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Instrument for preparation of reference gas mixtures with the use of the process of barbotage and permeation

CYPRIAN FIJAŁO[1], TOMASZ DYMERSKI[1], JACEK GĘBICKI[2], JACEK NAMIEŚNIK[1]
[1]GDANSK UNIVERSITY OF TECHNOLOGY, FACULTY OF CHEMISTRY, SUB-FACULTY OF ANALYTICAL CHEMISTRY,
[2]GDANSK UNIVERSITY OF TECHNOLOGY, FACULTY OF CHEMISTRY, SUB-FACULTY OF CHEMICAL AND PROCESS ENGINEERING

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ABSTRACT

Reference gas mixtures are classified as reference materials and are mainly used for quality monitoring and identification of impurities in atmospheric air. They can also be used for the calibration of measurement devices. Nowadays, there is a need to develop new techniques for the preparation of reference gas mixtures [1, 2]. In this paper, the design and the operating principles of an instrument based on the use of barbotage and permeation processes were presented.

Urządzenie do wytwarzania gazowych mieszanin wzorcowych z wykorzystaniem procesu barbotażu oraz permeacji

Słowa kluczowe: gazowe mieszaniny wzorcowe, barbotaż, generator gazowych mieszanin wzorcowych

STRESZCZENIE

Gazowe mieszaniny wzorcowe są zaliczane do materiałów odniesienia. Wykorzystuje się je przede wszystkim do monitoringu jakości powietrza atmosferycznego oraz identyfikacji występujących w nim zanieczyszczeń. Mogą być one również używane do kalibracji przyrządów pomiarowych. Obecnie dąży się do opracowania nowych technik przygotowywania gazowych mieszanin wzorcowych [1, 2]. W pracy przedstawiono opis konstrukcji oraz zasadę funkcjonowania prototypowego urządzenia przeznaczonego do wytwarzania gazowych mieszanin wzorcowych, którego działanie oparte jest na wykorzystaniu procesów barbotażu oraz permeacji.

1. INTRODUCTION

Reference gas mixtures are used in many branches of science and technology. For many years, there has been an intensive development of analytical techniques, which are used to conduct studies on the quality of atmospheric air, internal air and atmospheric conditions in workplaces. Because of that, there is a growing need for reference mixtures of appropriate meteorological parameters [3-7]. In order for a reference mixture to be deemed as a so-called non-matrix reference material, the following criteria must be fulfilled [8, 9]:

– constant and non-changeable concentration of analytes,
– capability of determining the concentrations with an accuracy 2.5-3 times bigger than the scale of the calibrated tool,
– commercial availability due to the need of conducting numerous analyses during the stage of equipment calibration,
– high purity (occurrence of contamination in the composition at the ultra-trace level of concentration),
– possibility of estimating the value of measurement uncertainty,
– documented traceability.

In practice, reference gas mixtures are obtained with the use of the following types of techniques [10-12]:

– static – introduction of a particular amount of each element of a given mixture to a container of a known volume,
– dynamic – constant introduction of the remaining elements of a given mixture into a stream of a carrier gas,
– combined – which combines static and dynamic techniques of their preparation.

The use of dynamic techniques is of special significance for employees of laboratories due to the possibility of the changing concentrations of components of a reference gas mixture in a smooth and quick way due to, among others, the possibility of changing the mass flow rate of a carrier gas stream. Currently, there are many constructional solutions allowing for the preparation of reference gas mixtures by dosing the component measured when introduced into a stream of a carrier gas with the use of a syringe or a pump in the process of diffusion, permeation or evaporation [13].

The tool we developed is designed to be used for the preparation of reference gas mixtures, which may be used for the calibration of equipment designed for measuring concentrations of atmospheric air contamination. Operation of the tool is based on the use of a dynamic technique, in which the processes of barbotage and/or permeation of a reference substance from the liquid to gas stage occurs. The generator allows for preparation of gas mixtures, in which analytes occur at a constant and controllable level of concentration. In addition, the construction solutions presented allow for the introduction of water vapour to a stream of a carrier gas, the presence of which may have an important influence on the results of tests conducted with the use of a gas analyser. The tool may be controlled with the use of a computer and that allows for constant monitoring and full automation of operation of each component of the generator.

2. DESCRIPTION OF THE OPERATING PRINCIPLE OF THE GENERATOR

The operating principle of the instrument presented is based on a dynamic technique, in which specific components generated during the process of barbotage and/or permeation are added to a carrier gas. A zero gas is used as a carrier and a dilution gas. As a result of the barbotage and/or permeation process, a gas mixture is created, which combines vapours of reference substances and the zero air.

The process of barbotage is based on passing a gas through a liquid capable of vapouring at a constant temperature. In the state of thermodynamic balance, the concentration of a substance in a stream of a carrier gas shall be determined on the basis of the vapour pressure at a given temperature. The amount of a given substance in a time unit (*W)* transferred in a stream of a carrier gas may be established with the use of the following equation (1):

$$W = \frac{P_s^o MQ}{10^3 RT} \qquad (1)$$

where: W [mg/s] – the mass flow of the evaporated substance, P_s^o [Pa] – the saturated vapour pressure at the given temperature, M [g/mol] – the molar mass of the evaporated substance, Q [ml/s] – the volumetric flow rate of the stream of the carrier gas, R [J/mol•K] – the gas constant, T [K] – the temperature at which the process of barbotage occurs. The concentration of a substance in a stream of a carrier gas at the temperature of 20°C may be calculated as follows (2):

$$C = \frac{24{,}04W}{10^{-6}QM} \tag{2}$$

where: C [ppm obj.] – concentration of the substance in a stream of a carrier gas at a Q volumetric flow rate.

By combining appropriately the stream of the carrier gas with the stream of the evaporated substance with a new portion of the carrier gas Q_n, we can obtain the desired value of concentration of the reference gas mixture – C_{wz}. This relation can be described by the following equation (3):

$$C_{wz} = \frac{Q}{Q + Q_n} \tag{3}$$

where: Q_n [ml/s] – the volumetric flow rate of the stream of the carrier gas.

The quotient of the volumetric flow rate of the gases referred to in the equation (4) may be called the degree of dilution of the evaporated substance:

$$\alpha = \frac{Q + Q_n}{Q} \tag{4}$$

The relation between the concentrations of components of the reference gas mixture at the temperature of 20°C and the degree of dilution of two chosen liquids (pyridine and butanol), assuming that the state of thermodynamic balance is maintained, as shown in Figure 1.

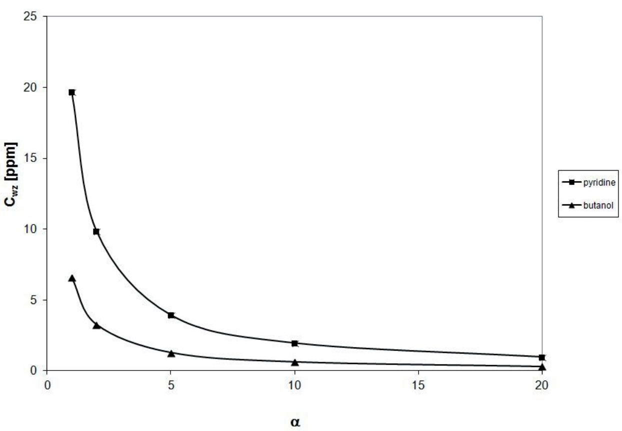

Figure 1 Dependence of components of the reference gas mixture, obtained with the use of barbotage process, on the degree of dilution

The process of permeation is based on the penetration of gases through barriers made of a semi-permeable material (a non-porous material) or a semi-permeable membrane. It may be divided into several stages, which are:

– dilution of the analytes on the material of the membrane,
– diffusion through the membrane,
– desorption from the external wall of the membrane perfused with a stream of a diluting gas.

The driving force of permeation is the difference between partial pressures of the component penetrating the membrane on both sides. The concentration of the measured component C in a stream of a diluting gas is calculated in accordance with the following equation (5):

$$C = \frac{E}{\rho Q} \tag{5}$$

where: E [ng/s] – the permeation ratio, *p* – the density of the gas component subject to the process of permeation (ng/nl), Q – the volumetric flow rate of the diluting gas (ml/s).

The E value is usually determined on the basis of calibration with the use of reference solutions obtained gravimetrically. The measurement of the loss of weight during appropriately long periods of time allows for determination of the value with sufficient accuracy. Figure 2 shows the dependence of changes in concentration of the measured component on the volumetric flow rate of the carrier gas stream at a constant E value.

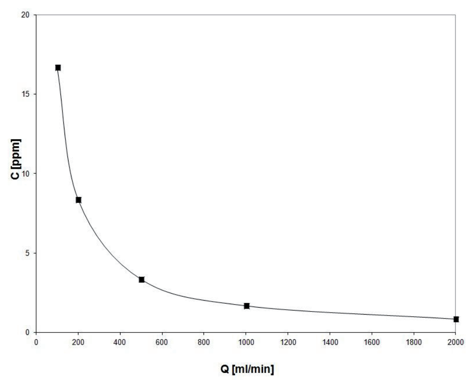

Figure 2 Dependence of concentration of components of a reference gas mixture on the volumetric flow rate for a stream of a carrier gas at the constant temperature and permeation rate

The structure of the instrument allows for the preparation of reference gas mixtures composed of several dozen measured components, which belong to various groups of chemical compounds, such as: alkanes, alcohols, aldehydes, ketones, mercaptans and sulphides. Independent determination of the temperature, the volumetric flow rate of a gas carrier and the type of the measured component subject to the process of barbotage and permeation allows for obtaining the determined concentration of a volatile substance in the gas phase. In order to provide constant and controlled conditions of conducting this process, a system of thermostatic elements was used, which allows for controlling the temperature of the sample within the range between 0°C and 60°C. However, to obtain a constant and determined value of the relative humidity parameter of the gas mixtures prepared, hygrostatic solutions and water were used, over or through which a dilution gas passed.

The most important advantages of the instrument for the preparation of reference gas mixtures with the use of the barbotage and permeation processes, in comparison to the currently used constructional solutions, are:

– A possibility of preparing reference gas mixtures, in which all components may occur in a wide range of concentrations,
– A possibility of preparing odoriferous gas mixtures, which are characterised by a similar value of the relative humidity parameter to the odoriferous gas mixtures occurring in real life,
– Simple operation of such instrument,
– A possibility of preparing gas mixtures directly from liquids, which is connected to:
• Increased safety during the preparation of gas mixtures than in the case of using gas mixtures from gas cylinders under high pressure,
• The fact that the concentrations of components of a gas mixture may be determined with a very high level of accuracy.

3. THE CONSTRUCTION OF THE INSTRUMENT DESIGNED FOR THE PREPARATION OF REFERENCE GAS MIXTURES

The main parts of the structure are a pneumatic system and a thermostatic system, together with a steering system controlling the pneumatic and thermostatic systems. The controlled concentrations of components of the gas mixture prepared are determined as a result of regulating the mass flow rate of a stream of a carrier gas through drilling fluids, regulation of chambers containing liquid samples and as a result of the regulation of the amount of the diluting gas provided. The regulation and control of humidity of the gas mixture prepared are done by regulating the mass flow of the stream of the diluting gas passing over or through the hygrostatic solution or water. To supply the pneumatic system, a carrier gas is used, which is zero air (of N5.0 purity class). The stream of zero air may be introduced to the prototype from a gas cylinder or a tool for cleaning and compressing atmospheric air. Cleaning of compressed atmospheric air usually takes place by removing particulates (with the use of a particulates filter), volatile organic compounds, carbon monoxide, nitric oxide and sulphur monoxide, water vapour, hydrocarbons, acid vapours and bacteria. The cleaned, dried and compressed zero air is then stored in the external container of the tool or directly introduced to the generator.

The instrument for dynamic generation of reference gas mixtures with the use of barbotage and permeation consists of the following units:

– Barbotage unit – ZB, which consists of barbotage chambers (KB),
– Permeation unit – ZP, which consists of permeation chambers (KP),
– Mixing unit – ZM, which consists of a mixing chamber and a concentration compensation container,
– Humidity determination unit – ZUW,
– Air distribution module – MD.

Figure 3 shows a flowchart of pneumatic units used in the instrument designed for the preparation of reference gas mixtures.

The pressure and mass flow rate of a stream of the carrier gas are regulated in the air preparation unit (ZPP), which is a part of the air distribution module (MD). The air preparation unit consists of a rotameter and a pressure regulator. The use of a divider of the stream of a gas guarantees an even division of the stream. The use of the stream divider also guarantees an even distribution of the stream of the given carrier gas between chambers, in which the processes of barbotage or permeation occur. The module of the carrier gas stream divider has another output for the carrier gas, which leads to the unit of mixture humidity determination (ZUW). When the carrier gas passes from the stream divider to appropriate barbotage (KB) or permeation chambers (KP), the amount of gas introduced into each chamber is regulated with the use of independently controlled mass flow regulators (MRP). The accuracy of regulation of the carrier gas flow has a significant and direct influence on the accuracy of the concentration obtained. In order to do that, mass flow regulators were used, which are characterised by the highest quality of operation. To provide a constant and controllable temperature in the chambers within the range between 0°C and 60°C, in which there is a transfer of analytes from the liquid to gas phase, the following procedures were adopted:

- within the range between 0°C and 20°C – thermostatic with the use of Peltier modules or a refrigerator,
- within the range between 20°C and 60°C – thermostatic with the use of Peltier modules or heaters made of a resistance wire.

Temperature regulation in each barbotage chamber in Figure 3 is marked as RTKB, while in permeation chambers, it is RTKP. The use of indices from 1 to N (Fig. 3) allows for the identification of further barbotage or permeation chambers.

The humidity determination unit (ZUW) is used for obtaining a constant and determined value of relative humidity for the gas mixture prepared. In order to do that, the diluting gas is passed over or through water or hygrostatic solution as the vapour pressure above specific saturated water solutions of salts of non-organic compounds is constant at the given temperature. The determination of the value of relative humidity of a gas mixture in the mixing chamber is done by changing the stream of the diluting gas passing over or through a hygrostatic solution and by changing the temperature of the chamber containing a hygrostatic solution or water. The temperature of a vessel filled with a hygrostatic solution or water is regulated with the use of a thermostat within the range of temperatures between about 20°C and 60°C. In the humidity determination unit (ZUW), the dividing valve (ZR) is used to change the direction of the diluting gas passing over a chosen hygrostatic solution or water. The stream of a diluting gas is determined with the use of a mass flow regulator.

The reference gas mixture mixing unit (ZM) consists of a mixing chamber and a container allowing for the compensation of analyte concentrations in a given gas mixture. It was also equipped with additional connections to an E-nos instrument, Tedlar bags or an olfactometric stub pipe. The temperature of the gas mixture located in the mixing chamber is regulated with the use of a thermostat, which allows for the regulation of a temperature within the range between 20°C to about 60°C. The use of separate, thermostatic mixing chambers allows for obtaining a constant temperature gradient, which prevents water condensation in pneumatic units.

All elements used to regulate the temperature, regulators of mass flow and hygrometers are connected to a central microprocessor driver with electrical wiring. Using such a connection allows for controlling the device operation with the use of an operator panel. Figure 4 shows a block diagram of the steering unit used in the reference gas mixture generator. The generator may be controlled with the use of a PC.

4. CONCENTRATIONS OF REFERENCE GAS MIXTURES OBTAINED WITH THE USE OF BARBOTAGE AND PERMEATION PROCESSES

On the basis of the tool presented, which is based on the barbotage and permeation processes, the concentration of each component of a reference gas mixture may be established.

In the equations presented below, in which a way of expressing concentrations was described, the constants are applicable at the temperature of 20°C.

A concentration of a given component in the mixing chamber, which is obtained as a result of a barbotage process, may be described with the use of the following equation (6):

$$C_1 = \frac{9{,}868 \cdot 10^3 P_s^o Q_1}{\sum Q} \tag{6}$$

where: C_1 [ppm volume] – the concentration of a given component in the mixing chamber obtained in a process of barbotage, P_s^o [Pa] – the vapour pressure of a saturated substance at the temperature of 20°C, Q_1 [ml/s] – the volumetric flow rate of a carrier gas passing through a given substance located in the barbotage drilling fluid, $\sum Q$ [ml/s] – the sum of all streams entering the mixing chamber.

A concentration of a component in the mixing chamber obtained in the process of permeation may be described with the use of the following equation (7):

$$C_2 = \frac{24{,}04 \cdot 10^9 E_n}{M_n \sum Q} \tag{7}$$

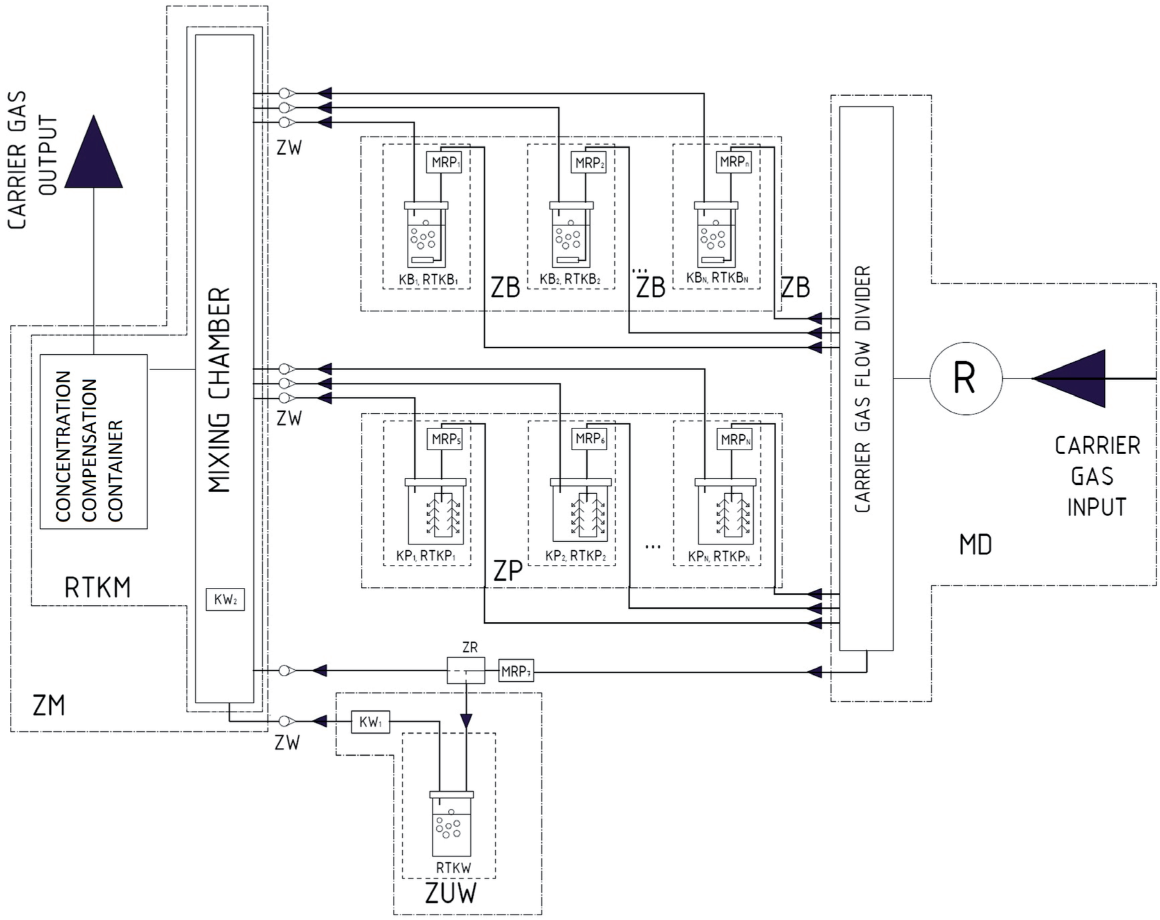

Figure 3 A block diagram showing the arrangement of pneumatic elements used in the reference gas mixtures generator

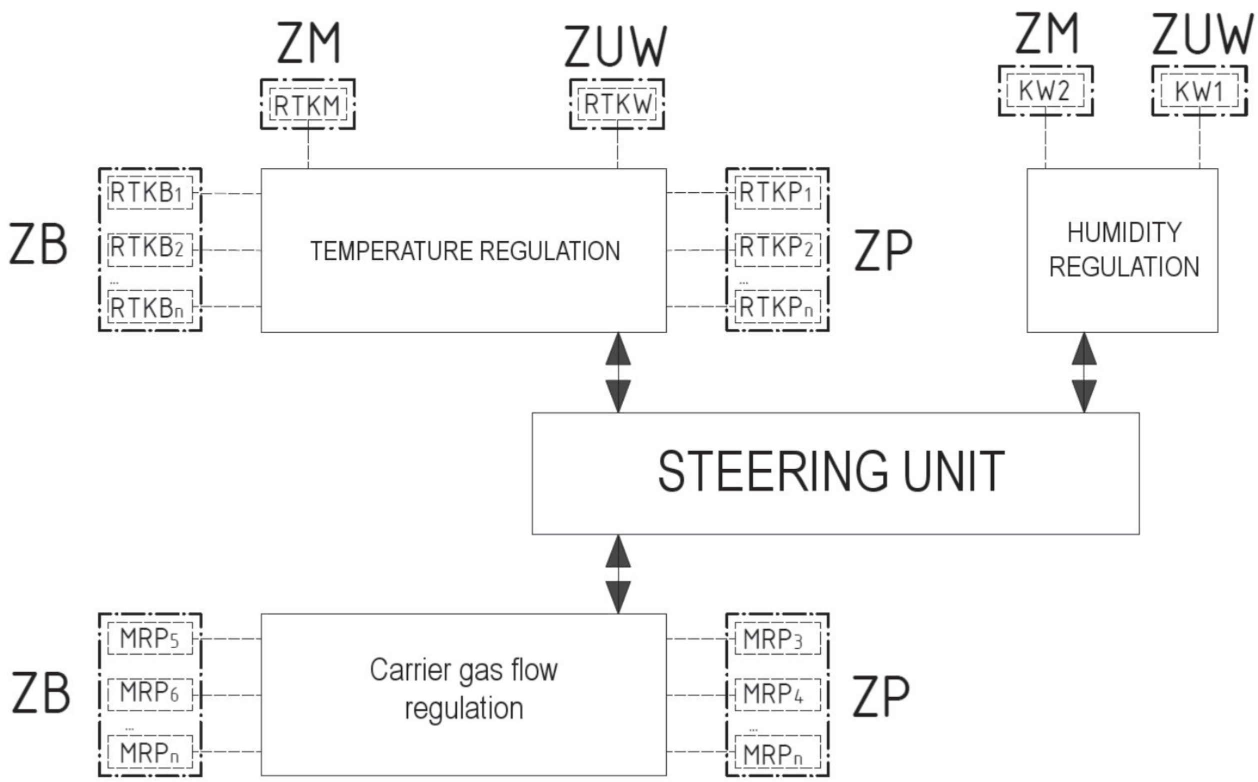

Figure 4 A block diagram of the steering unit of the reference gas mixture generator

Description of designations used in Figure 3 and Figure 4:
ZB – the barbotage unit, ZP – the permeation unit, ZM – the mixing unit, ZUW – the humidity determination unit, MD – the air distribution module, KB_1, KB_2 ... KB_N – the chambers, in which the process of barbotage occurs, KP_1, KP_2 ... KP_N – the chambers, in which the process of permeation occurs, $RTKB_1$, $RTKB_2$ ... $RTKB_N$ – independent regulation of the samples temperature in each chamber, in which the process of barbotage occurs, $RTKP_1$, $RTKP_2$ ... $RTKP_N$ – independent regulation of the samples temperature in each chamber, in which the process of permeation occurs, RKTM – independent regulation of the temperature of a gas mixture in a mixing chamber, RTKW – independent regulator of the temperature of a gas mixture in a chamber of the carrier gas humidity determination, MRP_1, MRP_2 ... MRP_N – the mass flow regulators, ZW – the check valves, ZR – the dividing valve, KW_1, KW_2 – the humidity controllers, ZPP – the air preparation unit.

where: C_2 [ppm volume] – the concentration of a given component in the mixing chamber obtained in the process of permeation, M_n [g/mol] – the molar mass of a given component of the reference gas mixture, E_n [g/s] – the permeation rate for a given component of the reference gas mixture.

A concentration of water vapour in the mixing chamber, which is obtained as a result of the process of passing of a stream of dry air over or through a hygrostatic solution or water, may be described with the use of the following equation (8):

where: C_w [ppm volume] – the concentration

$$C_w = \frac{9{,}868 \cdot 10^3 P_w^o Q_w}{\sum Q} \qquad (8)$$

of the water vapour in the mixing chamber, obtained as a result of the process of passing of a stream of dry air over or through a hygrostatic solution or water, P_w^o [Pa] – the saturated water vapour pressure at the temperature of 20°C, Q_w [ml/s] – the volumetric flow rate of a carrier gas passing through or over a hygrostatic solution or water.

5. SUMMARY

The generator of reference gas mixtures is an instrument for dynamic preparation of reference gas mixtures, the composition of which may be similar to the composition of real-life samples (the atmospheric air). The concentration of analytes obtained in a reference gas mixture depends on the volumetric flow rate of a gas carrier in the pneumatic system, the volumetric flow rate of the diluting gas stream and the temperature of the chambers, in which the processes of barbotage and permeation occur. The generator allows for introducing the desired amounts of water into the prepared gas mixture. The electronic system of controlling the operating parameters allows for automatic regulation of volumes of stream flows and the temperature. The solution presented allows for the preparation of reference gas mixtures, in which the measured components may occur in a wide range of concentrations.

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