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**GENERATING TEST GASES
FOR CALIBRATION OF METHODS
USED IN
ENVIRONMENTAL ANALYSIS**

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GENERATING TEST GASES FOR CALIBRATION OF METHODS USED IN ENVIRONMENTAL ANALYSIS

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INTRODUCTION

A reliable and comprehensive evaluation of an analytical method without calibration is possible in exceptional cases only. Gases of defined composition are required for the calibration. Examples from practical work show, however, that generation and application of these gases may cause difficulties mostly because the way apparatus is handled in practice. The problem begins - for example - when the test gas is passed through a 50 cm long rubber hose to the sampling vessel; this is the time when major sorption losses (e.g., of benzene) may occur in the connecting hose.

Another problem is often encountered when commercially available test gases with manufacturer's certificate of defined composition are used. In order to achieve a long shelf life of these "ready-made test gases", dry nitrogen is usually used as a basic gas. Such an artificial product when fed into the sampling equipment or analysis instrument produces a calibration curve which is valid for the test gas (e.g., benzene in dry nitrogen). However, in practice humid air which may also contain a generous sprinkling of other organic compounds is sent through the sorption material, thus making the original results for "adsorption capacity and desorption rate" somewhat invalid.

This IUPAC paper shall give information on methods for generating test gases; preference has been given to simple methods emphasizing notes for practical applications. Further information can be found in the literature (Refs. 1 to 24).

1. GENERAL

Test gases of defined composition are required to calibrate gas analysis instruments. Test gases consist of the basic gas (e.g., air) and one or several admixtures (e.g., CO); this definition corresponds to the VDI regulations (Ref. 15). Although "tailor-made" special apparatuses are mainly used, two basic principles can be distinguished: the static method and the dynamic method. Both methods will be described later; the variants in the equipment used will be taken into consideration. Points of importance to practitioners will be discussed in greater detail.

2. STATIC METHODS USED TO PREPARE TEST GASES

Static methods are based on the following general principle. A measured volume of the concentrated admixture is fed to a container which is filled with the basic gas. This gas and the admixtures are mixed. The test gas required for the measurement is obtained from the container through a connection nozzle.

Methods for mixtures up to 5000 ppm

The method is suitable for mixtures up to about a volume concentration of 5000 ppm (maximum). Even low concentrations (less than 1 ppm) can be set with this method.

Equipment. Container made of boron silicate glass, volume approx. 200 litres (calibrated), equipped with stirrer, evaporator dish (required for liquids), feed opening for the substance, sampling nozzle and ventilation valves (Fig. 1). Measure the liquids as starting substance for the admixture (e.g., benzene) by means of a syringe (Fig. 2) and proportion the substance through the feed opening to the evaporator dish. Measure gaseous substances as admixture by means of a piston-type sampler (Fig. 3) and proportion them. Homogeneous mixing is accomplished by means of the stirrer.

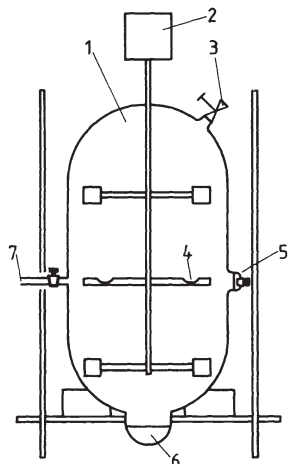


Fig. 1. 200-litre glass container for static test gas setting

1 container/2 stirrer/3 ventilation/
4 evaporator dish/5 feed opening for
admixture/6 cleaning opening/
7 sampling nozzle.



Fig. 2



Fig. 3

Fig. 2. Syringe for proportioning small amounts of liquids.

Fig. 3. Glass piston-type sampler (graduated, volume 100 cm³).

Special notes. (i) Flushing of the container: Before proportioning the admixture, clean the inside of the container carefully with pure air. (ii) Humidity content of the container atmosphere: Before proportioning the admixtures, the basic gas (atmosphere in the container) must be adjusted to the humidity content desired. Low humidity: Allow the basic gas to flow first through the drying tower (e.g. CaCl₂) and then into the container. In order to increase the humidity, pass the basic gas through a e.g. water-filled gas washing bottle. A dry container atmosphere can also be brought to the desired humidity content by proportioning the required quantity of water into the glass container and evaporating it. (iii) Check for undesirable gaseous contaminants: Before proportioning the admixture (gas, liquid), ascertain by an analysis that the container atmosphere (basic gas) does not contain any undesired foreign gases. (iv) Clean condition of the sampling nozzle: Introduce the (concentrated) admixture at a point other than the sampling nozzle if possible. Small quantities of admixture might be adsorbed to the inner surface of the nozzle; when the measurement is carried out desorption takes place into the test gas stream, and the result of the measurement would be falsified. The feed nozzle and the sampling nozzle do not have to be separate if adsorption-free proportioning has been ensured by preliminary tests. (v) Ignition danger: The concentration must be below the lower explosion limit. In the case of concentrations above 20 % of the lower explosion limit flushing the container first with inert gas (e.g., nitrogen) may be necessary. (vi) Complete mixing of admixtures and basic gas: The time required until a homogeneous mixture is obtained may have to be determined by preliminary tests. (vii) Complete evaporation of liquids: The liquid which has been pipetted in must evaporate completely; in the case of liquids with a higher boiling point, this may take several hours. The stirrer is in operation during evaporation. (viii) Supplementing the mixing procedure by means of piston-type sampler: Mixing of admixture and basic gas (during stirring) can be supplemented by means of a 100-cm³-piston-type sampler (Fig. 3). This

glass syringe is being connected to the sampling nozzle of the container and by moving the piston to and fro several times the whole mixing procedure is being intensified. (ix) Positive pressure in the container: Due to the addition of the admixture - especially after evaporation of liquids - a slight positive pressure is formed in the container. Establish pressure equalization between the container atmosphere and the ambient air before connecting the analytical device with the sampling nozzle. (X) Verifying test gas concentration: Verify according to Section 5. (Xi) Glass-on-glass connection: Connect the analytical device and the sampling nozzle by means of a short hose (glass on glass!). (Xii) Limitation of the test gas volume to be withdrawn: During the test, test gas is drawn from the container. Ambient air flows through the opened feed nozzle and reaches the container; the container atmosphere is diluted. For this reason, do not withdraw more than 5 % of the atmosphere (i.e., 10 litres for a 200-litre container).

Routine method for concentrations of 5000 ppm (maximum).

Fig. 4 illustrates a simple procedure utilizing a 20-litre-glass bottle (boron silicate glass). The measured volume (see Table 1) of the concentrated admixture is injected (through the opening of the bottle) onto the bottom of the bottle. The contents may then be mixed by means of a magnetic stirrer or tumbled with an aluminium foil inside. The 12 special notes given above have to be considered, particularly the limitation of the test gas volume to be withdrawn. Assuming the case of complete turbulent mixing (e.g., magnetic stirrer in operation) during withdrawal of the test gas, the change in concentration follows a mathematical relation (Ref. 1).

TABLE 1. Examples for the amount of admixture to be injected into a glass bottle

Volume of glass bottle	20 L	
Wanted concentration	10 ppm (vol./vol.)	
Admixture	Mass	Volume (liquid)
Acetaldehyde	0.37 mg	0.47 µL
Acetone	0.48 mg	0.61 µL
Benzene	0.65 mg	0.74 µL
Chlorobenzene	0.94 mg	0.85 µL
Ethanol	0.38 mg	0.49 µL
Hexane	0.72 mg	1.08 µL
Octane	0.95 mg	1.35 µL
Trichloroethylene	1.10 mg	0.75 µL
Xylene	0.89 mg	1.01 µL

Dilution of concentration in one bottle:

$$c = c_0 \cdot e^{-\frac{V_W}{V_B}}$$

c = residual concentration in bottle

c_0 = initial concentration

V_W = volume withdrawn

V_B = volume of bottle

Dilution of concentration in second bottle, when two bottles connected in series:

$$c_2 = c_0 \left[1 + \frac{1}{1!} \left(\frac{V_W}{V_B} \right) + \frac{1}{2!} \left(\frac{V_W}{V_B} \right)^2 \right] e^{-\frac{V_W}{V_B}}$$

c_2 = concentration in second bottle

c_0 = initial concentration

V_W = volume withdrawn

V_B = volume of bottle

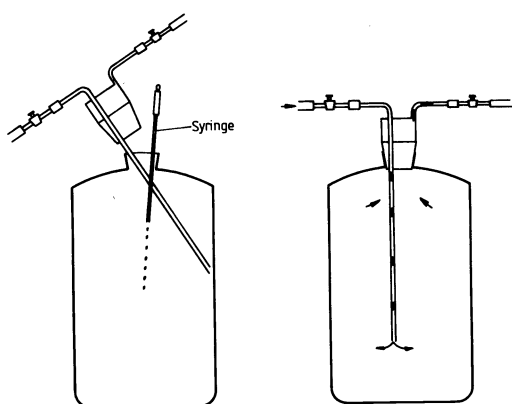


Fig. 4. Routine method for setting of vapour concentrations (admixture is injected, vapourized and mixed).

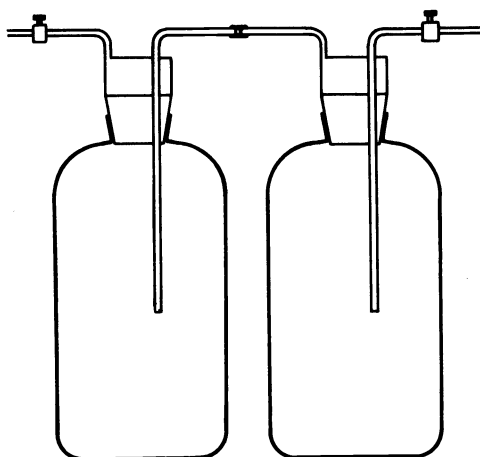


Fig. 5. Connection of two glass bottles in series to obtain larger volumes of test gases.

Connecting two of the 20-litre glass-bottles (each containing the same test gas concentration) in series (Fig. 5), it is possible to obtain relatively large volumes of test gases. Table 2 gives examples of the decrease in concentration versus volume withdrawn (assuming the case of complete turbulent mixing). The figures show that withdrawing a volume of 2 litres, lowers the concentration by approx. 10 %, when one bottle is being used. With two bottles in series, the concentration drops by approx. 1 % only, when a volume of 2 litres has been withdrawn. That means, a train of two 20-litre glass bottles allows sampling of approx. 7 litres before reaching the 5 % reduction of concentration (stated in paragraph Xii). When care is taken to mix thoroughly during the withdrawal procedure and to calculate the concentration by using the figures given in Table 2, larger volumes of test gases can be obtained.

TABLE 2. Residual concentration present in a 20 litre bottle (single or connected in series with second bottle) after removal of the following volumes:

Volume withdrawn (litre)	Residual concentration (at sampling nozzle) in percent of starting concentration	
	single bottle	two bottles in series
0	100	100
2	90	99
4	82	98
6	74	96
8	67	94
10	61	91
12	55	88
14	50	84
16	45	81
18	41	77
20	37	74

Method for concentrations up to several percent by volume

Theoretically concentrations up to 100 vol.% can be set.

Equipment. Bags made of special plastic foils, volume 10 litres (Fig. 6) with connection nozzle and septum (for injection of liquids).

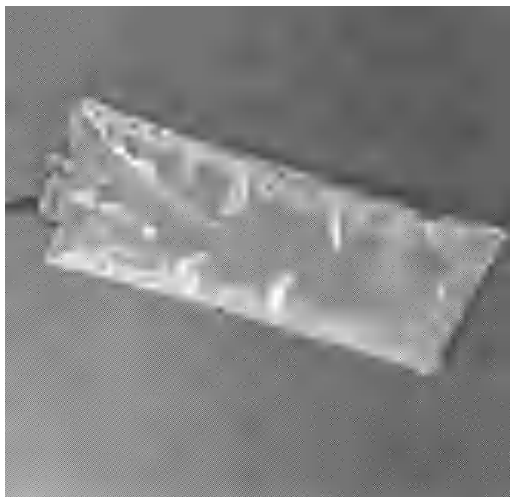


Fig. 6. Plastic bag with connection nozzle and septum (injection of liquids).

Special notes. The comments made under the heading in the earlier methods (glass containers) hold in analogy for plastic bags as well. Important: The selection of the foil is determined by the properties of the test gas (the plastic foil must not have any measurable permeability for test gas, the adsorption of the test gas on the foil must be negligibly small). Depending on the task at hand, the foil materials listed below have been used so far:

- Poly(tetrafluoroethylene) for hydrocarbons, halogenated hydrocarbons, ketones and esters
- Polyester for hydrocarbons, halogenated hydrocarbons, ketones and esters
- Polyethylene for carbon monoxide
- Poly(vinylidene dichloride) for hydrocarbons
- Rubber for carbon monoxide
- Metal coated plastic for carbon dioxide

3. DYNAMIC METHODS FOR PREPARING TEST GASES¹

Principle of the dynamic method: Basic gas and admixtures flow through a mixing section. The flow rates of both gases are measured before the inlet into the mixing section. After mixing, the test gas is withdrawn at a connection nozzle.

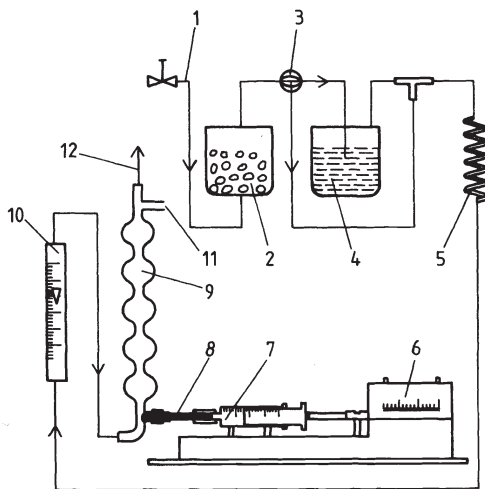
Continuous injection method for gases

Volume concentrations up to about 5000 ppm can be set by this method.

Equipment. A special glass syringe³ (piston-type sampler, volume 100 cm³) is filled with the admixture and placed into a transport device. The syringe is connected to a mixing tube via a capillary tube (Fig. 7). The flow rates of the basic gas and admixtures are set.

Fig. 7. Gas mixing equipment for continuous test gas settings

- 1 inlet of basic gas/2 filter container/3 change-over cock/4 humidifier/5 temperature compensation/6 transport device (with geared motor)/7 gas piston sampler (filled with the gaseous admixture)/8 capillary tube/9 mixing tube/10 flow meter (for basic gas)/11 sampling nozzle/12 to the exhaust.



Special notes. (i) Glass syringe (piston-type sampler): Use calibrated syringes only (calibration covers the volume released by the syringe, referred to the range of feed of the piston). Do not lubricate the syringe. The inside of the syringe and the surface of the piston must be clean. The polished surfaces of the piston and syringe chamber must seal perfectly with respect to one another, but must still move smoothly (precision polishing). (ii) Capillary tube: Length 25 to 35 mm, inside diameter 0.4 to 0.6 mm. (iii) Mixing tube: Material boron silicate glass; the dimensions must ensure homogeneous mixing. The inside diameter of the tube should be sufficiently large to prevent pressure drop during mixing (if necessary, determine the optimum dimensions by preliminary tests). (iv) Cleanness of the glass equipment (syringe, capillary tube, and mixing tube): Clean and dry the equipment before using it. To the extent possible, use different units for the various gases. (v) Flow rate of the basic gas and admixtures: The flow rates of the basic gas must be sufficiently large so that an adequate volume of test gas is delivered at the end of the mixing section for sampling (during the measurement). In the gas generating equipment, the flow rate must be adjusted to the sampling conditions. For most calibration purposes, this would amount to about three litres of test gas per minute. At least three litres of test gas per minute should thus be delivered. Towards the top, the flow rate is not limited theoretically; due to equipment parameters, an upper limit of 40 litres per minute has been found to cover most practical situations. The flow rate of the admixture is obtained from the concentration desired. The range from about 1 to about 20 cm³/min is preferred. Taking into account the lower and upper limits mentioned for the flow rates of basic gas and admixture, a concentration range from about 20 ppm to about 7000 ppm is covered (syringe filled with 100 % admixture). The concentration of the admixture in the syringe can be reduced by prior dilution (e.g., 10 vol.%); concentrations down to about 2 ppm can then be obtained at the end of the mixing section. Use inert gas (e.g., nitrogen having a high degree of purity) for prior dilution in the syringe; in case of prior dilution to less than 10 vol.% the conditions must be determined by preliminary tests. (vi) Humidity of the test gas: The basic gas must be conditioned by means of humidifiers or driers before it is fed to the mixing section. (vii) Running-in time: Adsorption is possible in the mixing section during the initial phase. The system must therefore be brought into equilibrium before it is used definitely; the running-in time is at least five minutes and may be up to several hours in some cases (if necessary determine the running-in time by preliminary tests). (viii) Verifying test gas concentration: Verifying according to Section 5.

Continuous injection method for volatile liquids with vaporization (concentrations from about 500 ppm to about 10.000 ppm can be set by this procedure).

The admixture is continuously injected as liquid from the glass syringe into a vaporizer section, through which air is flowing. The syringe is chucked into a transport device similar to the one described previously; the other data made in the previous section also hold in analogy to the proportioning of liquids. The principle of the method is shown in Fig. 8. The method has proved suitable in the case of liquids with a boiling point not much above 100 °C; at higher boiling points, the vaporizer section may have to be warmed up (e.g., with a hair-dryer). Make sure there is complete vaporization.

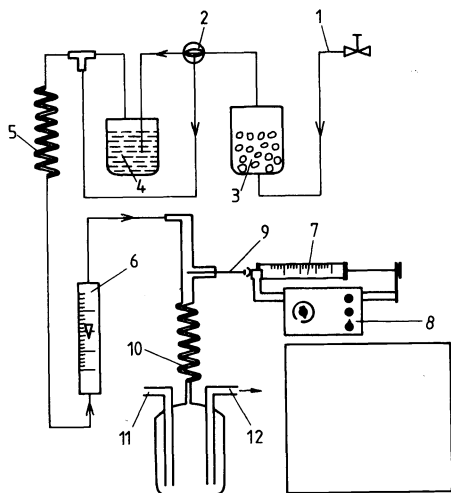


Fig. 8. Continuous injection of liquids with vapourization

1 inlet of basic gas/2 change-over cock/3 filter container/4 humidifier/5 temperature compensation/6 flow meter (for basic gas)/7 glass piston sampler (filled with the liquid admixture)/8 transport device with gear motor/9 capillary tube/10 evaporation section/11 sampling nozzle/12 to the exhaust.

Continuous injection method for vapours (volume concentrations from several ppm up to several hundred ppm; concentration range pre-determined by vapour pressure of admixture).

In a special glass syringe (piston-type sampler, volume 100 cm³) a known vapour concentration is being generated by "lubricating" the surfaces homogeneously and thoroughly (inside of syringe and surface of piston) with the (liquid) admixture (e.g. toluene). The total amount of liquid has to be selected in such a way that only the surfaces are being wetted; any excess of liquid must be prevented. The syringe (exit nozzle closed by a small polytetrafluoroethylene plug) has to be conditioned at constant room temperature for at least 15 min in order to get 100 % vapour saturation (resulting vapour concentration depends on vapour pressure, which is stated in respective literature, see table 3 and Ref. 14). Then the syringe is chucked into a transport device similar to the one described previously. Important: Temperature of the glass syringe during whole procedure (from saturation to injection) has to be constant and controlled.

TABLE 3. Examples of vapour concentration at 100 % saturation and temperature of 20 °C

Substance	Vapour concentration % by volume
Acetone	23.0
Acrylonitrile	11.5
Benzene	10.0
Carbon disulfide	39.2
Ethyl alcohol	5.8
n-Hexane	15.8
2-Propanol	4.3
Toluene	2.9
Trichloroethylene	7.9

Permeation method (concentrations from about 0.1 to 10 ppm).

The admixture to be proportioned is located in liquid form in a (closed) vessel (permeation tube) which is permeable to gas. In line with the VDI regulations (Ref. 16) substances (admixtures) with a critical temperature above 25 °C and a critical pressure below 10 bar are suitable. This includes all substances which are liquid at room temperature as well as gases which can be liquefied readily (e.g., NO₂). The basic gas sweeps around the permeation tube in a mixing section controlled by a thermostat. The substance diffuses through the walls of the permeation tube into the mixing section and gets into the stream of the basic gas there. The test gas concentration is calculated from the rate of diffusion and the flow rate of the basic gas. The substance quantity released per time unit (rate of diffusion) is determined by difference weighing of the permeation tube. Due to the low rates of

diffusion (range: microgram per minute) and the test gas stream of at least three litres required for equipment calibrations, the concentrations which can be reached by the permeation method are usually a few ppm at the most.

4. DETERMINATION OF THE FLOW RATES

The composition of the test gas (dynamic setting) is determined by the flow rates of the basic gas and the admixture. These flow rates must be measured. Calibrated flow meters (float principle) are used for the basic gas. The admixture is proportioned by means of the devices described in section 3. The flow meters are calibrated by gas meters (wet design) at pre-determined intervals. The gas meters as well must be calibrated, i.e., by means of a defined air volume (known pressure and temperature) which is obtained by displacement by water (Fig. 9). This air volume is taken as original standard, while the gas meters (wet design) are used at what is called intermediate standard. Calibration of the special glass syringe (section 3) are handled according to the soap bubble method or by water displacement in the case of low flow rates while higher flow rates are measured by means of gas meters (wet design). The soap bubble method is illustrated in Fig. 10. The graduated burette is calibrated. A flat liquid film is produced by a wetting agent in the lower area of the burette. The air to be measured enters the burette below the liquid film, and this film is moved upwards by the air. The air volume can be calculated from the initial and end positions of the liquid film. The time difference between the two positions is measured by means of a stop watch.

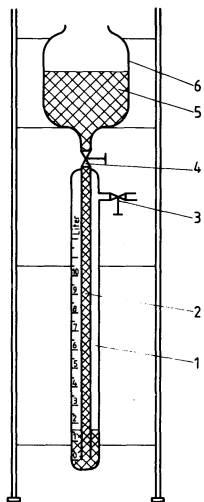


Fig. 9. Device for making defined flow rates (displacement by water)

1 cylindrical glass vessel (calibrated to 10 litres)/2 feed tube (for displacement liquid)/3 shut-off valve (the air stream is obtained at this point)/4 shut-off valve (for regulating the liquid stream)/5 displacement liquid (water)/6 supply vessel for displacement liquid.

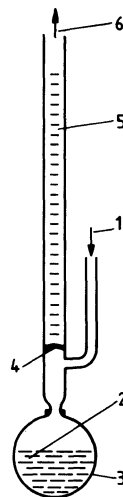


Fig. 10. Soap bubble flow meter

1 gas inlet/2 wetting agent (aqueous solution)/3 rubber ball/4 soap bubble/5 calibrated glass tube/6 gas outlet.

5. VERIFYING THE SET CONCENTRATION

The following procedure has proved suitable. As a matter of principle, only analyzed material is used as a starting substance (liquid or concentrated gas) for the admixture. The starting substances are either procured with an analysis certificate or are analyzed (purity check). The methods used are those known and described in literature (e.g., gravimetry, volumetric analy-

sis, gas chromatography, volumetry and adsorption). Experience has shown that it is not difficult to analyze the (concentrated) starting substance. The analytical determination of the test gas concentration may, however, present problems; sometimes this is, with justifiable effort, not possible at all. For this reason, the concentration of the admixture in the test gas is determined preferably by means of the comparison method described in the VDI regulations (Ref. 17 and 18) and in ISO 6143 (Ref. 10).

Description of the comparison method: Using several stable and homogeneous gas mixtures which have been prepared in a particularly careful manner (the concentration of the admixture is calculated), an analysis apparatus (e.g., flame ionization detector, gas chromatograph) is calibrated. The calibrated analysis apparatus is then used for analyzing the test gases as they are normally prepared.

Examples of preparing methods and analysis methods for a number of gases and vapors are listed in the Table 4.

TABLE 4. Generating methods and analysis

	Static 200-litre container (glass)	Static 10-litre container (plastic)	Dynamic (gases) Continuous injection (syringe)	Dynamic (vapours) Continuous injection (syringe)	Dynamic (liquids) Continuous injection + vapourization	Dynamic (gases) Permeation method	Analysis method for verifying the test gas concentration (see also Ref. 24)
Acetic acid				X			titration
Acetone	X			X	X		gas chromatography
Ammonia	X		X				titration (Ref. 20)
Benzene	X			X			gas chromatography
Carbon dioxide	X	X	X				gravimetric, volumetric
Carbon monoxide	X	X	X				VDI regulation (Ref. 18)
Chlorine			X				titration
<u>N,N</u> -Dimethyl formamide	X						gas chromatography
Ethanol	X			X	X		gas chromatography
Formaldehyde	X						photometric (Ref. 23)
Hydrogen chloride			X				titration
Hydrogen sulfide	X		X			X	titration (Ref. 20)
Methyl bromide	X		X				VDI regulation (Ref. 18)
Nitrogen dioxide	X		X			X	titration (Ref. 21)
Nitrogen monoxide			X				titration (Ref. 21)
Phosgene			X				VDI regulation (Ref. 18)
Sulfur dioxide	X		X				titration (Ref. 22)
Trichloroethylene	X			X			gas chromatography
Vinyl chloride	X		X				VDI regulation (Ref. 18)

6. HINTS FROM PRACTITIONERS FOR PRACTITIONERS

Taking off liquid gases (e.g. propane) from compressed-gas containers: Contaminations may accumulate in the gaseous phase which is in equilibrium with the liquid phase. The composition of the gaseous phase therefore does not always correspond to that of the liquid phase. Sampling of liquid gases should be carried out from the liquid phase of the container content. This is done either by means of a plunger tube, or the bottle must be turned upside down (Ref. 19).

Reactions in the gaseous phase: Reactions between the admixture and the basic gas or the foreign substances which may appear in the basic gas lead to uncontrollable changes in the test gas concentration. For instance, hydrazine (N_2H_4) may react with carbon dioxide or with oxygen. The use of atmospheric air as basic gas is therefore not always to be recommended in the case of adjustments of hydrazine concentrations. Another example would be the reaction of the admixture with the humidity of the air while aerosols are formed. This reaction can be observed particularly in the case of concentration adjustments of hydrogen fluoride, hydrogen chloride and nitric acid. The stability of ammonia test gases is also affected by humidity (Fig. 11). Sulfur dioxide is much more stable in air having a low degree of humidity than in air having a high H_2O content (Fig. 12).

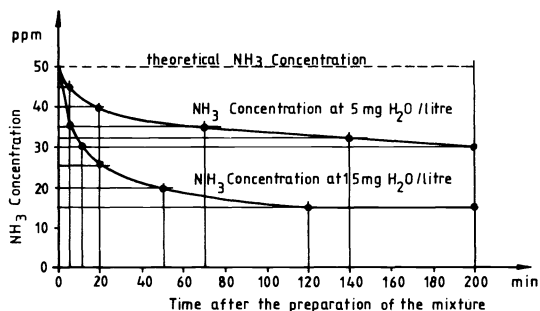


Fig. 11. Change in the NH_3 concentration (in air) as function of time at various degrees of humidity (setting in 200-litre glass container).

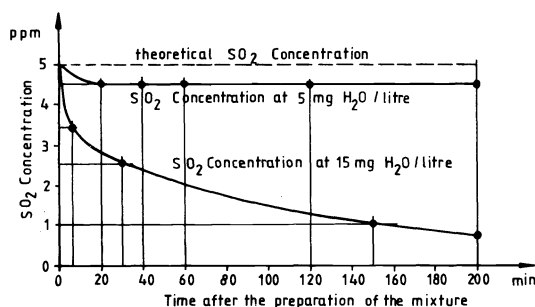


Fig. 12. Change in the SO_2 concentration (in air) as function of time at various degrees of humidity (setting in 200-litre glass container).

Test gases in compressed-gas cylinders: Preparing and storing of test gases in compressed-gas cylinders may present problems. If sufficient experience has not been acquired, the manufacturers of these test gases should definitely be consulted. Gas mixtures with an appropriate certificate can be procured from them. In addition to the concentration, the minimum and maximum storage temperature as well as the maximum storage time are listed in the certificate. For reasons of stability, the pressurized test gases are very dry (in most instances); the humidity may be less than 1 mg/m^3 . Difficulties may arise when such dry gases are used for calibration. The basic gas of such test gases is often nitrogen. Consideration has been given to this fact, since analytical devices, calibrated with nitrogen test gases, may give faulty results, when being used for air testing.

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