CHREV. 171

# GENERATION OF STANDARD GASEOUS MIXTURES

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## 1. INTRODUCTION

The problem of the preparation of standard gaseous mixtures is becoming increasingly important. The use of continuous air analysers, based mainly on relative measurements, requires calibration and checking of these instruments. Frequent calibration of the analysers is required before and, sometimes, immediately after a measurement, and the requirements concerning standard gas mixtures are also increasing. Several mixtures with various concentrations of the component to be measured and also a so-called "zero gas" are necessary for checking the linear dynamic range of employed detectors. Alternatively, convenient variation of the concentration of a given component in the mixture must be possible. In addition, standard mixtures are also mandatory for the calibration of chromatographs, model investigations of various reactions and processes (*e.g.*, adsorption, oxidation, reduction) and evaluation of the effectiveness of, *e.g.*, sorbents[1,2] or catalysts[3–5].

The mixture obtained must fulfil a number of practical requirements. First, it should be stable, *i.e.*, maintain a definite concentration of the component to be measured for prolonged periods of time[6]. It should also be available in sufficient amounts to permit the performance of the required investigations. Large amounts of a standard mixture (of the order of cubic metres) are necessary for calibration of continuous analysers. Additionally[7], the accuracy of determination of the composition of

a mixture should be better by a factor of 2.5–3 than the accuracy of a calibrated instrument, contamination should not influence the results at a given concentration level of the component to be measured, variations in the composition of the mixtures should not exceed 2–5 % (relative), mixtures should be prepared using only measurements of fundamental quantities such as mass, temperature and pressure and all sources of errors should be precisely defined and their values known.

A number of reviews on the generation of standard gas mixtures have been published[8–21], but some of them[10,13,14,17] deal only with certain groups of methods. In general, the methods can be divided into two groups: static and dynamic. Static methods are based on the introduction of measured amounts of individual components (diluting gas and components to be measured) in the form of gas or liquid into a vessel of known volume, whereas continuous (dynamic) methods are based on a continuous flow of components (in amounts controlled by means of suitable devices) into a chamber or a tube wherein their mixing occurs. A more detailed classification[8] is shown in Fig. 1.
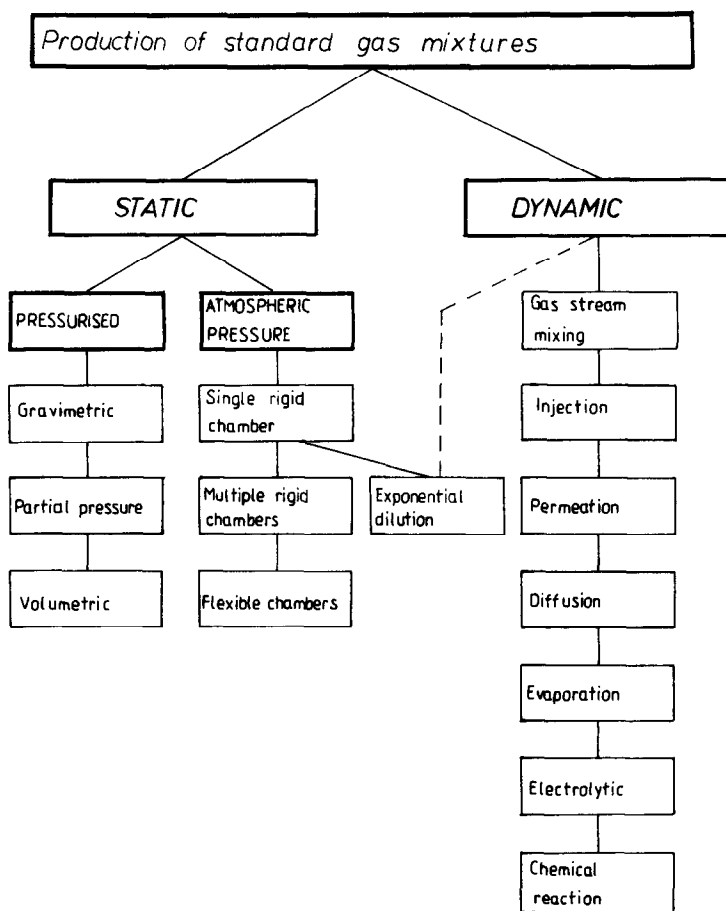


Fig. 1. Classification of methods of generation of standard gaseous mixtures[8].

## 2. STATIC METHODS

This group of methods is particularly suitable for the preparation of small volumes of mixtures, *e.g.*, for the calibration of gas chromatographic (GC) detectors[22–24]. The mixtures are prepared in metal cylinders[25–31], glass bottles[32,33] and plastic containers[30,34,35]. The advantage of these methods is that they do not require complex apparatus, but the disadvantages are the necessity for the elimination of effects such as adsorption and condensation on the walls of a container (preliminary conditioning[36,37] or covering the walls with appropriate coatings[26,37]) and the errors associated with an introduction of small amounts of a component to be measured into diluting gas[26]. In practice, static methods are employed for the preparation of gaseous mixtures containing the component to be measured in the concentration range from less than 1 ppm to several tens percent[27,37–42]. On an industrial scale, the preparation of mixtures by static methods involves the following steps: control of the inner surface of the container and valves; evacuation or purging with an inert gas (usually nitrogen) of the container with simultaneous heating; introduction of individual components; homogenization of the mixture; and analysis of the prepared mixture. The amounts of the individual components should be measured in order to obtain a gaseous mixture of known composition, and the pressures[43,44], volumes[22,44,45] or masses[26,28,29,44,46] of the mixed components should also be measured.

Type of material suitable for making containers in which standard mixtures are stored constitutes a separate problem which has been discussed in a number of papers[30,34,35,47–49]. Plastic bags have definite advantage over rigid containers, being cheap, light and having the possibility of changing their volume and hence changing the volume of a gaseous mixture. This results in avoiding displacement of the mixture by means of air and its dilution. However, it is necessary to test the suitability of a given bag material for various compounds at different concentration levels. Such studies have been carried out for a number of plastics, such as poly(vinyl chloride), polyethylene, Teflon (PTFE), Kel-F, Mylar, Tedlar, Saran and Scotchpak[30,34,35,47–52].

### 2.1. Pressure methods

The gas pressure in a container is measured by means of a precision manometer. Assuming that the components being mixed obey the ideal gas law, the concentrations will be proportional to the partial pressures of the individual components[53]:

$$C_i = \frac{P_i}{P} \cdot 10^6 \tag{1}$$

where $C_i$ and $P_i$ are the concentration (ppm) and partial pressure, respectively, of a given component, $i$, and $P$ is the total pressure. However, owing to the occurrence of a spherical barrier, hydrogen bonding, quantum effects and various forces (intermolecular, electrostatic, etc.), mixed gases do not obey the ideal gas law and, consequently, it is necessary to introduce into eqn. 1 the expression for the so-called compressibility

factor ($z$):

$$z = \frac{P_i V}{nRT} \tag{2}$$

where $V$ is the gas volume, $n$ the number of moles of gas, $R$ the gas constant and $T$ temperature.

## 2.2. Volumetric methods

A container of known volume $V$ is filled with pure gaseous components under atmospheric pressure and at temperature $T$. If under these conditions the value of the compressibility factor $z$ differs considerably from 1.00, it should be determined. The number of moles of the component to be measured ($n_i$) in a mixture can be calculated from

$$n_i = \frac{(P - P_s)V}{zRT} \tag{3}$$

where $P_s$ is the equalizing pressure. The amount of diluting (complementary) gas, $n_g$, is usually determined gravimetrically:

$$n_g = \frac{m_g}{M_g} \tag{4}$$

where $m_g$ is the mass and $M_g$ the molecular weight of the diluting gas. The final equation for calculating the concentration of a component to be measured in the mixture is then

$$C_i = \frac{n_i}{n_g} \approx \frac{(P - P_s)\,VM_g}{zRTm_g} \cdot 10^6 \tag{5}$$

## 2.3. Gravimetric methods

Gravimetry, being an absolute method, enables the errors associated with sampling components by measuring pressure or volume to be avoided. In this instance the concentration of a given component can be calculated from

$$C_1 = \frac{\dfrac{m_1}{M_1}}{\displaystyle\sum_{i=1}^{n} \dfrac{m_i}{M_i}} \cdot 10^6 \tag{6}$$

where $m_1$ is the mass of component 1 with molecular weight $M_1$ and $m_i$ is the mass of component $i$ with molecular weight $M_i$. Using this method of preparation of standard mixtures it is necessary to employ special balances[54] with a large weighing capacity and high sensitivity. Much progress has recently been achieved in this field. At pres-

ent, balances with a weighing capacity of 30 kg and a sensitivity of 0.1 mg are used for this purpose, which permits standard mixtures to be prepared with sufficient accuracy.

## 2.4. Pressureless methods

The second group of static methods constitute methods of preparation of gaseous mixtures under atmospheric pressure. The following containers are used for this purpose:

(1) Single rigid chambers of various total capacity[30,49,55–57] into which a measured amount of gas or liquid is introduced. Such a chamber should be provided with a heater for evaporation of liquid and a stirrer. Air is commonly used to displace the mixture from the chamber, which results in a continuous decrease in the concentration of the component to be measured. For this reason, not more than 10% of the content of the chamber can be withdrawn without taking into account the decrease in concentration of the component to be measured[58].

(2) Multiple rigid chambers. A specified number of chambers of identical volumes are connected in series. When the mixture is withdrawn from the last chamber, the mixture from the previous chamber takes its place instead of air. This method allows the preparation of mixtures in amounts depending on the number of chambers (bottles) connected in series[58,59], e.g., the connection of five chambers in series permits the preparation a mixture in an amount equal to 3 volumes of the chamber[58].

(3) Flexible chambers[34,35,60–63]. These are made of plastics[34,35,64–66], PTFE[67–69] or aluminized plastics[59,61,70]. The volume of such chambers can be as high as 14 m³ (refs. 69, 70) and their utilization is sometimes combined with preliminary dilution of a mixture[71]. A diagram of the generation of a standard gaseous mixture in a Mylar bag[34] is shown in Fig. 2.

Long-term storage of such prepared mixtures is not recommended owing to possible losses of the component to be measured (adsorption, diffusion). In order to decrease the effect of adsorption on the walls[63], it is recommended that the container is washed with nitric acid, followed by distilled water, purged with oxygen and, finally, preliminarily conditioned with an appropriate standard mixture.
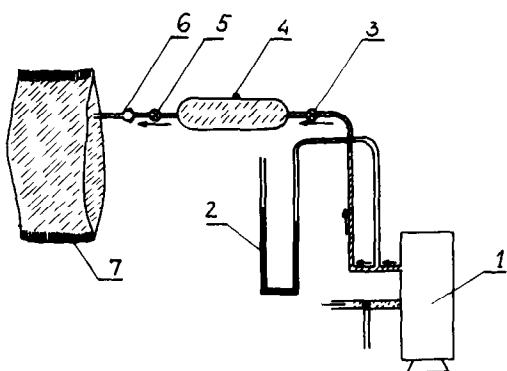


Fig. 2. Diagram of preparation of gaseous mixture in a plastic container[34]. 1 = Wet gas meter; 2 = water manometer; 3 = valve; 4 = rubber septum; 5 = valve; 6 = ball ground-glass joint; 7 = Mylar container.

## 3. EXPONENTIAL DILUTION METHOD

This is a particular case of a single rigid chamber method, at the same time belonging to dynamic methods of preparation of standard mixtures owing to the continuous supply of a stream of diluting gas. The principle of the method is shown schematically in Fig. 3. By using the exponential dilution method (EDM), a gaseous mixture is generated in which the concentration of a component of interest decreases exponentially with time. The method is especially suitable for the calibration of GC detectors and continuous gas analysers. EDM has been described by Lovelock[72] and its modifications by Williams and Winefordner[73]. A small amount of a pure component (gas, liquid) is introduced into a flask of known volume, provided with a stirrer, through which passes diluting gas at a constant flow-rate. The concentration of a component in the gaseous mixture leaving the flask can be expressed by the following equation (assuming constant temperature):

$$C = C_0 \exp\left( - \frac{Qt}{V} \right) \tag{7}$$

where $C_0$ is the initial concentration of the measured component in the flask, $Q$ the flow-rate of diluting gas, $V$ the volume of the flask and $t$ the time from the moment of introduction of the component to be measured into the flask.

A number of direct applications of this technique have been described[74-82] as well as its combination with the permeation method[83,84]. As mentioned earlier, the EDM can be employed not only for gases but also for liquids[85] and, after appropriate modifications, for the generation of multi-component mixtures[86].

The method is very versatile, as the component introduced into the diluting gas can be any gas or mixture of gases of known composition or any volatile liquid.

The accuracy of the composition of mixtures prepared by means of EDM depends on the quality of the apparatus and the technique used. In order to ensure
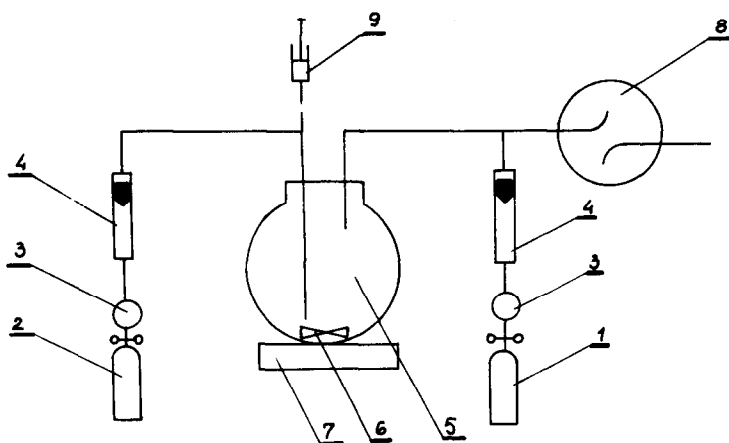


Fig. 3. Schematic diagram of the apparatus for the exponential dilution method with an additional dilution stage. 1 = Tank with diluting gas; 2 = tank with purging gas; 3 = control valve; 4 = flow meter; 5 = flask; 6 = stirring bar; 7 = magnetic stirrer; 8 = mixing chamber; 9 = sampling syringe.

good accuracy and precision of preparation of a mixture, the component to be measured should be introduced into the flask automatically using a sampling device of known, constant volume. In addition to obvious sources of error such as variations in the volume of the introduced component, temperature, pressure and flow-rate of the diluting gas and inaccurate measurement of time, there is also an inherent error resulting from non-ideal mixing of components in the container. However, this error is repeatable and has a constant value. It can also be minimized by careful design of the chamber. It is necessary to eliminate dead volumes, as the gas present there diffuses to the stream of standard mixture, resulting in a disturbance of the exponential dependence of concentration on time. As mixtures prepared using the exponential dilution method are always "freshly" mixed, they undergo only such degradation as is brought about by incorrect selection of components of the mixture or unsatisfactory transport of the generated mixture to the analyser being calibrated.

Hence, the method has the following advantages: versatility, low cost, no additional accessories required, a wide range of mixtures can be generated and the data on linearity of the detector being tested are provided "automatically". The EDM also has certain drawbacks: it requires highly trained personnel, portable devices are difficult to construct, continuous operation is impossible and the accuracy of preparation of the mixture depends to a large extent on the accuracy of introduction of the component to be measured.

## 4. DYNAMIC METHODS

It follows from the requirements for standard gaseous mixtures that the dynamic methods are of particular importance and have definite advantages over static methods. Their variety[87] (see Fig. 1) permits the selection of the most suitable method of mixing the generated components with a stream of diluting gas for a particular purpose. Dynamic methods are especially valuable in the preparation of mixtures of reactive or labile components when their storage is practically impossible.

In general, it is impossible to recommend the best method of preparing a standard mixture for a given purpose; however, the most widely used methods are those based on the diffusion of molecules of the component to be measured into a stream of gas (diffusion methods) and the diffusion of molecules of this component through permeable barriers (permeation methods), owing to their versatility and suitability under both laboratory and field conditions.

### 4.1. Mixing of gas streams

These methods are also called "dilution of streams" and are based on the mixing of two or more gas streams, the flow-rates of which are known and regulated by means of appropriate flow meters[4,88–90]. Naturally, multi-stage dilution is also easily accomplished[91–93]. A schematic diagram of an apparatus for two-stage dilution is shown in Fig. 4. For the simplest case of mixing two streams, the concentration of the component to be measured can be calculated from

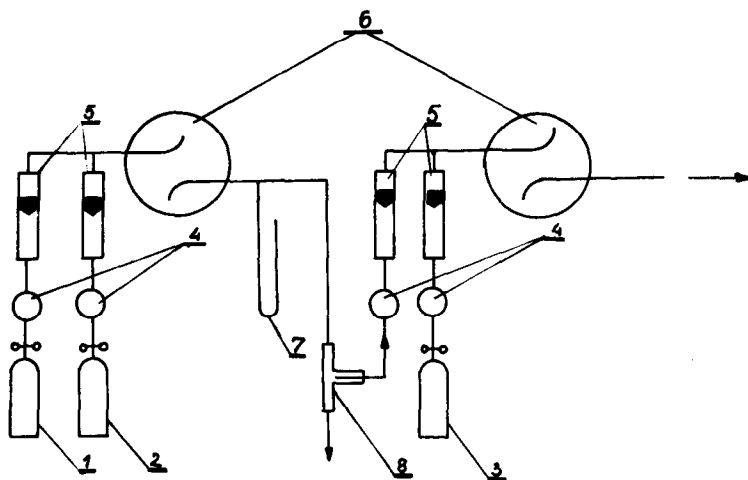$$C = C_1 \cdot \frac{Q_1}{Q_1 + Q_2} \qquad (8)$$

Fig. 4. Apparatus for two-stage dilution of a gas stream. 1 = Tank with diluting gas I; 2 = tank with measured component; 3 = tank with diluting gas II; 4 = control valves; 5 = flow meters; 6 = mixing chambers; 7 = manometer; 8 = stream splitter.

where $C_1$ is the concentration of the measured component in a stream of gas of flow-rate $Q_1$ and $Q_2$ is the flow-rate of the diluting gas.

The concentrations of the component to be measured obtained when using a single-stage system usually range from 0.01 to 1 %, whereas two-stage dilution results in a concentration of less than 1 ppm.

A device for multi-stage dilution consists of a number of elements of identical design equal to the number of stages of dilution. A mixture generated in the first element of the apparatus is accurately divided with respect to the flow-rate by means of, e.g., capillaries[94-104] into two streams representing (most favourably) 10 % and 90 % of the primary stream, the stream constituting 10 % of the mixture volume being introduced into the next element and the second stream being removed outside the apparatus. A stream of diluting gas in an amount corresponding to 90 % of the mixture volume removed outside the device in the first stage is also fed to the second element. In such a manner, the concentration of the measured component in the second element is ten times lower than in the first element.

Frequently, a standard mixture from a bottle is mixed with a stream of air provided by a pump[105,106]. A modification of this method is based on employing pumps that mix gases in a definite ratio[107,108]. Such devices usually consist of two piston pumps driven by a synchronous motor through a system of gears. By changing the gear ratio, the volume ratio of gases drawn by the pumps from containers is also changed and hence the concentration of the measured components in the mixture is varied.

The accuracy of preparation of a mixture by stream dilution methods depends to a large extent on the accuracy of measurement of the flow-rate of mixed streams and, particularly, of the stream containing the component of interest. Bubble meters[97], capillary flow meters[98], rotameters with various ranges[102] or precision manometers[104] are used for this purpose. Portable gas dilution apparatus[109] and

commercially available devices for gas stream mixing[110–113] are also known. In order to prevent adsorption on the walls of an apparatus it should be made of glass or PTFE. Proper design of the mixing chamber is also essential in order to eliminate stratification effects of the mixed components.

## 4.2. Injection methods

A comparative evaluation of this group of methods has been published by Nelson[59]. Injection methods are used for the preparation of standard mixtures of liquids of various volatility in the diluting gas[6,105,106,114–117] and thus it is imperative to design an injection device that will prevent condensation of liquids. A schematic diagram of the simplest injection device is shown in Fig. 5. The component to be measured is injected into the diluting gas stream manually using a syringe or a micro-syringe[118,119], a motor-driven syringe[6,120–122], syringe pumps[107,123–125] or a syringe provided with a paddle wheel driven by a stream of air[85]. Both the accuracy and reproducibility of preparation of the mixture and the concentration of the component to be measured greatly depend on the manner of injection[126–129]. In order to accelerate the process of preparation of the mixture, special atomizers[118–121], glass-wool plugs[130,131], heating of the device[124,125,127,132] or injection of liquid into a small stream of an inert gas[133] that it subsequently diluted to obtain the desired concentration are frequently used.

A stage involving additional dilution of a mixture is commonly employed[126,134]. Devices for the preparation of standard gaseous mixtures by means of injection methods are available commercially[113,135,136].

## 4.3. Permeation methods

All permeation methods are based on Fick's diffusion law. According to this law of diffusion of gases, the permeation rate ($R$) of any gas through a plastic membrane (polyethylene, PTFE, silicone rubber) of thickness $L$ and surface area $A$ can be expressed by the following equation[137–140]:
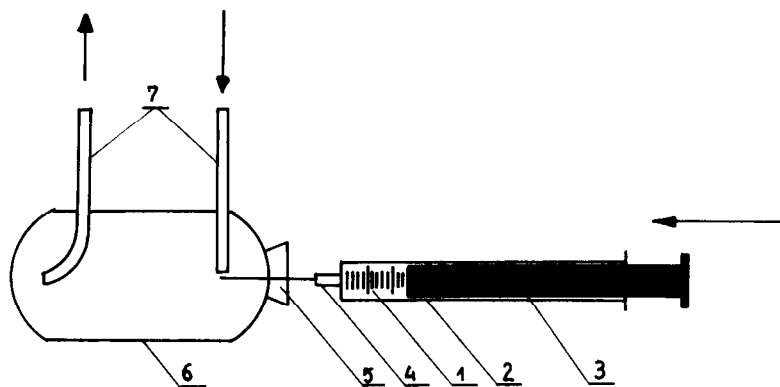
$$R = DS \left(p_1 - p_2\right) \frac{A}{L} \tag{9}$$

Fig. 5. Diagram of a simple injection device. 1 = Component to be measured; 2 = gas-tight syringe; 3 = syringe plunger; 4 = needle; 5 = rubber septum; 6 = mixing chamber; 7 = chamber by-passes.

where $D$ is the diffusion coefficient, $S$ the solubility constant and $p_1$ and $p_2$ the partial pressures on the two sides of the membrane. The permeation coefficient $(B)$ can be defined as

$$B = DS \tag{10}$$

Further, the dependence of $B$, $D$ and $S$ on temperature is expressed by the Arrhenius equation:

$$B = B_0 \exp\left(-\frac{E_p}{RT}\right) \tag{11}$$

$$B = D_0 \exp\left(-\frac{E_d}{RT}\right) S_0 \exp\left(\frac{H_s}{RT}\right) \tag{12}$$

where $E_p$ and $E_d$ are the activation energies for permeation and diffusion, respectively, and $H_s$ is the heat of solution.

The concentration of the component to be measured that passes through the permeable membrane into the stream of diluting gas can be calculated as follows[141-143]:

$$C = \frac{RK}{Q} \tag{13}$$

where $R$ is the permeation rate, $K$ the reciprocal vapour density of the permeating component and $Q$ the flow-rate of diluting gas. The value of $K$ can be calculated from

$$K = \frac{22.45}{M} \cdot \frac{T}{273} \cdot \frac{760}{P} \tag{14}$$

where 22.45 is the molar volume of the permeating component at STP, $M$ is its molecular weight, $T$ is temperature and $P$ is pressure. If $t = 25°C$ and $P = 760$ mmHg, the equation is simplified to

$$K = \frac{22.45}{M} \tag{15}$$

and the final equation for calculating the concentration is

$$C = \frac{22.45\ R}{MQ} \tag{16}$$

All permeation systems can be divided into three categories:

(a) two-phase system: liquid and its vapour[144-148] or liquified gas and its vapour[149-151];

(b) two-phase system: solid (polymers: paraformaldehyde and polyoxymethylene) and formaldehyde vapour at elevated temperature[152-154];

(c) one-phase system: a standard gas or its mixture with an inert gas under atmospheric or elevated pressure[140,143,155,156].

In various designs of permeation devices the following materials have been used for membranes: PTFE[140,143,155,156], silicone rubber[140,152,157–160], polypropylene[155,156,161], polyester[155,156,161], poly(vinyl fluoride)[155,156,161], polyamide[155,156,161], nylon[162], polyethylene[146,147,162] and wood[163]. Combination of permeation tubes with the chemical reaction of permeating components has been employed for the generation of CO and NO as components of standard mixtures[164].

Among permeation devices of various design, permeation tubes are most commonly used[145–147,165–173]. They were described for the first time in 1966 by O'Keefe and Ortman[137] for application to the generation of gaseous components of standard mixtures. Permeation tubes are now being produced on a mass scale[150,151,162,174] and the selection of a suitable tube can be made on the basis of lists compiled by manufacturers[162,174], giving parameters such as operating temperature, tube material, wall thickness, permeation rate and lifetime. A permeation tube is prepared by closing a given liquid or gas in a tube made of PTFE or other plastic material. After an initial induction period of 1–3 weeks, the permeation rate reaches a constant value if the tube is kept at constant temperature.

Calibration of permeation tubes or other permeation devices is an important problem. The apparatus for preparation of mixtures using this method[175,176] and methods of calibration (volumetric, manometric, colorimetric, coulometric and gravimetric) have been described[148,166,175–178]. The absolute, gravimetric method of determining the loss in weight of the tube after a prolonged period of time has found most widespread use for calibration purposes.

In order to obtain a standard mixture in which the concentration of the component to be measured is determined with an accuracy of 1 %, the flow-rate of the diluting gas must be measured with an accuracy of 1 %. The value of the permeation rate must also be known with this accuracy. A significant factor influencing permeation rate is temperature, according to the following equation[162]:

$$\log \frac{R_2}{R_1} = 2950 \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \tag{17}$$

where $R_1$ and $R_2$ are the permeation rates at temperatures $T_1$ and $T_2$, respectively. This equation is an empirical relationship determined for various materials from which permeation devices are made. On the basis of eqn. 17, the values of $R$ can be predicted for temperatures different from the calibration temperature. It follows from eqn. 17 that the value of the permeation rate varies by 10 % with a change in temperature of 1°C. Thus, in order to prepare a mixture with 1 % accuracy it is necessary to thermostat the device to within ±0.1°C.

In practice, permeation tubes are not refillable and for this reason it is an important task to determine the lifetime of a tube, i.e., the period during which, at constant temperature, its permeation rate remains constant. The lifetime of a tube depends only on the tube volume, the mass of the component placed inside the tube and its permeation rate. For standard tubes with wall thickness of 0.062 and 0.125 in., the lifetime (months) can be calculated as follows[162]:

$$\text{Life} = \frac{1465}{R} \cdot D \tag{18}$$

whereas for tubes with wall thickness 0.030 in. the lifetime (months) is given by[162]

$$\text{Life} = \frac{3386}{R} \cdot D \qquad (19)$$

where $R$ is the permeation rate per 1 cm length, $D$ is the density of liquid inside the tube. The lifetime of a tube is independent of the tube length. Eqns. 18 and 19 were derived assuming that the tube was filled to 90% of its volume and that 10% of the volume remained filled with the liquid, *i.e.*, that the effective volume of a given liquid component constitutes 80% of total volume of the tube. In terms of characteristic parameters, permeation vials are devices similar to permeation tubes. These two types of devices differ only in their permeation rates, which are considerably smaller for permeation vials owing to the small permeation area. On the other hand, the lifetime of permeation vials is substantially longer as a result not only of the smaller permeation rates but also of the considerably larger volume of liquid that is placed in a reservoir of permeation vials. As mentioned earlier, there are a variety of designs of
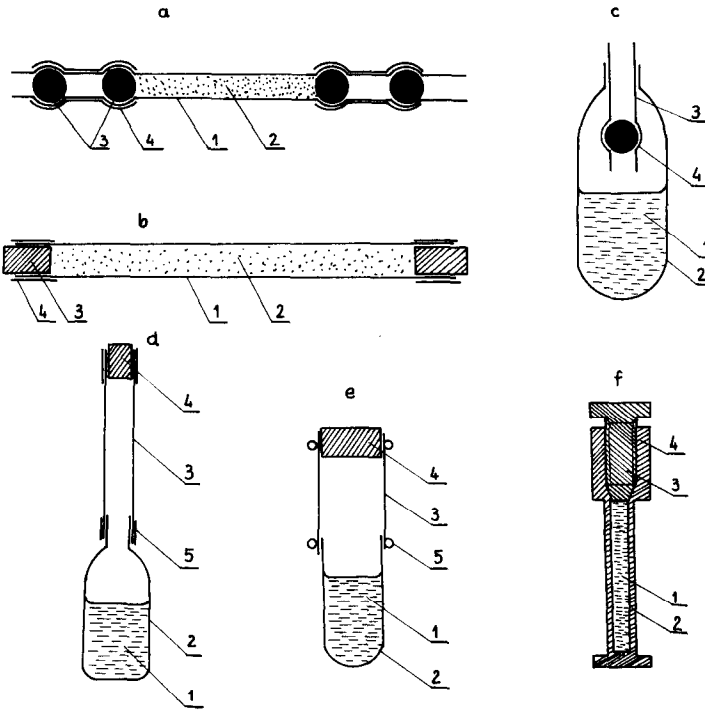


Fig. 6. Designs of permeation devices. (a)[137] 1 = PTFE tube; 2 = component to be measured; 3 = stainless-steel balls; 4 = reinforcing collar. (b)[179,180] 1 = PTFE tube; 2 = component to be measured; 3 = PTFE stoppers; 4 = reinforcing collar. (c)[181] 1 = Component to be measured in the form of a liquid; 2 = microvial; 3 = PTFE tube; 4 = stainless-steel ball. (d)[159] 1 = Component to be measured in the form of a liquid; 2 = microvial; 3 = PTFE tube; 4 = PTFE stopper; 5 = reinforcing collar. (e)[182] 1 = Liquid component; 2 = glass tube; 3 = permeation surface; 4 = PTFE stopper; 5 = stainless-steel reinforcing collar. (f)[143] 1 = Liquid component; 2 = permeating part of PTFE tube; 3 = threaded PTFE stopper; 4 = threaded body of tube.
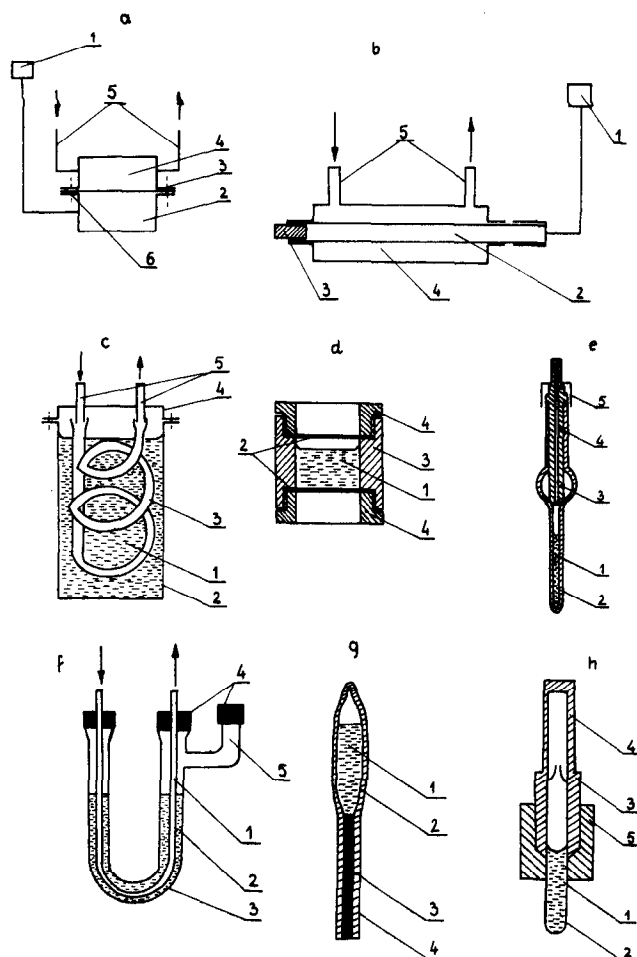
Fig. 7. Further designs of permeation devices. (a)[140,143,155,156,161] 1 = Source of component to be measured (in the form of a gas); 2 = lower chamber of the device; 3 = permeable membrane; 4 = upper chamber; 5 = gas inlet and outlet. (b)[143] 1 = Source of gaseous component; 2 = PTFE tubing; 3 = PTFE stopper; 4 = chamber purged with diluting gas; 5 = inlet and outlet. (c)[144,177] 1 = Liquid component; 2 = container; 3 = PTFE tubing; 4 = cover; 5 = inlet and outlet. (d)[144] 1 = Liquid component; 2 = PTFE membranes; 3 = body with threaded orifices; 4 = fixing nuts. (e)[184] 1 = Liquid component; 2 = glass vial; 3 = PTFE plug with permeable area (at the top); 4 = channel in plug; 5 = screw-cap. (f)[180,183] 1 = PTFE tubing; 2 = component to be measured; 3 = glass U-tube; 4 = stopper; 5 = by-pass for filling of the device. (g)[157] 1 = Component to be measured; 2 = glass container; 3 = permeable membrane; 4 = glass capillary connected to the container. (h)[185] 1 = Liquid component; 2 = glass vial; 3 = PTFE cover; 4 = permeable part of the cover; 5 = body.

permeation devices, a number of which[137,140,143,144,155,156,159,161,174,179-185] are shown in Figs. 6 and 7. Owing to ever increasing applications of various types of permeation devices in analytical chemistry, not only devices generating gaseous components but also complete apparatus for the preparation of standard gaseous mixtures using the permeation technique, called calibrators[43,132,151,186-192], are commercially available. Most recent applications of the permeation devices include the cali-
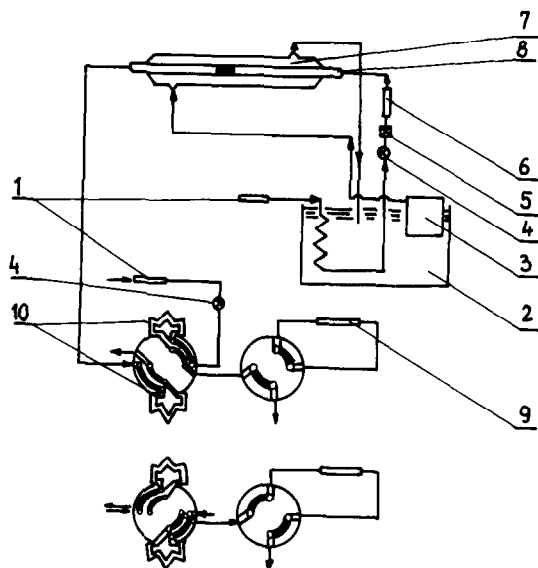
Fig. 8. Apparatus for generation of standard gaseous mixtures employing the permeation phenomenon[199].
1 = Purifier with molecular sieve; 2 = water thermostat; 3 = pump; 4 = pressure regulator; 5 = flow regulator; 6 = flow meter; 7 = thermostating device; 8 = permeation tube; 9 = tube with sorbent; 10 = sampling loop.

bration of passive monitors for many components of workplace atmospheres[145,159,193–196]. The method is commonly employed for the preparation of standard mixtures containing halocarbons[197] and sulphur compounds[198].

Numerous examples of laboratory apparatus for the generation of gaseous mixtures using permeation devices have been described[143,186,196,199]. Thermostated water-baths were usually employed for maintaining a constant temperature of permeation devices. A diagram of such an apparatus is shown in Fig. 8, although there also exist multi-channel systems[145,191,192] that permit the preparation of multi-component standard mixtures.

Basic features of permeation methods for the preparation of standard gaseous mixtures can be summarized as follows:

advantages: versatility;
ease of automation;
portability and easy service;
availability of sources for many components;
drawbacks: long initial induction period;
relatively high cost;
necessity of using special instrumentation for every permeation device;
continuous emission of a component from the source
(it is impossible to "shut off" the source).

## 4.4. Diffusion methods

The application of the diffusion phenomenon for the preparation of standard

gaseous mixtures was proposed over 25 years ago[200,201]. In addition to permeation methods, these methods are currently the most commonly employed. They also have similar advantages and drawbacks.

Diffusion methods are based on the principle of dilution of the vapour of a liquid diffusing from a container through a capillary or directly from a capillary into a space through which a stream of diluting gas is passed[202–204]. The theoretical background of diffusion methods was reported by Altshuller and Cohen[205]. The fundamental theoretical equation is

$$R = 2.21 \cdot 10^6 \cdot \frac{DMPA}{TL} \cdot \log\left(\frac{P}{P-p}\right) \qquad (20)$$

where $R$ is the diffusion rate, $D$ the diffusion coefficient, $M$ the molecular weight of the diffusing compound, $p$ the vapour pressure of this compound at temperature $T$, $P$ the total pressure, $A$ the cross-sectional area of the diffusional part of the device and $L$ the length of this part.

The diffusion coefficient also depends on pressure and temperature, which is expressed by the following relationship:

$$D = D_0 \left(\frac{T}{T_0}\right)^m \left(\frac{P_0}{P}\right) \qquad (21)$$

where $D_0$ is the diffusion coefficient under normal conditions ($T_0 = 298°K$ and $P_0 = 760$ mmHg) and $m$ is a constant, usually assumed to be 2.00 but sometimes 1.75.

Combination of eqns. 20 and 21 yields the following final equation:

$$R = 6.169 \cdot 10^6 \, D_0 M \left(\frac{A}{L}\right) \left(\frac{T_0}{T}\right)^{m-1} \log\left(\frac{P}{P-p}\right) \qquad (22)$$

On the basis of the $R$ value the concentration of a diffusing compound in the mixture can be calculated using eqn. 13. Maintaining constant diffusion conditions, i.e., geometric dimensions of a diffusion vessel, temperature, pressure and flow-rate of the diluting gas, a gaseous mixture containing a constant concentration of the diffusing component is obtained.

Among the various types of diffusion vessels the most commonly employed are the McKelvey–Hoelscher vessel[201], the Stefen-type vessel[205] and diffusion tubes[141,162]. The first vessel consists of two spherical chambers connected by a capillary. The lower chamber serves as a container for the investigated liquid, and mixing of the diluting gas with vapour of the liquid diffusing through the capillary occurs in the upper chamber. Maintenance of a constant liquid level (constant geometric conditions) is essential. The McKelvey–Hoelscher vessel has been described in numerous papers[206–208], including modified versions[142,209–211].

In the Stefen-type vessel adapted by Altshuller and Cohen[205] a capillary (being simultaneously a container with the liquid) is permanently connected with a chamber in which mixing of the components occurs. Losses of liquid are read from a scale etched on the capillary. This type of vessel also has several modifications[16,212–214].

The third type, diffusion tubes, consist of a glass container filled with liquid

and connected with a long neck of exactly defined diameter. The container is usually filled with 3–4 ml of liquid, which diffuses through the neck at a constant rate (at constant temperature) into the chamber in which the tube is placed and through which passes a stream of diluting gas. The effect of temperature control can be ascertained by assuming an average change of vapour pressure of a given liquid of 50 % with a temperature change of 10°C. This will change the logarithmic term in eqn. 22 by 50 %. The same temperature change will result in a variation of the temperature term of this equation of *ca.* 3 % in the same direction. Generally, a change in temperature of 1°C will change the diffusion rate (*R*) by *ca.* 5 %. Hence the temperature should be controlled and stabilized with an accuracy $\pm 0.2$°C in order to maintain the accuracy of preparation of a standard mixture within $\pm 1$ %. For a given tube, the best method of varying the concentration of a component in a mixture is to vary the flow-rate of the diluting gas, whereas a change in concentration when changing the measured component (liquid in the container) is best accomplished by using the term in eqn. 22 expressing geometric parameters.

In analytical practice, most diffusion vessels are calibrated by the determination of the loss in weight of the device[141,142,208–210,215–218] after a prolonged period of time during which it is thermostated and diffusing vapours are removed by a stream of an inert gas. Calibration can also be performed by means of gas chromatography[214,218] or by the measurement of the volume of liquid that diffuses from a
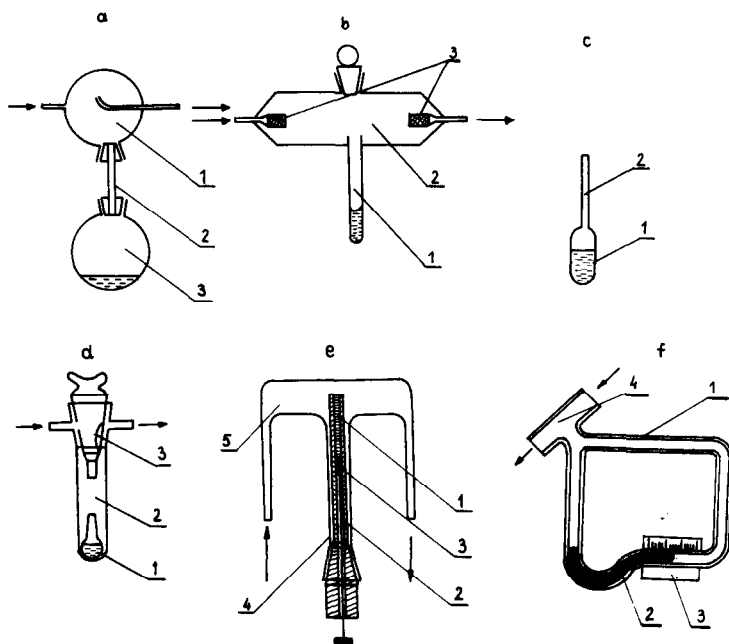


Fig. 9. Designs of diffusion devices. (a)[201] 1 = Mixing chamber; 2 = interchangeable capillary tube; 3 = lower chamber with liquid component. (b)[205] 1 = Glass tube with liquid; 2 = mixing chamber; 3 = gas inlet and outlet with sintered-glass frits. (c)[141] 1 = Glass vial with liquid; 2 = capillary. (d)[215] 1 = Ampoule with liquid; 2 = glass container with ground-glass joint; 3 = stopper with ground-glass joint. (e)[212] 1 = Liquid; 2 = calibrated capillary; 3 = plunger; 4 = capillary mounting; 5 = mixing chamber. (f)[222] 1 = Glass capillary; 2 = liquid component; 3 = scale; 4 = diluting gas line.
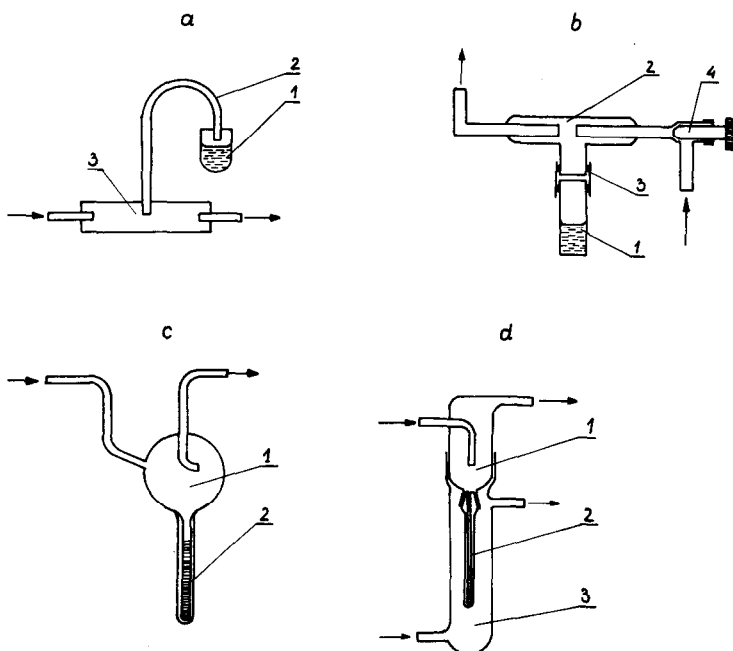
Fig. 10. Further designs of diffusion devices. (a)[221] 1 = Vial with liquid; 2 = diffusion tube; 3 = mixing chamber. (b)[217] 1 = Container with liquid; 2 = mixing chamber; 3 = connection with seal; 4 = needle valve. (c)[213] 1 = Mixing chamber; 2 = calibrated capillary with liquid. (d)[220] 1 = Mixing chamber; 2 = calibrated capillary with liquid; 3 = thermostated jacket.

calibrated capillary[34,205,212,219,220]. Methods of determining the stabilization time, *i.e.*, the period after which the diffusion rate becomes constant, have also been described[185,219]. Semimicro- or microbalances are used to determine the loss in weight of diffusion devices. Immediately after weighing, the diffusion vessel is re-placed in a thermostated chamber and the entire procedure is repeated. In order to minimize weighing errors, the loss in weight of the vessel should be of the order of 100 mg and hence the time between two successive weighings should be sufficiently long. As with permeation devices, it is essential for practical reasons to determine the lifetime of a diffusion vessel. It can be calculated from the following equation:

$$\text{Life} = \frac{23.48\ VD}{R} \tag{23}$$

where $V$ is the volume of liquid in the container, $D$ is its density and $R$ is the diffusion rate.

It should be pointed out that diffusion vessels should not contain multi-component mixtures. If a need arises to generate multi-component gaseous mixtures, one should employ several diffusion vessels filled with pure components[218]. Schematic diagrams of designs of diffusion vessels and their modifications[141,201,205,212,213,215,217,220–222] are shown in Figs. 9 and 10.

Naturally, the methods of preparation of standard mixtures described in this

section can be combined with others, *e.g.*, with the inclusion of additional dilution of gas streams[223] or chemical reactions[154]. Commercially available generators of gaseous mixtures utilizing diffusion method have also been described[141,162]. Among other applications, the use of the Stefen-type diffusion vessel for the determination of the diffusion coefficients of vapours of various compounds can be mentioned here[224].

## 4.5. Evaporation methods

Evaporation is an important phenomenon utilized for the preparation of standard gaseous mixtures using both static[225] and dynamic[4,64,226–230] methods. The technique is the simplest to realize in practice and is based on passing a pure diluting gas through[50,231,232] or over[233] a liquid layer. A schematic diagram of the apparatus for the generation of standard mixtures by an evaporation method[234] is shown in Fig. 11. In this instance the amount of the component to be measured in the gas is calculated from the relationship

$$m = \frac{p_i V_s M}{RT} \tag{24}$$

where $m$ is the amount of the component to be measured in a mixture of volume $V_s$ in channel A, $p_i$ is the vapour pressure of the component with molecular weight $M$ at temperature $T$ and $R$ is the gas constant. However, the volume $V_s$ can be calculated as follows:

$$V_s = \frac{V_G P_a}{P_G} \tag{25}$$

where $V_G$ is the total volume ($V_G = St$), $S$ is the flow-rate through the regulator 2A, $t$ is the sampling time, $P_a$ is the total gas pressure, $P_v$ is the pressure in channel A and
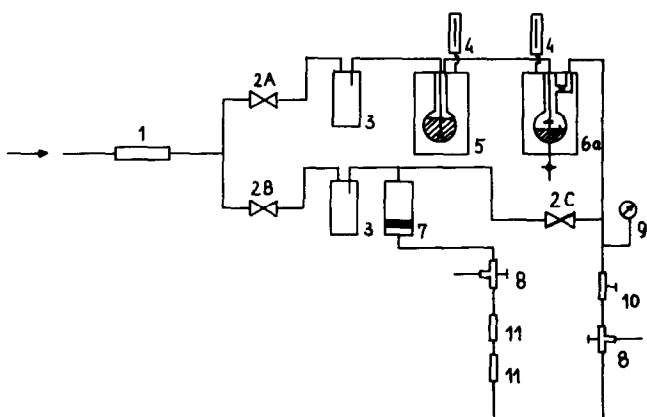


Fig. 11. Apparatus for generation of gaseous mixtures using the evaporation method[234]. 1 = Purifier with molecular sieve; 2A, 2B = flow regulators; 3 = safety flasks; 4 = resistance thermometer; 5 = container with liquid component; 6 = condenser; 7 = mixing chamber; 8 = stream splitter; 9 = manometer; 10 = valve; 11 = adsorption tubes.

$P_G = P_v + P_a$. Thus, the final equation for calculating $m$ can be written as

$$m = \frac{p_i St P_a M}{RT (P_a + P_v)} \tag{26}$$

The most important problem is the generation of a stream of saturated vapour that is subsequently diluted with an additional gas stream. In order to fulfil the condition that the concentration of the measured component in the primary gas stream corresponds to the saturated vapour pressure, the flow-rate of the gas should be sufficiently small and the device in which the saturation process occurs should be of special design. Bubblers of various types[136,235-238], sometimes connected in series[239,240] and U-shaped absorbers[241-243] are used for this purpose and, additionally, the standard compound can be coated on a solid support[241,244]. In this manner, the surface of contact between the measured component and the diluting gas is substantially increased.

A system of coupled rotameters or capillary flow meters[242,245] is ordinarily used to measure the flow-rate. Another design of flow meter for the measurement of small flow-rates has also been described[246]. The preparation of multi-component mixtures employing a multi-channel system is also possible[237]. Other procedures include the generation of saturated vapour at low temperature[247], continuous sampling of a substance to a mixer and its evaporation at elevated temperature[248] or evaporation at elevated temperature of a substance that is solid under normal conditions[249]. In many instances air is preliminarily humidified using the same technique[102,239,240,244].

It should be pointed out that the methods discussed in this section have found widespread application for the preparation of standard gaseous mixtures containing exactly known concentrations of water vapour in the relative humidity range 7–98 %. Evaporation techniques can be utilized in both static and dynamic methods. Hygostatic solutions of various salts are sometimes employed[250-252]; lists of such solutions can be found in physico-chemical handbooks. Evaporation methods are particularly suitable for the calibration of various types of explosimeters[136,238]. This group of methods also includes the generation of such components as $SO_2$, $NO_x$, $H_2S$, HCN and $NH_3$ from aqueous solutions appropriate salts by passing a stream of gas over the solutions[233].

## 4.6. Electrolytic methods

The process of electrolysis of an appropriate solution can be utilized for the preparation of certain components of standard gaseous mixtures. This problem has been discussed in numerous papers[13,14,17,253-255]. The amount of a gaseous component generated at the electrode can be calculated from

$$Q = \frac{Vi}{Fn} \tag{27}$$

where $Q$ is the flow-rate of a gaseous component generated at one of the electrodes, $F$ is the Faraday constant, $V$ is the experimental molar volume of the generated gaseous

component, $n$ is the number of electrons exchanged in the electrode process and $i$ is the electrolysis current. For steady conditions (constant flow-rates of the diluting gas and gases generated electrolytically), the following equation expressing the concentration of the component to be measured in a mixture is valid:

$$C = \frac{Q_1}{Q_1 + Q_2 + Q_3} \cdot 10^6 \qquad (28)$$

where $Q_1$ and $Q_2$ are the flow-rates of gases generated at the two electrodes and $Q_3$ is the flow-rate of the diluting gas. Assuming that $C < 1000$ ppm and $Q_1 + Q_2 \ll Q_3$, a simplified equation can be applied[15]:

$$C = \frac{Vi}{FQ_3 n} \cdot 10^6 \qquad (29)$$

The electrolysis process can be successfully employed for the following purposes: anodic generation of $CO_2$ from a saturated aqueous solution of oxalic acid[256-259]; anodic generation of oxygen and cathodic generation of hydrogen from acidic or basic aqueous solutions[104,254,260,261]; cathodic liberation of NO during electrolysis of nitrosylsulphuric acid solution[11,262-264]; generation of $H_2S$ by cathodic reduction of bis($\beta$-ethylcarboxy)trisulphane[265].

The possibilities of generation of other gaseous components have also been studied[14,246] and the literature data on this subject are compiled in Table 1.

TABLE 1

ELECTROLYTIC GENERATION OF COMPONENTS OF GASEOUS MIXTURES

| *Desired gaseous component* | *Electrolytic system* | *Gas generated at second electrode* | *Yield (moles of gas/Faraday)* |
|---|---|---|---|
| $O_2$ ($H_2$) | Pt, $H_2SO_4$, Pt<br>Pt, $K_2SO_4$, Pt<br>Pt, KOH, Pt | $H_2$ ($O_2$) | 1/4, 1/2 |
| $N_2$ | Pt, $N_2H_4 \cdot H_2SO_4$, Pt | $H_2$ | 1/4 |
| $Cl_2$ | Pt, NaCl, Pt | $H_2$ | 1/2 |
| $CO_2$ | Pt, $H_2C_2O_4$, Pt | $H_2$ | 1 |
| NO | Pt, $NOHSO_4 + H_2SO_4$, Pt | $O_2$ | 1 |
| $C_2H_6 + 2CO_2$ | Pt, AcONa, Pt | $H_2$ | < 1/2 (Kolbe reaction) |
| $O_3 + O_2$ | Pt, $H_2SO_4$, Pt | $H_2$ | ≪ 1/6 |
| $AsH_3 + H_2$ | Pt, $Na_3AsO_3 + H_2SO_4$, Pt | $O_2$ | ≪ 1/3 |
| $SbH_3 + H_2$ | Pt, $KSbC_4H_4O_7$, Pt | $O_2$ | ≪ 1/3 |
| CO | Pt, HCOONa, Pt | $H_2$ | No data available |
| $H_2S$ | Pt, $Na_2S_2O_3$, Pt | $H_2$ | No data available |
| $SO_2$ | Pt, $Na_2S$, Pt | $H_2$ | No data available |
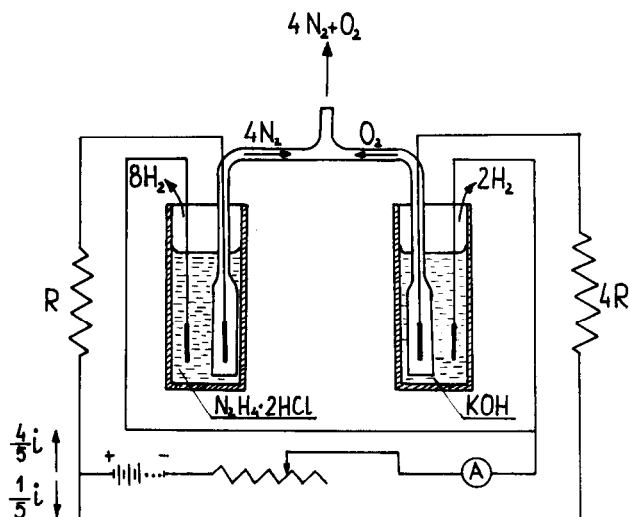
Fig. 12. Apparatus for generation of "electrolytic air"[13].

An interesting example of the application of electrolysis is the generation of "electrolytic air"[13]. A diagram of suitable apparatus is shown in Fig. 12.

New possibilities have been created by the combination of electrolysis with chemical conversion of the products of the electrolysis reactions. This approach permits one to obtain carbon monoxide after catalytic reduction of electrolytically generated carbon dioxide[266], nitrogen dioxide after oxidation of electrolytic NO with
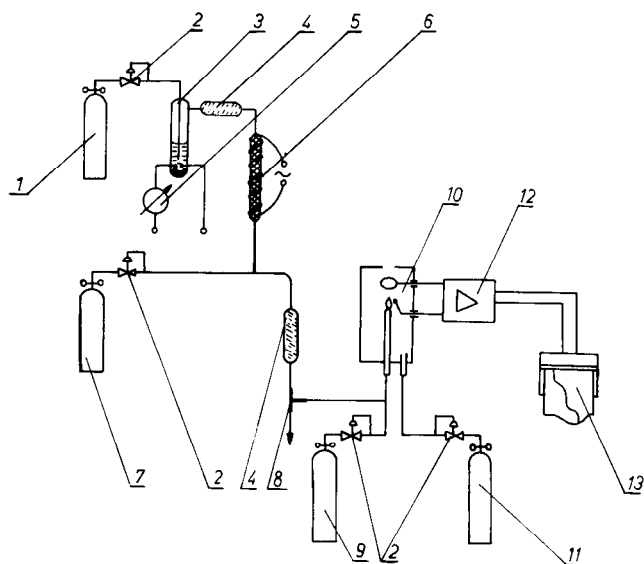


Fig. 13. Apparatus for generation of methane using electrolysis and chemical conversion of the products[271]. 1 = Hydrogen tank; 2 = valve; 3 = electrolyser; 4 = dryer; 5 = amperometer; 6 = tube with catalyst; 7 = nitrogen tank; 8 = stream splitter; 9 = hydrogen tank; 10 = flame-ionization detector; 11 = air tank; 12 = amplifier; 13 = recorder.
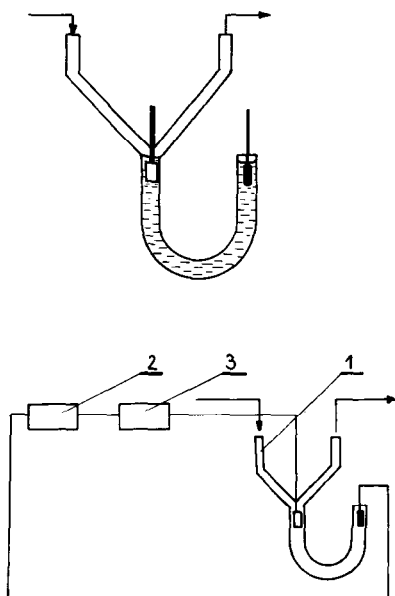
Fig. 14. Schematic diagram of electrolyser proposed by Hersch and apparatus for electrolytic generation of gases[13]. 1 = Electrolyser; 2 = amperostat; 3 = amperometer.

electrolytic oxygen[262], water through catalytic oxidation of electrolytically generated hydrogen in the presence of an excess of oxygen[254,255,267] or a stoichiometric amount of electrolytic oxygen[254,255,268–270] and methane through catalytic reduction of carbon dioxide generated in an electrolysis process[271], which is shown in Fig. 13.

In a number of papers[13,14,263], serious attention has been drawn to the prob-

TABLE 2

GENERATION OF GASES THROUGH THERMAL DECOMPOSITION OF SOLID SUBSTANCES

| Desired gaseous component | Thermal decomposition reaction |
|---|---|
| $O_2$ | $7KMnO_4 \xrightarrow{250°C} K_3MnO_4 + 2K_2MnO_4 + 4MnO_2 + O_2$ |
| $N_2$ | $NH_4NO_2 \xrightarrow{70°C} N_2 + 2H_2O$ |
|  | $Ba(N_3)_2 \xrightarrow{150°C} 3N_2 + Ba$ |
| $N_2O$ | $NH_4NO_3 \xrightarrow{200°C} N_2O + 2H_2O$ |
|  | $4NH_4NO_3 \xrightarrow{200°C} 2NO_2 + 3N_2 + 8H_2O$ |
| $NO_2$ | $Pb(NO_3)_2 \xrightarrow{O_2} PbO + 2NO_2 + \frac{1}{2}O_2$ |
| $CO$ | $CaC_2O_4 \xrightarrow{440°C} CaCO_3 + CO$ |
|  | $Ni(CO)_4 \xrightarrow{200°C} Ni + 4CO$ |
| $CO_2$ | $2NaHCO_3 \xrightarrow{200°C} Na_2CO_3 + H_2O + CO_2$ |
|  | $MgCO_3 \xrightarrow{540°C} MgO + CO_2$ |
| $(CN)_2$ | $2AgCN \xrightarrow[vacuum]{400°C} 2Ag + (CN)_2$ |
| $Cl_2$ | $2AuCl \xrightarrow{\Delta} 2Au + Cl_2$ |
| $CH_4$ | $CH_3COONa + NaOH \xrightarrow{400°C} CH_4 + Na_2CO_3$ |

lems associated with designs of electrolysers that would ensure quantitative purging of electrolysis products with simultaneous separation of anodic and cathodic compartments. A diagram of an electrolyser proposed by Hersch[13] and a diagram of the apparatus for the generation of standard mixtures are shown in Fig. 14.

Basic advantages and drawbacks of electrolytic methods of generation of gaseous mixtures should also be mentioned. The advantages include specificity, the possibility of constructing portable apparatus, the ease of building a given instrument as a calibration module, ease of automation, possibility of interruption of the generation process at any moment and short response times. The drawbacks are limited application, the necessity to use special technologies and the possibility of deviations from the Faraday law owing to evaporation of water or exhaustion of the electrolyte.

However, both direct and indirect methods of electrolytic generation of standard gaseous mixtures can obviously complement other methods. The ease of effecting changes in concentration of the component to be measured in a mixture (through variation of the electrolysis current) permits checks on the instruments being calibrated at various points of their dynamic ranges.

TABLE 3

UTILIZATION OF CHEMICAL REACTIONS FOR GENERATION OF COMPONENTS OF GASEOUS MIXTURES

| Reactants in the form of gas or vapour | Reaction conditions | Gaseous components obtained |
|---|---|---|
| $C_2H_5OH$ | $\xrightarrow{Al_2O_3}$ | $C_2H_4 + H_2O$ (in $N_2$) |
| $C_6H_5OH$ | $\xrightarrow{\Delta}$ | $CO + 3H_2 + 5C$ (in $N_2$) |
| $Fe(CO)_5$ | $\xrightarrow{200\,C}$ | $5CO + Fe$ (in $N_2$) |
| $2H_2 + O_2$ | $\xrightarrow{Pt}$ | $2H_2O$ |
| $C_{10}H_8 + 12O_2$ | $\xrightarrow{\Delta}$ | $10CO_2 + 4H_2O$ |
| $Cl_2 + H_2$ | $\xrightarrow{uv}$ | $2HCl$ |
| $RNH_2 + H_2$ | $\xrightarrow{Ni}$ | $RH + NH_3$ (in $N_2$) |
| $O_2 + 2C$ | $\xrightarrow{\Delta}$ | $2CO$ (in $N_2$) |
| $H_2O + C$ | $\xrightarrow{\Delta}$ | $CO + H_2$ (in $N_2$) |
| $H_2 + Ag_2S$ | $\xrightarrow{500\,C}$ | $H_2S + Ag$ (in $N_2$) |
| $H_2 + NiCl_2$ | $\xrightarrow{600\,C}$ | $2HCl + Ni$ (in $N_2$) |
| $H_2 + CoF_4$ | $\xrightarrow{300\,C}$ | $2HF + 2CoF_2$ (in $N_2$) |
| $6H_2O + Mg_3N_2$ | $\rightarrow$ | $2NH_3 + 3Mg\,(OH)_2$ |
| $6H_2O + Al_2S_3$ | $\rightarrow$ | $3H_2S + 2Al\,(OH)_3$ |
| $3H_2O + Al(OR)_3$ | $\rightarrow$ | $3ROH + Al(OH)_3$ |
| $HCl + Na_2S_2O_3$ | $\rightarrow$ | $SO_2 + NaHSO_3 + NaCl$ |
| $2CF_3COOH + CaC_2$ | $\rightarrow$ | $C_2H_2 + (CF_3COO)_2Ca$ |
| $H_2O + CaC_2$ | $\rightarrow$ | $C_2H_2 + CaO$ |
| $2Cl_2 + N_2H_4\,H_2SO_4$ | $\rightarrow$ | $4HCl + H_2SO_4 + N_2$ |
| $Cl_2 + 2NaClO_2$ | $\rightarrow$ | $2ClO_2 + 2NaCl$ |
| $SO_2 + 3NaClO_2$ | $\rightarrow$ | $2ClO_2 + NaCl + Na_2SO_4$ |
| $3NO + 2CrO_3$ | $\xrightarrow{200\,C}$ | $3NO_2 + Cr_2O_3$ |
| $3NO + 2HMnO_4$ (aq) | $\rightarrow$ | $3NO_2 + 2MnO_2 + H_2O$ |
| $H_2O + CH_3MgI$ | $\rightarrow$ | $CH_4 + MgOHI$ |
| $H_2O + PCl_5$ | $\rightarrow$ | $2HCl$ |
| $2HCl + 2NaHCO_3$ | $\rightarrow$ | $CO_2$ |
| $H_2O + 2RCOCl$ | $\rightarrow$ | $2HCl + (RCO)_2O_2$ |
| $5H_2 + Ag_2SO_4$ | $\xrightarrow{\Delta}$ | $H_2S + 4H_2O + 2Ag$ |

## 4.7. Chemical reaction methods

Thermal decomposition reactions constitute a fundamental type of reaction that can be employed for the preparation of certain components of standard gaseous mixtures[22,164,261,272-276]. Examples of such reactions are given in Table 2.

This group of methods also includes pyrolysis of organic compounds[277], partial oxidation of carbon layers in order to generate carbon monoxide[278], catalytic oxidation of sulphur dioxide[279] and conversion reactions of stable mixtures. Reactions of stable mixture are used for the dynamic generation of unstable, highly reactive mixtures. Stable reagents from gas cylinders are mixed in a constant ratio of streams in a reaction chamber where the generation of the component to be measured occurs. As the mixture is generated only during actual use, the component to be measured does not undergo degradation even if it is highly reactive. The technique described here has been applied to the generation of controlled amounts of water[267,280] and the preparation of gaseous mixtures containing nitrogen oxides[281,282] and ozone[106,283-286]. Table 3 lists examples of other conversion reactions that can be utilized for the generation of standard gaseous mixtures[13,246,287,288].

In the most comprehensive review of methods of preparation of standard gaseous mixtures[8] there is a section discussing the methods of preparation of standard aerosols. In the present review this topic has been omitted owing to a recent publication dealing with the subject[289].

## 5. SUMMARY

Static and dynamic methods for the preparation of standard gas mixtures are discussed. The principles of the design of devices for the generation of gas mixtures and fundamental equations for calculation of the concentration of a component of interest in a mixture are given. Advantages and shortcomings of the methods are also described.

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