

# Gas Extraction Generation of Gas Mixtures of Polar Organic Compounds at the Level of Trace Concentrations

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Received April 18, 2023; revised May 10, 2023; accepted May 10, 2023

**Abstract**—The generation of gas mixtures of polar organic compounds at the level of their maximum permissible concentrations (several  $\mu\text{g}/\text{m}^3$ ) by continuous gas extraction from aqueous solutions with known concentrations in combination with dilution with a diluent gas flow was studied. The distribution coefficients of phenol, isomeric cresols, nitrobenzene, and  $\text{C}_4$ – $\text{C}_6$  alkanols between aqueous and gas (nitrogen) phases necessary for this study were determined. A two-stage generation technique based on the saturation of a sorbent (activated carbon) with an extractant gas flow with a given concentration of target components followed by their desorption by a flow of pure extractant gas was proposed.

**Keywords:** gas mixtures, generation, continuous gas extraction, distribution coefficients in the aqueous phase–gas phase system, volatile organic compounds

**DOI:** 10.1134/S1061934824030110

Currently, there are no ready-made methodological solutions and means for obtaining standard gas mixtures (SGMs) with concentrations of volatile organic compounds (VOCs) at a ppb ( $\mu\text{g}/\text{m}^3$ ) level. It is necessary to evaluate the trueness of techniques for determining highly toxic organic compounds, such as phenols and aliphatic  $\text{C}_4$ – $\text{C}_6$  alcohols, in air at the level of their maximum permissible concentrations (MPCs) based on the results of analysis of liquid media into which the analytes were extracted. However, extrapolation of the established patterns of pre-concentration in air analysis to the region of lower analyte concentrations is incorrect because the recovery at the stages of sorption and desorption and the manifestation of a memory effect depend on the concentrations of the analytes [1]. Among the variety of methods used for preparing SGMs [2, 3], equilibrium dynamic methods based on an equilibrium distribution of target components between gas and condensed (liquid or solid) phases have undeniable advantages from the point of view of minimal time consumption and labor intensity in relation to the generation of SGMs with trace concentrations of VOCs [4, 5].

The simplest choice for the technical implementation of the above methods is continuous gas extraction (CGE), which consists in passing a relatively slow flow (to ensure interphase equilibration) of extractant gas through the volume or above the surface of the condensed phase with a certain concentration of target components. Under certain conditions, the concentrations of the target components in the outgoing

extractant gas stream remain almost constant. Continuous gas extraction is simple and well studied; there are certified devices for its implementation, so-called headspace sources of gas mixtures (HSGMs), the use of which is included in the state verification scheme for instruments measuring the concentrations of components in gaseous media [6]. The disadvantages of traditional CGE versions include relatively small volumes of generated SGMs with a constant concentration of target components and low volumetric flow rates of the generated mixtures. In addition, HSGMs are non-renewable and non-repairable products, which provide gas mixtures with analyte concentrations starting from  $0.5 \text{ mg}/\text{m}^3$  [7], which is significantly higher than the MPCs of many highly toxic VOCs.

Some of the disadvantages of the traditional technique of continuous gas extraction implemented in HSGMs have been overcome in other equilibrium methods for generating SGMs: chromatomembrane [8, 9] and chromatodesorption methods [10, 11]. However, these methods are characterized by the complexity of the hardware design, and they require the use of commercially unavailable devices.

The purpose of this work was to develop a methodological basis for the generation of gas mixtures of polar VOCs at the level of their MPCs (several  $\mu\text{g}/\text{m}^3$ ) using the continuous gas extraction of VOCs from aqueous solutions with known concentrations in combination with dilution with a flow of diluent gas.

## THEORY

The principles of CGE have been studied in detail in connection with its widespread use in headspace gas-chromatographic analysis of liquids [12, 13]. The recovery of VOCs is determined primarily by the distribution coefficients  $K$  of target components between the liquid and gas phases and the relative volatility  $F$  of the liquid in which they are dissolved:

$$K = \frac{c_L}{c_G}, \quad F = \frac{p_L^0 M}{RT \rho_L},$$

where  $c_L$  and  $c_G$  are the equilibrium concentrations of a component in the liquid and gas phases, respectively, mol/L or g/dm<sup>3</sup>;  $p_L^0$  is the saturated vapor pressure of the liquid (Pa) at a given temperature  $T$ , K;  $M$  is the molar mass of the liquid, g/mol;  $R$  is the universal gas constant, Pa dm<sup>3</sup> mol<sup>-1</sup> K<sup>-1</sup>; and  $\rho_L$  is the density of the liquid, g/L. The quantities  $K$  and  $F$  are dimensionless.

In the case of highly volatile liquids ( $KF > 1$ ), passing an extractant gas flow through the liquid leads to an increase in the concentration of the target component due to intense evaporation of the liquid and, accordingly, a decrease in its volume. Evaporation can be prevented by initially saturating the extractant gas flow with the vapor of the liquid by passing it through a vessel with this liquid. On the contrary, if  $KF < 1$ , the concentration of the target component inevitably decreases in the course of CGE. Finally, if  $KF = 1$ , the concentration of the target component in the process of CGE remains constant and theoretically creates the most favorable conditions for the generation of an SGM. However, it is very rarely possible to select a suitable liquid that would meet the specified condition, and, if it is possible, the vapor concentration of the liquid itself in the generated SGM is too high to use it for monitoring the trueness of procedures for the determination of VOCs in air at the MPC level [14]. For this reason, it seems to us more rational to use a two-stage technique based on a combination of continuous gas extraction of VOCs with dilution of the main extractant gas flow with an additional flow of pure diluent gas in order to obtain SGMs with trace concentrations of analytes.

The following well-known equation [12] describes the regularities of CGE from a relatively nonvolatile liquid solution of components having  $K > 100$ :

$$c_G = c_G^0 \exp\left(-\frac{v_G}{KV_L}\right), \quad (1)$$

where  $c_G^0$  and  $c_G$  are the concentrations of the target component in the extractant gas flow at the initial point in time and after passing the extractant gas volume  $v_G$ , respectively;  $V_L$  is the volume of the liquid solution. As follows from Eq. (1), the greater  $K$ , the lower the degree of a decrease in the component concentration as the extractant gas flow is passed through

and, accordingly, the greater the volume of the resulting SGM with a conditionally constant component concentration.

The need to ensure an equilibrium distribution in CGE limits the gas flow rate and makes necessary a high degree of gas dispersion in the liquid. The possibility of fog and foam formation and spray entrainment complicates the design of the equipment used; however, these processes are typical for very high extractant gas flow rates (higher than 0.5 L/min). It is advisable to use continuous gas extraction to obtain SGMs of substances with high distribution coefficients ( $K > 500$ ).

Water is the most suitable liquid for generating SGMs of polar VOCs. In the aqueous phase–gas phase system,  $K \gg 10^3$  for aliphatic alcohols, and  $K \gg 10^4$  for phenols; this creates the necessary prerequisites for obtaining sufficiently large volumes of SGMs with a constant concentration of analytes. On the other hand, the nature of the extractant gas itself has almost no effect on the value of  $K$  because the interaction of molecules in an ideal gas is reduced to elastic collisions. This circumstance makes it possible to use purified laboratory air or nitrogen as the cheapest inert gas to generate SGMs.

## EXPERIMENTAL

*Equipment and Reagents*

Reagents of at least analytical grade were used. Aqueous solutions of phenols and alcohols were prepared by the volumetric weight and volumetric volume methods, respectively, using Light pipette dispensers (Thermo scientific, the United States) and a VL-21 analytical balance (Gosmetr, Russia). Time was measured using a stopwatch. In the generation of gas mixtures and determination of the distribution coefficients of analytes in the liquid–gas system, the extractant gas flow was set using a Chromatec-Kristall FGP gas flow generator (Chromatec, Russia) and passed through aqueous solutions of analytes with known concentrations. In the former case, Zaitsev's device, which was filled with 4 mL of solution, was used; for the generation of gas mixtures, 1 L of solution was in a glass bottle (the height of a liquid column was 20 cm) equipped with a stopper with two outlet tubes. The inner diameter of the tube through which the extractant gas flow was supplied was 3 mm. The vessels with solutions were placed in a LOIP LB 200 circulating liquid thermostat (LOIP, Russia), which maintained the temperature with an accuracy of  $\pm 0.1^\circ\text{C}$ . If necessary, the flow of an extractant gas through the vessels was monitored with a soap-film flow meter.

A Kristall 5000.2 chromatograph (Chromatec, Russia) equipped with a flame ionization detector and a BPX-1 (100% dimethyl polysiloxane) capillary column (10 m  $\times$  0.53  $\times$  2.65 mm) was used for the gas chromatographic determination of test substances in

**Table 1.** Distribution coefficients of volatile organic substances in the aqueous solution–nitrogen system at 25°C depending on their concentrations (mg/L) in solution with separate (;) and joint (+) presence in solution ( $P = 0.95$ ;  $n = 4$ )

Concentrations of phenol and <i>o</i> -cresol in solution	$K \times 10^{-3}$		Concentrations of 1-butanol and 1-pentanol in solution	$K$	
	phenol	<i>o</i> -cresol		butanol-1	pentanol-1
30; 30	47.9 ± 1.9	19.5 ± 0.2	1.00; 1.00	3100 ± 110	2040 ± 160
30 + 30	48.2 ± 1.8	19.4 ± 0.3	1.00 + 1.00	3020 ± 160	2020 ± 110
100; 100	48.6 ± 2.0	19.9 ± 0.2	10.0; 10.0	3050 ± 180	2010 ± 50
100 + 100	48.7 ± 2.3	19.8 ± 0.3	10.0 + 10	3020 ± 150	2050 ± 70
300; 300	47.8 ± 1.8	19.5 ± 0.2	100; 100	3040 ± 60	2030 ± 40
300 + 300	48.5 ± 2.2	19.5 ± 0.2	100 + 100	3010 ± 50	2030 ± 60

the flow of an extractant gas. The extractant gas samples were taken into the chromatograph using an automatic heated sampling valve at regular intervals of 2 min. The HPLC determination of phenols was performed on a Shimadzu LC-20 Prominence liquid chromatograph with a Shimadzu RF-20A fluorimetric detector (Shimadzu, Japan) and a chromatographic column (250 × 4.6) mm packed with Supelco Discovery C<sub>18</sub> sorbent with a particle size of 5 μm. The temperature was 35°C, the excitation wavelength was 215 nm, the emission wavelength was 300 nm, and the sample loop volume was 20 μL.

#### *Determination of Distribution Coefficients in the Liquid–Gas System*

Gas extraction generation of SGMs involves the use of information on the distribution coefficients  $K$  of analytes between the liquid and gas phases. The value of  $K$  was determined by the decrease in the concentration of test substances in a model aqueous solution located in a bubbler (Zaitsev's device) after passing a certain extractant gas volume through it according to the well-known formula [15]

$$K = \frac{V_G}{V_L \ln \frac{c_L^0}{c_L}} - \frac{V_G}{V_L},$$

where  $V_G$  is the gas phase volume in the bubbler. The ratio of analyte concentrations in the solution ( $c_L^0/c_L$ ) was replaced by the corresponding ratio of the peak areas of the test substances in the chromatogram upon gas chromatographic analysis of an aqueous solution before and after passing a given extractant gas volume  $v_G$ . The random error  $\varepsilon$  in the determination of  $K$  was calculated using the following well-known [16] formula:

$$\varepsilon = \pm \frac{t(P, n)s}{\sqrt{n}},$$

where  $t$  is the Student coefficient, which depends on the confidence level  $P$  and the number of parallel determinations  $n$ , and  $s$  is standard deviation.

## RESULTS AND DISCUSSION

Preliminarily, we experimentally determined the distribution coefficients of the target components in the liquid–gas system; these coefficients do not depend on the concentration in an aqueous solution (Table 1), and this fact indicates the fulfillment of Henry's law [12]. In addition, if the concentrations of components did not exceed (100–300) mg/L, their distribution coefficients were not affected by the mutual presence of the components. This creates the necessary prerequisites for the generation of multi-component SGMs with predetermined concentrations of target components by the CGE method.

It was established that the flow rate of the extractant gas has almost no effect on the concentration of analytes in a gas phase if this flow rate does not exceed 200 mL/min. Table 2 summarizes the concentrations of analytes in aqueous solutions required to obtain SGMs with concentrations of 1 mg/m<sup>3</sup> and 10 ppb and maximum permissible concentrations in atmospheric air [14], which were calculated based on the distribution coefficients. As follows from Table 2, aqueous solutions of analytes with extremely low concentrations of components are required to prepare SGMs at the MPC level; at these concentrations, the negative effect of the adsorption of analyte molecules on the walls of vessels used to prepare solutions by repeated dilution begins to affect. In addition, there is a possibility of their volatilization in the course of this dilution. In contrast to the works [7, 13, 17] in which a traditional procedure was implemented for continuous gas extraction, we think it is more preferable to use a procedure for obtaining SGMs based on the dynamic dilution of a more concentrated SGM generated with a flow of purified laboratory air or nitrogen by a factor of (10–100). A procedure of this kind can be easily implemented using a two-channel gas flow former (Fig. 1). Because the distribution coefficients of ana-

**Table 2.** Required concentrations of volatile organic substances in aqueous solutions for the gas-extraction generation of standard gas mixtures with certain concentrations of analytes and their distribution coefficients ( $K$ ) between the aqueous and gas (nitrogen) phases ( $n = 4$ ;  $P = 0.95$ )

Analyte	$K$ (25°C)	MPC, $\mu\text{g}/\text{m}^3$ [14]	Concentrations (mg/L) of analytes in aqueous solution for the generation of SGMs with given concentrations		
			1 mg/m <sup>3</sup>	10 ppb	MPC
Phenol	47900 ± 1800	10	48.6	1.87	0.486
<i>o</i> -Cresol	19500 ± 700	5	19.6	8.68	0.098
<i>m</i> -Cresol	41200 ± 1900	5	41.4	18.3	0.207
<i>p</i> -Cresol	39800 ± 1700	5	40.0	17.7	0.200
<i>n</i> -Butanol	3020 ± 120	100	3.01	0.091	0.301
Isobutanol	1630 ± 70	100	1.63	0.049	0.54
Pentanol	2030 ± 110	10	2.03	0.074	0.020
Isopentanol	1920 ± 80	10	1.92	0.070	0.019
<i>n</i> -Hexanol	1390 ± 60	200	1.38	0.057	0.274
Nitrobenzene	870 ± 40	8	0.87	0.046	0.007

lytes strongly depend on temperature, the vessel with generating solution was placed in a liquid thermostat, which is not shown in Fig. 1.

Despite the apparent simplicity of this dilution, in order to obtain reproducible results that comply with the laws of ideal gases, the diluent gas pressure at the inlet of the mixing chamber should be at least 30 kPa (0.3 atm) lower than the pressure in the vessel with a solution of the target component, from which the gas flow is supplied to the mixing chamber through a throttle. In this case, the concentration  $c_G$  of the target

component in the generated SGM flow after dilution can be calculated using the formula

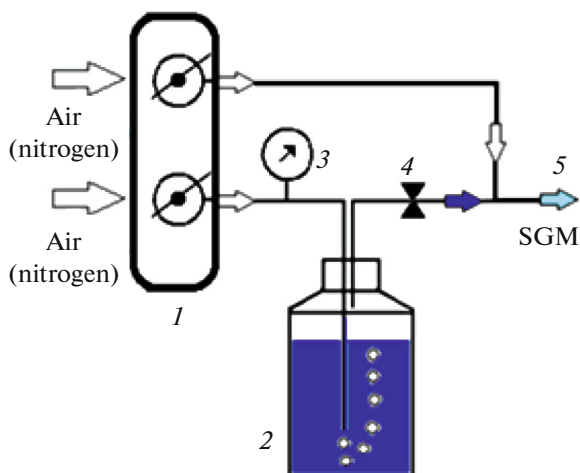
$$c_G = c_G^0 \frac{W_0}{(W_0 + W)} \frac{P_{\text{atm}}}{P_0}, \quad (2)$$

where  $c_G^0$  is the concentration of the target component at the outlet of the vessel with solution;  $W_0$  and  $W$  are the volumetric flow rates of air (nitrogen) passing through the analyte solution and the diluting flow, respectively; and  $P_{\text{atm}}$  and  $P_0$  are atmospheric pressure and pressure in the vessel with a solution of the target component.

To evaluate the trueness of the method developed for generating SGMs, we compared the concentrations of phenols in SGMs calculated using formula (2) and found experimentally. The determination method consisted in the sorption preconcentration of analytes from the SGM flow, the elution of sorbed phenols using an organic solvent, and the subsequent determination of analytes in the eluate by liquid chromatography with fluorimetric detection. Preconcentration was carried out in a column (3 × 0.3) cm packed with FAD active carbon with a particle size of (0.5–0.9) mm for 50 min. The extractant gas flow rate for phenols was set so that the sum of  $W_0$  and  $W$  was 400 mL/min. Desorption of phenols was carried out with 1.5 mL of acetonitrile. Previously, Vitenberg et al. [18] found that the quantitative extraction of phenols with a recovery of at least 97% occurred under the selected conditions. Experimentally, the concentrations of phenols in the SGMs were found using the formula

$$c_{G\text{exp}} = S_x c_L V_L / (S_{\text{st}} W_G t),$$

where  $S_x$  is the peak area of an analyte in the chromatogram after desorption;  $S_{\text{st}}$  is the peak area of the analyte in the analysis of its standard aqueous solution



**Fig. 1.** Schematic diagram of the generation of standard gas mixtures with dilution: (1) two-channel gas flow generator with two gas flow regulators; (2) vessel with an aqueous solution of the analyte; (3) deformation pressure gauge; (4) adjustable mechanical throttle; and (5) output of a standard gas mixture with the analyte.

**Table 3.** Calculated ( $c_{G\text{calcd}}$ ) and experimentally found ( $c_{G\text{expt}}$ ) concentrations of phenols in the generated standard gas mixtures ( $n = 4$ ;  $P = 0.95$ )

Analyte	$W_0$ , mL/min	$W$ , mL/min	$c_{G\text{calcd}}$ , $\mu\text{g}/\text{m}^3$	$c_{G\text{expt}}$ , $\mu\text{g}/\text{m}^3$
Phenol	40	360	$206 \pm 6$	$196 \pm 10$
<i>o</i> -Cresol	40	360	$472 \pm 14$	$442 \pm 22$
Phenol	8	392	$41.2 \pm 1.1$	$39.1 \pm 1.8$
<i>o</i> -Cresol	8	392	$94 \pm 3$	$88 \pm 4$

with the concentration  $c_L$ ;  $V_L$  is the volume of acetonitrile used for the desorption of phenol;  $W_G$  is the flow rate of the gas mixture through the sorption column; and  $t$  is the time of passing the gas mixture through the column.

The experimental results obtained (Table 3) indicated the trueness of the developed method for generating SGMs. The errors in calculated values were found based on the errors in determining the distribution coefficients of analytes.

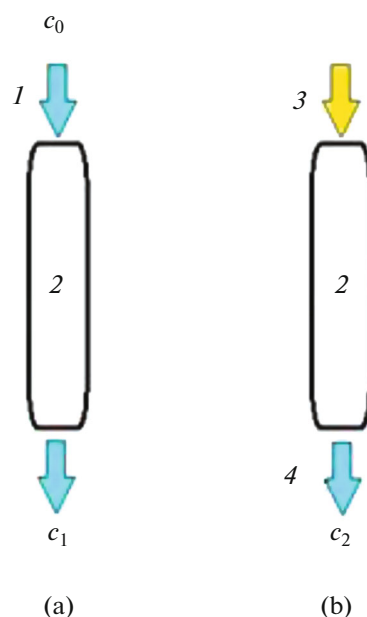
The considered generation method requires the use of special equipment and highly qualified personnel. From the point of view of practical implementation, a two-stage gas extraction—adsorption—desorption scheme for generating SGMs seems more rational. Its essence is that, at the first stage of gas extraction—adsorption, which is performed in a specialized laboratory, an SGM generated using the above dynamic gas extraction procedure with known concentrations of analytes is passed through a column packed with a sorbent until the complete saturation of this latter (Fig. 2). The saturation process is completed after the analyte concentration at the outlet of the sorption column ( $c_1$ ) is equal to the concentration at the inlet ( $c_0$ ). If a flow of pure gas is supplied to the inlet the sorption column after saturation (the stage of desorption), the analyte concentration at the column outlet ( $c_2$ ) will remain constant and equal to  $c_0$  for a sufficiently long time, which depends on the capacity of the sorbent.

Provided an air-tight sorption column, the time interval between stages can be several months. In this case, the temperatures of sorbent saturation and the subsequent generation of SGM should be as close as possible to each other. A similar principle of obtaining SGMs forms the basis for the functioning of the above headspace sources of gas mixtures (HSGMs). However, the obvious disadvantage of the latter, which is overcome in this work, is the impossibility of obtaining SGMs with predetermined concentrations of analytes, for example, at the MPC level.

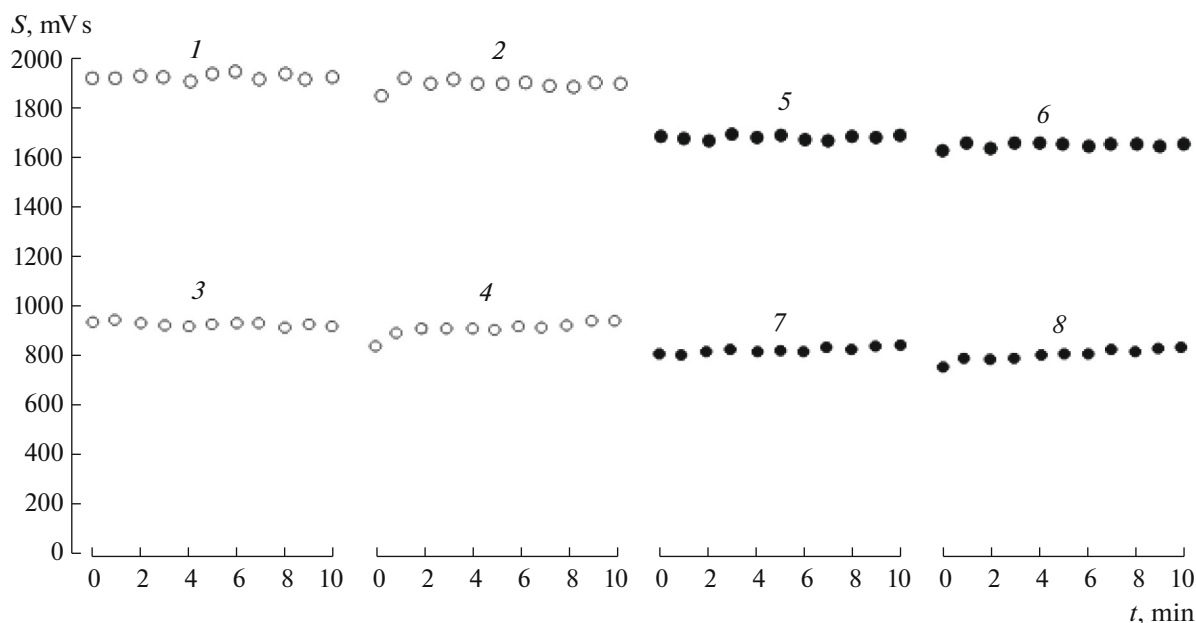
Figure 3 illustrates the capabilities of the proposed two-stage generation of SGMs. It shows the dynamics

of changes in the concentrations of phenol and butanol in a gas-phase flow at the outlet of the sorption column, or rather their peak areas in the chromatogram when analyzing this phase during saturation and the subsequent desorption. As can be seen in Fig. 3, the peak areas on saturation and the subsequent desorption were almost the same.

The relative non-excluded systematic error (RNSE) of the concentration  $\theta_r$  in an SGM generated by the proposed method consists of the RNSE of the measurement of the distribution coefficient of the analyte ( $\theta_r K = 0.05$ ), its concentration in the generating solution ( $\theta_r c_L = 0.02$ ), the flow rates  $W_0$  ( $\theta_r W_0 = 0.05$ ) and  $W$  ( $\theta_r W = 0.05$ ) upon dilution, and RNSE associated with concentration changes in time ( $\theta_r I =$



**Fig. 2.** Two-stage scheme for generating standard gas mixtures: (a) first stage (saturation) and (b) second stage (desorption); (1) input of a standard gas mixture; (2) sorption column; (3) clean gas inlet; and (4) output of a standard gas mixture.



**Fig. 3.** Dynamics of changes in the concentrations (peak areas in the chromatogram) of (1–4) phenol and (5–8) butanol in the gas phase flow at the outlet of the sorption column on (1, 3, 5, 7) saturation and (2, 4, 6, 8) desorption. The concentrations of the analytes in the gas phase were (1, 2, 5, 6) 20 and (3, 4, 7, 8) 10 mg/m<sup>3</sup>.

0.02) and with temperature inequality on saturation and desorption ( $\theta_r c(T) = 0.02$ ). With a confidence

probability of  $P = 0.95$ , the total RNSE can be estimated using the formula

$$\theta_r = 1.1 \sqrt{(\theta_r K)^2 + (\theta_r c_L)^2 + (\theta_r I)^2 + (\theta_r W_0)^2 + (\theta_r W)^2 + (\theta_r c(T))^2}.$$

Substituting the numerical values of the quantities included in this formula leads to  $\theta_r \approx 10\%$ , which can be considered a good result, taking into account the very low concentrations of analytes and the multi-stage procedure for preparing SGM. In the absence of temperature control, the error increases to (20–25)%. Such error values are comparable to the errors of HSGMs [19].

The most important characteristic of a device for generating SGMs is the maximum volume of the resulting SGM ( $V_G^{\max}$ ) with a permissible deviation of the actual concentration from the specified initial value. The volume of the gas flow the volatile content

of which decreases by no more than a given value ( $\delta$ ) is found according to the following formula known from the theory of dynamic gas extraction:

$$V_G^{\max} = -KV_L \ln(1 - \delta),$$

where  $V_L$  is the volume of the liquid phase, and  $\delta$  is the decrease in an analyte concentration (in fractions of the initial value). Table 4 summarizes the obtained experimental data.

Thus, the developed methods make it possible to generate up to several cubic meters of SGMs with analyte contents at the MPC level from just one liter of the generating solution.

**Table 4.** Maximum volumes (m<sup>3</sup>) of standard gas mixtures of analytes generated without dilution and with dilution of the main flow ( $V_L = 1$  L)

Analyte	Maximum volume without dilution		Maximum volume with dilution by a factor of 50	
	$V_G^{\max}$ for $\delta = 1\%$	$V_G^{\max}$ for $\delta = 3\%$	$V_G^{\max}$ for $\delta = 1\%$	$V_G^{\max}$ for $\delta = 3\%$
Phenol	0.489	1.481	24.5	74.1
<i>o</i> -Cresol	0.197	0.598	9.9	29.9
1-Butanol	0.030	0.092	1.5	4.6
1-Pentanol	0.020	0.062	1.0	3.1

## ACKNOWLEDGMENTS

This article is dedicated to the 300th anniversary of St. Petersburg State University.

## FUNDING

This work was supported by ongoing institutional funding. No additional grants to carry out or direct this particular research were obtained.

## CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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Translated by V. Makhlyarchuk

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