 5 (13, 83) and 6 (79–81).
Evaporation (13, 89–94)	Passing a stream of pure diluent gas through a layer of a liquid or over its surface. The flow rate of diluent gas should be sufficiently low to ensure that the analyte concentration corresponded to its saturated vapor pressure. In this technique, the evaporation process can be carried out in a variety of devices, such as: • Spargers, sometimes connected in series; • U-shaped absorbers; • Analyte can be coated onto the surface of a support, thus expanding the surface area of the analyte being in contact with the diluent gas. Generation of multicomponent mixtures by way of multichannel systems is also possible.	• Difficulty of preparation of a stream of gas saturated with the analyte vapor (which is subsequently diluted with an additional gas stream).	• Simple, inexpensive technique, not requiring sophisticated apparatus. • Short stabilization period for the process of generation of a mixture.	The technique has found numerous uses for the preparation of gaseous standard mixtures containing known concentration of water vapor in the range of 7–98% relative humidity. It is also used for the calibration of a variety of explosimeters. This group of techniques also includes generation of SO_2, NO_x, H_2S, HCN and NH_3 from aqueous solutions of appropriate salts by passing a stream of gases over the surface of the solution. Concentration C_i of the analyte in the gas can be calculated from the following equation [78]: $$C_i = \frac{p_i M}{RT} \cdot \frac{P}{P - p_i} \quad [14]$$ where: p_i - vapor pressure of the component having a molar mass of M at temperature T; M - molar mass of the analyte; R - gas constant; P - total pressure of the gas.

Miscellaneous Techniques				
Exponential dilution (13, 35, 87–91)	Special case of a single chamber of constant volume, classified as both a static and dynamic technique due to continuous supply of the diluent gas. The main part of the apparatus is a mixing chamber, filled with a gas mixture of known composition. Two approaches are possible: • Introduction of a specific amount of liquid or gas to a known volume of gas in the chamber; • Purging the chamber with a gas mixture of known concentration. After thorough mixing of the content of the chamber, both inlet and outlet valve are opened, and a stream of diluent gas is introduced at a constant flow rate. Concentration of the analyte in the gas mixture leaving the chamber varies exponentially with time.	• Highly trained operators are required to use the apparatus; • Portable devices are difficult to design; • Continuous operation is impossible; • Accuracy of composition of the prepared mixture depends on the close control of parameters of introduction of the analytes; • Possible problems associated with adsorption of analytes on the chamber walls; • The fundamental requirement for gaseous standard mixtures, i.e. constant concentration of the analyte during the entire period of its generation, is not met.	• Possibility of generation a wide range of concentrations in a single experiment; • High accuracy and precision of generation of a gaseous standard mixture; • Simple, inexpensive technique for the preparation of multicomponent standards, not requiring sophisticated apparatus; • General applicability: a variety of analytes can be used; • Possibility of generation of multicomponent gaseous mixtures at concentration levels ppbv and pptv using static dilution technique.	Concentration of the analyte in the gas mixture leaving the chamber varies exponentially with time and it can be calculated from the following equation [13, 35]: $C_t = C_o \exp\left(-\frac{Qt}{V}\right)$ [13] where: C_o - initial concentration of the analyte in the chamber; C_t - concentration at time t Q - flow rate of the diluent gas; V - volume of the mixing chamber; t - time. – Accuracy of the composition of the prepared mixture depends upon the quality of the apparatus and the method of introduction of the analytes. In order to obtain high accuracy and precision of the composition of the mixture, it is recommended that the introduction of the analytes into the chamber is automated and makes use of a sampling device of known volume. – The technique is especially suitable for the calibration of GC detectors and gas analyzers operating on a continuous basis. – It is possible to combine exponential dilution with permeation, which yields better results than using exponential dilution alone.

TABLE 5
Examples of generation of gaseous components by way of appropriate chemical reactions (13, 83)

Reagents as vapor or gas	Conditions of chemical reaction	Gaseous products
C_2H_5OH	Al_2O_3	$\boxed{C_2H_4} + H_2O$
$Fe(CO)_3$	200°C	$\boxed{3CO} + Fe$
$C_{10}H_8 + 12O_2$	Δ	$\boxed{10CO_2} + 4H_2O$
$RNH_2 + H_2$	Ni	$RH + \boxed{NH_3}$
$O_2 + 2C$	Δ	$\boxed{2CO}$
$2CF_3COOH + CaC_2$		$\boxed{C_2H_2} + (CF_3COO)_2Ca$
$H_2O + CH_3MgI$		$\boxed{CH_4} + MgOHI$
$HCl + AgNO_3$		$\boxed{HNO_3} + AgCl$

- uniform distribution of active sites on the surface of particles;
- well defined porosity; and
- high mechanical strength.

Characteristics of individual supports of immobilized compounds used in the process of thermal decomposition for the generation of analytes of gaseous standard mixtures are compiled in Table 7.

All chemically modified supports can play the role of source of analyte(s) of a certified gaseous standard mixture only if they have certain required properties (Figure 6).

- high purity of the material
- decomposition temperature
- degree of surface coverage of the support with immobilized compound
- degree of homogeneity of coverage of the support surface with immobilized compound

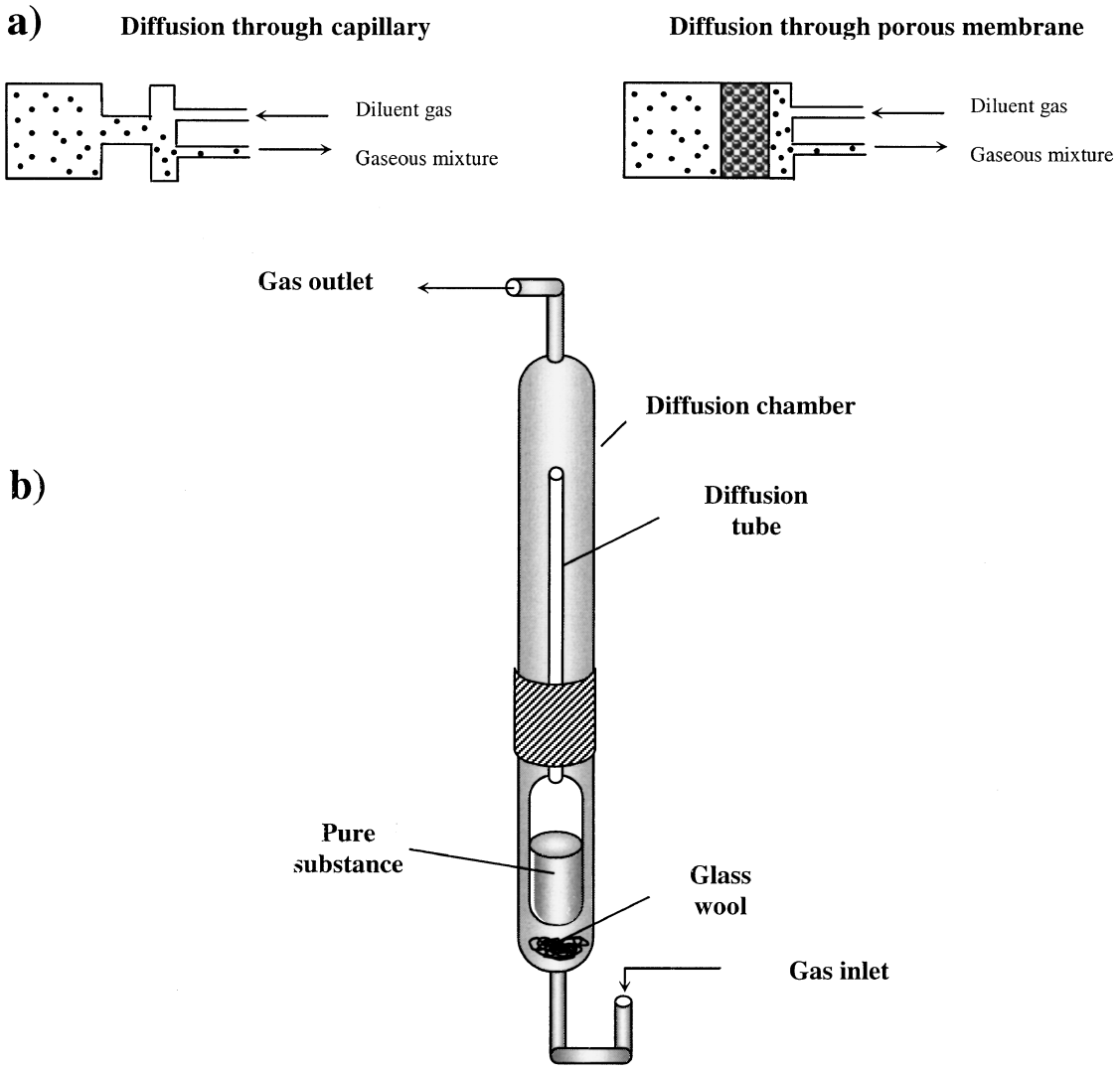
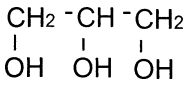
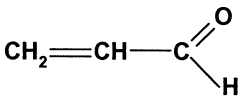
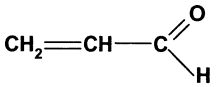
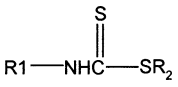


FIG. 4. (a) Diagram of introduction of analytes into a stream of diluent gas using diffusion, (b) design of a diffusion tube.

TABLE 6
Examples of generation of components of standard gaseous mixtures using appropriate chemical reactions (79, 80, 83)

Type of reaction	Reagents	Elimination of problem	Gaseous products	Literature
Electrolytic decomposition of thiocyanates	$SCN^- + 11H_2O$	Nontoxic thiocyanates → toxic hydrogen cyanide	$SO_4^{2-} + 7H_3O^+ + \mathbf{HCN} + 6e^-$	(83)
Dehydration of glycerol		Nontoxic glycerol → carcinogenic acrolein		(79)
Oxidation of allyl alcohol	$CH_2 = CH - CH_2OH$	Nontoxic allyl alcohol → carcinogenic acrolein	$+ 2H_2O$  $+ H_2$	(79)
Thermal decomposition of dithiocarbamates		Odorless dithiocarbamates are heated in the injection chamber of gas chromatograph → Mixture of thiols with foul odor	$\mathbf{R_1NCS + R_2SH}$	(80)

A schematic diagram of the apparatus for generation of gaseous standard mixtures using thermal decomposition of immobilized compounds is depicted in Figure 7 (108).

The four-way valve (4 in Figure 7) is in position allowing the passage of a stream of gas directly onto the GC column, whereas in Figure 8 the valve is in position enabling the desorber to be included into the sampling loop system.

In order to generate a stream of gaseous standard mixture using the apparatus shown in Figure 8, one should prepare a glass tube containing a sample of chemically modified material placed between two glass wool plugs. Silica gel, porous glass, or glass fibers of a known length can be used as a support. Prior to use, the glass tubes should be silanized to minimize the interactions between the container wall and the analyte. Thus, the prepared tube with the sample is placed in the chamber of a thermal desorber, previously heated to a desired temperature. The time required to heat the chamber of the thermal desorber depends on the kind of support used. After this time has elapsed, the position of the four-way valve is switched to direct the gas mixture formed onto the head of the GC column, which results in sampling of the mixture. Following the sampling step, the four-way valve is returned to its initial position (107).

In addition to the way the support surface is modified, the composition of a standard mixture is also affected by the parameters of thermal decomposition of a particular batch of modified support, such as (109):

- amount (mass/length) of sample of modified support,
- temperature of thermal decomposition of immobilized compound,
- flow rate of diluent gas (w przypadku, gdy strumień gazu rozcieńczającego przepaywa przez generator strumienia analitu),
- duration of preparation of a gaseous standard mixture,
- geometry and kind of support of immobilized compound.

So far, this method has been used for the preparation of gaseous standard mixtures containing the following compounds as the analytes (110–124): acetone, acetaldehyde, amines, ammonia, methyl chloride, ethene, thiols, isothiocyanates, carbon monoxide, and/or carbon dioxide (Table 8).

An important aspect of preparation of reference materials is the possibility of placing a length of chemically modified glass fiber in an SPME device in order to generate a specific gaseous standard mixture in a measuring device at the right

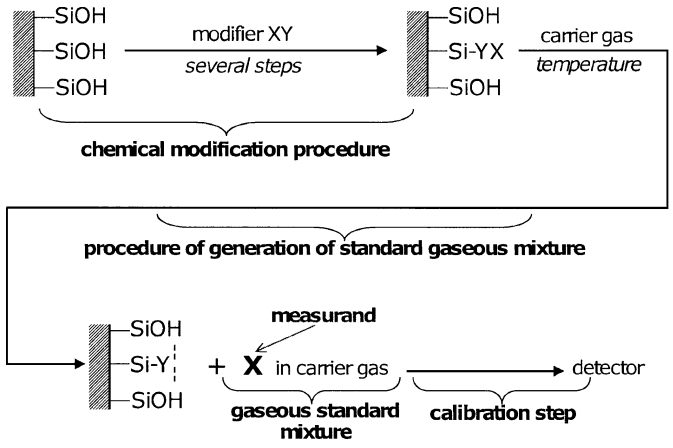


FIG. 5. Generation of a standard gaseous mixture using thermal decomposition of the immobilized compound formed on the surface of support (93).

TABLE 7
Characteristics of supports used for the preparation of immobilized compounds serving as a source of analytes for standard gaseous mixtures (94–106)

Type of support	Properties	Specific surface area [m^2/g]	Particle size [μm]	Pore size [nm]
Silica gel (MN-Kieselgel 60)	– Surface hydroxyl groups; – Readily available in different forms, varying with respect to particle shape and size, size and diversity of pores, and specific surface area; – Favorable physical-chemical properties, such as: • Mechanical resistance (it is not destroyed at pressures up to 65 MPa), • Chemical inertness (over pH range 2 to 8), • Thermal stability up to 250°C, • Possibility of replacement of silicon atoms with others, such as boron, magnesium or aluminum, • Possibility of modification of both the surface and the geometric structure of pores (through hydrothermic processing or chemical binding of phases), • High specific surface area and a large number of active sites per unit area => possibility of adsorption or binding a larger amount of compounds, • Highly homogeneous surface structure.	480–540	0.063–0.2	
Porous glass	– Possibility of manufacturing porous glass of specific properties (pore diameter, pore volume, specific surface area) and limited distribution of pores on the surface => specific surface area is smaller than that of silica gel; – Spongelike structure with SiO_2 groups => higher thermal stability and resistance to pH changes compared to silica gel; – Stronger adsorbing power than silica gel.	20–100	100–500	30–300
Glass fibers	– Coated with a thin film of stationary phase can be used for extraction in SPME => direct introduction of a length of fiber into the heated injection chamber of gas chromatograph => possibility of simplification of the process of thermal decomposition of immobilized compound (generation of the desired amount of a volatile component); – Elimination of the error related to sample weighing; – Specific surface area lower by three orders of magnitude than that of silica gel and porous glass.	Fiber diameter: 100 μm		

moment. It is a novel approach which can be described as "fit for purpose" (107). An undisputed advantage of this device is its simplicity, ease of automation and the possibility of use in field studies.

Investigations were carried out for various lengths of glass fibers modified using trimethylamine as well as a solution of silylating agent and N-methylmorpholine. In both cases methyl chloride was the analyte. The results obtained clearly demonstrated that the amounts of the analyte generated using the SPME device (Figure 9) are larger compared to those obtained by placing the fiber in the desorber chamber (107).

Using thermal decomposition of immobilized compounds for the generation of analytes of gaseous standard mixtures solves a

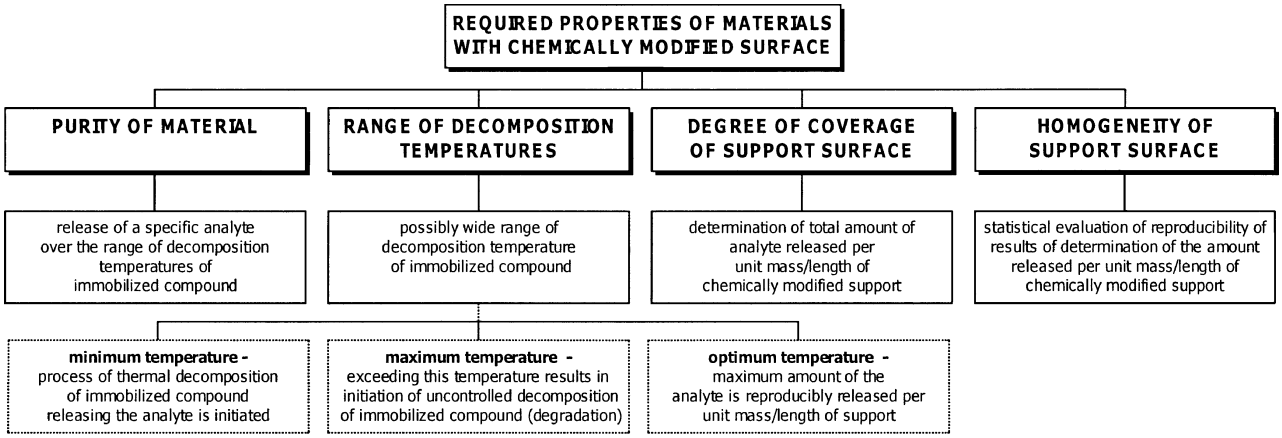


FIG. 6. Listing of parameters used to evaluate suitability of materials with chemically modified surface for the generation of standard gaseous mixtures (93, 107).

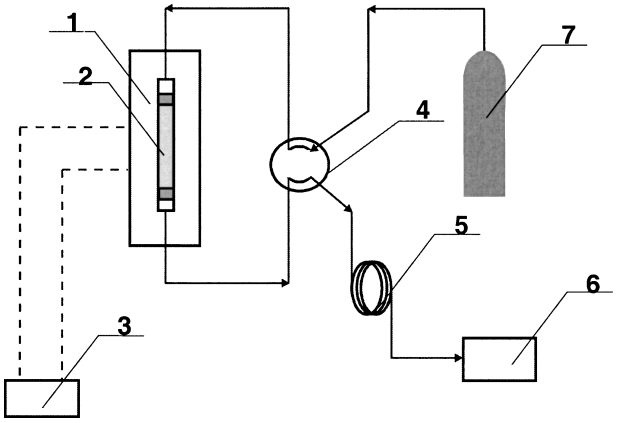


FIG. 7. Schematic diagram of the apparatus for the generation of standard gaseous mixtures using thermal decomposition of immobilized compounds (108): 1 = thermal desorber; 2 = glass tube containing sample of the investigated material; 3 = temperature controller; 4 = four-way value (chromatographic analysis); 5 = chromatographic column; 6 = detector; 7 = carrier gas tank.

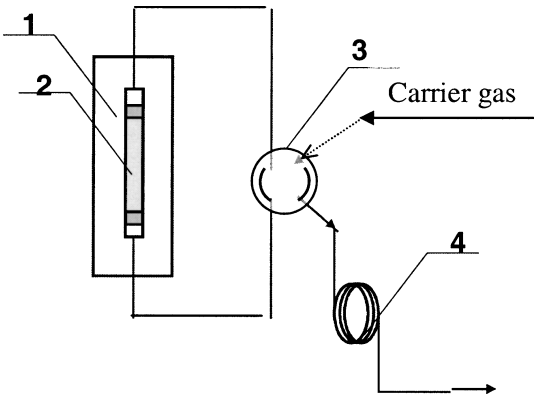


FIG. 8. Schematic diagram of position of a four-way valve enabling placement of the thermal desorber into the sampling loop: 1 = thermal desorber; 2 = glass tube containing sample of the investigated material; 3 = four-way valve; 4 = chromatographic column.

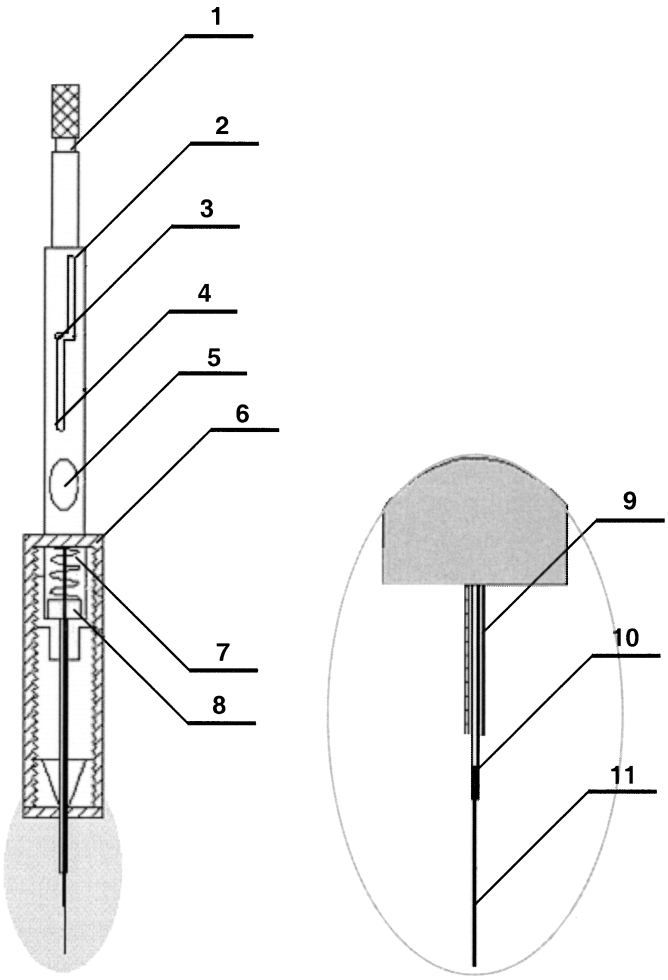


FIG. 9. Design of the SPME device (solid-phase microextraction): 1 = plunger; 2 = barred; 3 = plunger retaining screw; 4 = z-slot; 5 = hub-viewing window; 6 = dustable needle guide/depth gauge; 7 = tensioning spring; 8 = sealing septum; 9 = septum piercing needle; 10 = fiber attachment tubing; 11 = coated fused silica fiber.

TABLE 8
Volatile analytes obtained through thermal decomposition of immobilized compounds

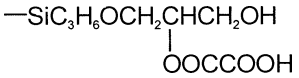
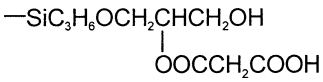
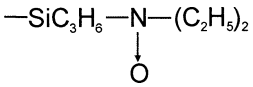
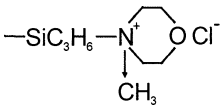
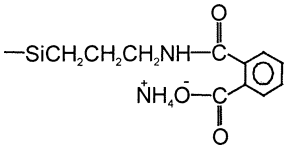
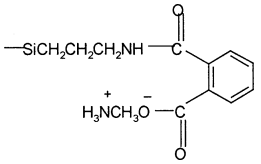
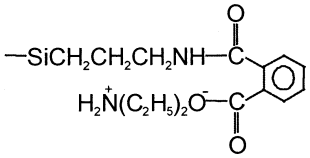
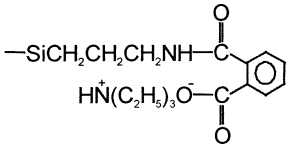
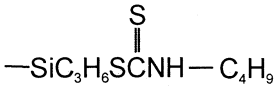
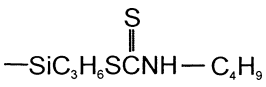
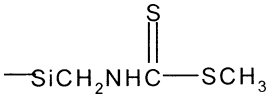
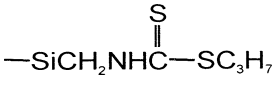
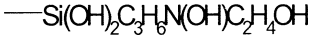
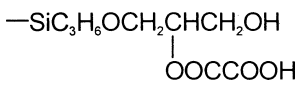
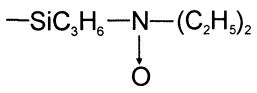
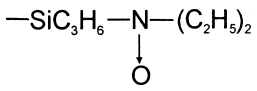
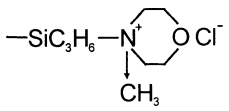
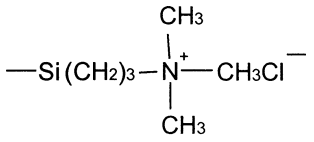
Type of support	Type of immobilized compound	Volatile analyte released	Optimum decomposition temperature of immobilzed compound [°C]	Literature
Silica gel		CO, CO_2	250	(115, 116)
Silica gel		CO_2	250	(114)
Silica gel		C_2H_4	245	(124)
Silica gel		CH_3Cl	270	(118)
Silica gel		NH_3	200	(119)
Silica gel		CH_3NH_2	310	(119)
Silica gel		$(C_2H_5)_2NH$	320	(119)
Silica gel		$(C_2H_5)_3N$	340	(119)
Silica gel		CH_2CHCH_2NCS	150	(120)
Silica gel		C_4H_9NCS	150	(120)
Silica gel		CH_3SH	150	(123)
Silica gel		C_3H_7SH	150 170	(121) (109, 122)
Silica gel		CH_3CHO	180	(112)

TABLE 8
Volatile analytes obtained through thermal decomposition of immobilized compounds

Type of support	Type of immobilized compound	Volatile analyte released	Optimum decomposition temperature of immobilzed compound [°C]	Literature
Rods coated with silica gel		CO, CO_2	300	(117)
Porous glass		C_2H_4	245	(124)
Glass fibers		C_2H_4	245	(111)
Glass fibers		CH_3Cl	270	(107)
Glass fibers		CH_3Cl	280	(107)

number of problems discussed in this article. It allows generation of both single- and multicomponent gaseous standard mixtures. By varying parameters such as: kind of support, type of procedure for modifying support surface, quantity (mass/length) of chemically modified support, and conditions of thermal decomposition process (time, temperature), it enables generation of standard mixtures having a wide and controlled range of concentrations of the analyte. It also enables safe storage of standard mixtures containing volatile, reactive, toxic and malodorous compounds at ambient temperature without any losses of analytes. Another significant advantage of the method is the possibility of carrying out calibration of a measuring device either online or offline (125).

When using glass fibers as a support, an important advantage is elimination of errors associated with weighing samples and the lack of effect of water content on the amount of released analyte—this amount is determined from the length of the fiber (107).

The results of investigations demonstrate that the amount of analyte released from chemically modified silica gel depends on the mass of the gel, while in case of chemically modified glass fibers it depends on their length. Thus, for chemically modified glass fibers possible adsorption of contaminants on the fiber surface has no effect on the amount of analyte released per unit length of the fiber.

SUMMARY

Extensive research on the techniques of preparation of gaseous standard mixtures containing trace and ultratrace amounts of analytes carried out over the last 12 or so years has resulted in elimination or minimization of a number of problems related to these techniques.

In order to minimize the problems resulting from adsorption and desorption of analytes on the walls of containers, the materials from which vials and containers used for storage of gaseous standard mixtures are made have been changed (126). Mechanical and chemical properties of the container material have to be considered when selecting a suitable device. In addition, preparation of concentrated mixtures and their dilution just prior to the calibration step is recommended.

The use of air as a diluent gas increased the similarity of matrix of gaseous standard mixtures to that of real samples.

Introduction of autodilution has simplified the calibration step, because it made possible the use of just a single primary gaseous mixture. This technique allows us to obtain standard mixtures with a wide range of analyte concentrations. Further simplification and shortening of calibration resulted from the introduction of techniques permitting preparation of multicomponent gaseous mixtures, thus enabling a single calibration step for more than one analyte. The role of permeation and diffusion techniques should be emphasized, since in this case each of the mixture components is released from a separate permeation or diffusion vial and any required combination of analytes is thus possible.

The problem of generation of gaseous standard mixtures containing components that are toxic, volatile, and malodorous has been solved by introducing the analyte into a stream of the diluent gas just before the calibration step. It also is possible to use a

suitable chemical reaction. For example, the mixture containing hydrogen cyanide can be prepared using electrolytic decomposition of nontoxic thiocyanates and dehydration of nontoxic glycerol can yield a carcinogenic product—acrolein. Another reason for generating such a mixture component directly before the calibration step is the high volatility of the analyte.

A novel approach to the problem was the utilization of chemically modified silica gel to generate gaseous standard mixtures by way of thermal decomposition of immobilized compounds. As this technique developed, silica gel was replaced with porous glass, and then with glass fiber. This allowed the preparation of standard mixtures with a wide and adjustable range of analyte concentrations. In addition, it provided safe storage of standard mixtures containing volatile, reactive, toxic, and malodorous components under ambient conditions without any losses of the analyte. An additional advantage of the technique making use of glass fibers as a support is elimination of the errors associated with sample weighing and the lack of effect of water content on the amount of released analyte; this amount is determined by the length of the fiber (107). Utilization of the SPME device in order to introduce chemically modified glass fibers into the hot injection chamber of a gas chromatograph is an undisputed improvement of this technique. As a result of this innovation, larger amounts of the analyte are obtained than in the case of placing the fiber in the chamber of a thermal desorber (107). Other advantages of using the SPME device include its simplicity, low cost, ease of automation, and field use.

A significant progress in the development of techniques of preparation of gaseous standard mixtures has been observed recently. This is partly due to the intense development of new analytical procedures for the analysis of indoor air pollutants at increasingly lower concentration levels, requiring multicomponent gaseous standard mixtures. A growing demand for reference materials of this type results in further research on the techniques of preparation of gaseous standard mixtures containing lower and lower concentrations of the analytes.

Another serious challenge is the creation of new reference materials for volatile analytes in gaseous media, since at present there are just a few materials of this type commercially available.

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