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Using chromatography – desorption method of manufacturing gas mixtures for analytical instruments calibration

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Abstract. In this paper, the chromatography desorption method of obtaining gas mixtures of known compositions stable for a time sufficient to calibrate analytical instruments is considered. The comparative analysis results of the preparation accuracy of gas mixtures with volatile organic compounds using diffusion, polybarbotage and chromatography desorption methods are presented. It is shown that the application of chromatography desorption devices allows one to obtain gas mixtures that are stable for 10…60 hours in a dynamic condition. These gas mixtures contain volatile aliphatic and aromatic hydrocarbons with a concentration error of no more than 7%. It is shown that it is expedient to use such gas mixtures for analytical instruments calibration (chromatographs, spectrophotometers, etc.)

1. Introduction

To analyze the qualitative and quantitative compound of gas substances of natural and technogenic origin by instrumental methods, it is necessary to use graduation gas mixtures (GGM) with the known concentration of components. This fact is conditioned by the needs of not only metrological estimation of measurements and calibration of gas analytical equipment, but also by the need of creating model mixtures for accelerated testing and study of a number of chemical reactions and technological processes, of creation of artificial atmospheres and other tasks.

The increase in the methods of preparation of GGM is associated with today’s stricter requirements for the control of the environment contamination. The research of the authors dealing with these problems is devoted to the creation of new instrumental and methodological solutions aimed at improving the accuracy of maintaining the composition of calibration gas mixtures prepared by known methods. Particular attention is paid to the certification of the methods for preparing gas mixtures and studying the stability of the gas mixtures composition during storage and operation of the reference sample [1 - 5]. The EU has developed and operates a set of normative acts regulating the preparation of GGM in the standard range of concentrations [6], among which the manometric and the gravimetric methods are the most popular.
The manometric method is based on an accurate dosing of the components of the gas mixture at a certain pressure in the vessel. The gas pressure in the vessel is determined by means of a precision manometer. The composition of the mixture is calculated following the equations of pure gases state and gas mixtures. However, due to the influence of various factors (molecular, electrostatic interactions, the formation of hydrogen bonds, quantum effects, etc.), the real gas mixtures differ from the ideal, which makes it necessary to use computer systems and programs for controlling the mixture preparation [7 - 8]. When implementing standard procedures, the improvement of the accuracy of the GGM composition is important.

The gravimetric method makes it possible to avoid the errors associated with the selection and accurate metering of components and errors that occur when measuring pressure and volume. This method is based on the sequential introduction of the gas mixture components, weighted with high accuracy, into the vessel. When combining a gravimetric method with a dynamic dilution of the flow, it becomes possible to expand significantly the range of operating concentrations [9 - 12], but the accuracy of the method is limited by the accuracy of the weights, to which the high loads work requirements are applied, and the operator's qualification.

A common method of obtaining GGM is a static gas extraction, which uses the distribution of the target components between the liquid and the gas phases in a closed system. With a sufficiently large number of target components in a liquid phase, the specified concentrations of these components in the gas phase are kept constant due to the dynamic equilibrium between phases, even with appreciable adsorption of the components of the gas phase by the walls of the vessel [13, 14]. But at the present time there is no information about the distribution coefficients of a wide range of volatile organic substances in liquid-gas systems, which limits the spread of this method in analytical practice. The dynamic realization of the method is based on the introduction of the target components into the diluent gas stream, which is pure air or an inert gas (carrier gas).

The disadvantage of the method is the length of the production of the GGM with low concentrations of the target components, as well as an increase of the error of the GGM as it is diluted. The method of mixing flows is based on the mixing and dilution of several gas streams, the speed of which is known and controlled by the corresponding flowmeters. In practice, the degree of dilution is limited by the technical characteristics of the measuring instruments and the design features of the gas mixing plant [16 - 17].

A wide range of devices for obtaining GGM by dynamic thermos diffusion is presented on the world market, devices and methods of instrumental implementation of which are diverse and provide the possibility of obtaining poly-component gas mixtures, including reactive compounds. In Russia, the vapor-phase sources of gas mixtures, a thermos-diffusion generator of gas mixtures "Microgas", calibration gas mixtures in balloons are the most popular.

However, the expediency of their use is limited by the following main drawbacks: to prepare a gas mixture with different concentrations of the components, it is necessary to use the equipment for precise dilution of the gas flows or to use several sources of gas components. Besides, they are intended for the production of mono-component gas mixtures, which considerably the complicates the multicomponent grading and makes it more expensive; these sources are often unsuitable for obtaining gas mixtures of aggressive and corrosive compounds due to the instability of their composition over time, which causes a short period of their storage. The complexity of using such mixtures in the field conditions is stipulated by the inability to store them even for an insignificant period of time due to adsorption losses.
2. Description of the chromatographic desorption method
The methods of the continuous gas extraction are free from the aforementioned shortcomings [13, 19]. The chromatography-desorption method makes it possible to obtain gas mixtures of the 2nd level. It is characterized by the simplicity of the instrumental design, the accuracy and the economy. The method is based on the equilibrium saturation of the inert gas flow by volatile organic compounds (VOC) as it passes through the chromatographic desorption system (Figure 1), which presents tubular flow container 2 connected to gas flow regulator 1 and placed into thermostat 4. A tubular flow container is filled with a sorbent with a known amount of VOC. Such systems can be miniaturized, which makes them irreplaceable in the conditions of a non-laboratory or a field analysis. It also minimizes the use of organic solvents.

![Figure 1. A schematic diagram of the chromatographic desorption device. 1 - Gas flow regulator; 2 – Tubular flow container filled with sorbent; 3 – Flowmeter; 4 - Thermostat; \(C_0\) is the flow of the pure inert gas; \(C_x\) is the flow of a gas mixture "an inert gas-analyte"](image)

The process of obtaining gas mixtures by a chromatographic-desorption method is carried out in two stages: 1 - chromatographic-sorption stage consists of the equilibrium saturation of the VOC sorbent at a temperature above the operating temperature of the system; 2 - chromatographic desorption stage consists of the desorption of VOC during the inert gas flow through the system at a temperature below the saturation temperature. Thus, the value of the distribution constant of substances in the sorbent-gas system is being regulated. It ensures the production of flows with a specified VOC content without the additional dilution or the change of other parameters. The regularities of the chromatographic desorption method are well described within the limits of the theory of the adsorption equilibrium concentration method [13]. In [18], the practical realization of the chromatographic-desorption process for obtaining mono- and poly-component gas mixtures containing micro concentrations of aliphatic hydrocarbons, polar, aromatic and halogen-containing organic compounds is shown.

3. The experimental part
Table 1 presents the comparison of the accuracy of preparation of mono- and poly-component gas mixtures of VOC with use of polyabarbotage (PB) and chromatographic desorption (ChDS) methods.

To estimate the accuracy of the gas mixtures preparation, the gas mixtures obtained by means of a thermos-diffusion generator of gas mixtures "Microgas" were chosen as sample gas mixtures.

| VOC       | \(C_{G_{m}}\), mg/m³ | Polyabarbotage (PB) method | Chromatography-desorption (ChDS) method |
|-----------|-----------------------|----------------------------|----------------------------------------|
|           | \(\delta_{1}\), %    | \(\tau_{1}\), h            | \(\delta_{1}\), %    | \(\tau_{1}\), h            | Weight of nonvolatile liquid, g | Weight of nonvolatile liquid, g |
|           |                       |                           |                          |                          | \(\tau_{1}\), day'          | \(\tau_{1}\), day'            |
| Mono-component mixtures |                     |                           |                          |                          |                            |                            |
| benzene   | 0.24                  | 3                         | 10                       | 7                        | 4                          | 12                          |
| toluene   | 0.07                  | 5                         | 50                       | 167.4                    | 7                          | 6                          | 48                          |
| ethyl-    | 0.15                  | 5                         | 30                       | 10                       | 5                          | 30                          | 17.8                        | >90                          |
Poly-component mixtures

|                | benzene | n-hexane | n-octane |
|----------------|---------|----------|----------|
| benzene        | 0.24    | 5        | 10       |
| toluene        | 0.07    | 6        | 50       |
| ethyl-benzene  | 0.15    | 5        | 30       |
| n-hexane       | 0.20    | 7        | > 60     |
| n-octane       | 0.03    | 7        | > 60     |

*storage time of the working system (storage conditions: the impermeability of the vessels, the normal pressure and humidity, T = 23±2°C), the system is assumed to be stable at up to 10% of its composition change.

As it is seen from the presented data, both methods allow one to obtain gas mixtures which are stable for \( \tau = 10 \ldots 60 \) hours, with the accuracy of preparation \( \delta = (3 \ldots 7)\% \). Figure 2 shows the dependence of correlation coefficient \( K_R \) of the linear calibration function obtained with the use of polyabarbotage and chromatographic desorption systems for the generation of gas mixtures in the concentration range of 0.1...10 mg/m\(^3\) with the help of which the gas chromatograph "Kristall-5000.1" (produced by the plant "Chromatek") with a flame ionization detector was calibrated.

**Figure 2.** Dependence of correlation coefficient \( K_R \) of the linear calibration function obtained with the use of polyabarbotage (a) and chromatographic desorption systems (b)

As it can be seen from the presented data, both methods make it possible to obtain stable gas mixtures to further calibrate the analytical instruments, as indicated by the proximity of the correlation coefficient of the calibration function to 1. However, the CDS method has an advantage of 5 ... 10\%, which is important when working with a low concentration of GGM.

**4. Discussion**

For the purpose of obtaining of the same volume of calibration gas mixtures, the chromatographic-desorption method needs 10 times less reagents compared to the polyabarbotage method, there is no
need to utilize waste solutions, which corresponds to the principles of the "green" chemistry. Systems CDS are stable during storage for at least 3 months, the calibration error for the CDS systems is 5 ... 10% lower.

Besides, the possibility of obtaining poly-component gas mixtures in one cycle, the simplicity of the instrumental design and of the operation present an important advantage. It opens the possibility to use the chromatographic-desorption method in non-laboratory conditions. The chromatographic desorption devices can be miniaturized. A medical needle, when used as a tubular flow container (discrete-type chromatography-desorption microsystems) or microfluidic systems [20], presents examples of such use.

At the same time, an important factor determining the capacity of the system is not only the properties of the sorbent, but also the dead volume due to the ratio of the geometric dimensions of the container and sorbent particles. In general, the trend of miniaturization is inherent to all areas of the analytical chemistry development, since a methodical and instrumental basis for the implementation of the "in situ" analysis is created this way.

5. Conclusion

The improvement of the methods of gas mixtures preparation of the known composition has recently become one of the trends of the analytical chemistry. At the same time, the requirements imposed on them are becoming tougher: in addition to the accuracy and the reproducibility of the results, the miniaturization, the automation and the compliance with the principles of the "green" chemistry are important. By the number of its advantages, the dynamic methods of obtaining gas mixtures of a known composition are the most popular methods today.

It should be noted that while solving complex analytical problems, it is necessary to take into account the individual features of a particular case, choosing not only the most expedient method of graduation, but also the method of preparation of graduation mixtures, which makes it possible to obtain the standard samples that are closest in both composition and matrix.

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References

[1] McKinley J and Majors R E 2000 A Question of Traceability LC-GC Europe 13 892
[2] Slominska M, Koniczka P, and Namiesnik J 2010 Trends Anal Chem 29(5) 419
[3] Slominska M, Koniczka P, and Namiesnik J 2014 Trends Anal Chem 62 135
[4] Rhoderick G C 2013 Anal Bioanal Chem 405(1) 369
[5] Harsch D E 1980 Atmos Environ 14(9) 1105
[6] International standard Gas analysis - Preparation of calibration gas mixtures using dynamic volumetric methods 1-10 ISO 6145
[7] Hu S, Wu H, Wang D, and Li J 2013 J. of the Int. Measurement Confederation 46(3) 1084
[8] Richter M, Jann O, Horn W, Pyza L, and Wilke O 2013 Gefahrstoffe Reinhaltung der Luft V73(3) 103
[9] Brewer P J, Brown R J C, Miller M N, Minarro M D, Murugan A, Milton M J T, and Rhoderick G C 2014 Anal Chem 86(3) 1887
[10] Matsumoto N, Shimosaka T, Watanabe T, and Kato K 2008 Anal Bioanal Chem 391(6) 2061
[11] Haffkenscheid T, Baldan A, Quincey P, Gerboles M, and Saunders K A 2005 Atmos Environ 39(21) 3947
[12] Milton M J T, Vargha G M, and Brown A S 2011 Metrologia 48(5) 1
[13] Vitenberg A G, Efremova O V, and Kotov G N 2002 Russ J Appl Chem 75(1) 39
[14] Morris C, Berkeley R, and Bumgarner J 1983 Anal Lett 16 1585
[15] Greenhouse S, and Andrewes F 1990 Anal Chim Acta 236 221
[16] Talbert B, Benesch R, Haouchine M, and Jacksier T 2004 LCGC North America 22(6) 562
[17] Kim M E, Kim Y D, Kang J H, Heo G S, Lee D S, and Lee S 2016 Talanta 150 516
[18] Platonov I A, Kolesnichenko I N, and Lange P K 2017 Measurement Techniques 59(12) 1330-1333
[19] Slominska M, Koniecza P, and Namiesnik J 2014 Trends Anal Chem 62 135
[20] Platonov I A, Kolesnichenko I N, Novikova E A, Pavlova L V, Lobanova M S, and Mikheenko A E 2017 Measurement Techniques 60(8) 848-852