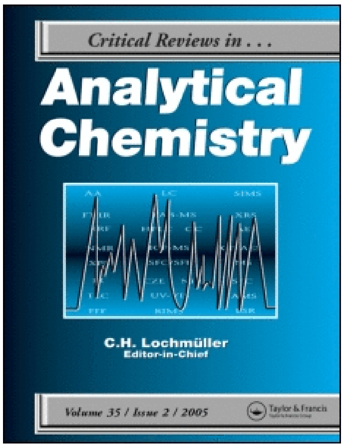

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Analytical Application of Liquid-Gas and Liquid-Gas-Solid Chromatography

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ABSTRACT: Physicochemical fundamentals of two new chromatographic methods—the liquid-gas (LGC) and the liquid-gas-solid chromatography (LGSC) are stated. The mechanism of the stationary gas phase retention in the pores of hydrophobic supports is explained and practical results of the effect obtained are considered. Examples of the LGC and LGSC application for preconcentration of gases and volatile organic compounds dissolved in water are discussed. These methods have substantial advantages in comparison with the common head-space analysis.

KEY WORDS: Chromatography, capillary effects, stationary gas phase, aqueous solutions, concentration, dissolved gases, volatile organic admixtures.

Until the early 1980s, chromatographic methods were generally reduced to four combinations of the stationary and mobile phases (the mobile phase is the primary process): gas-solid, liquid-solid, and liquid-liquid. Liquid-liquid is subdivided into two versions differing as to whether polar liquid or nonpolar liquid plays a role in the stationary phase. At this juncture attention finally focused on possibly expanding the chromatographic process to conditions in which the mobile phase is a substance in the supercritical state, giving birth to supercritical fluid chromatography. In all these cases the stationary phase was condensed. One could hardly imagine the possibility of the stationary gas phase in the chromatographic process.

In 1982, when studying analytical methods of gases dissolved in water, Moskvin and colleagues[1] discovered a new chromatographic process in which a gas fixed in the pores of a solid served as the stationary phase and a liquid support served as the mobile phase. When filtering through the column with porous polytetrafluoroethylene (PTFE), the water containing dissolved gases (oxygen, nitrogen, hydrogen), the latter have been found in the filtrate. The aqueous sample volume exceeded the interstitial volume of the column several-fold. Thus, gas concentrations changed with the volume of passed sample corresponding with the principles of the frontal chromatographic process. The increase of the retention parameters along with the increase in temperature, and the absence of any apparent connection between retention volumes and the specific surface of the supports employed gave evidence that the retention in the chromatographic column is determined by the distribution process in the system liquid (mobile phase)-gas (stationary phase). This version was classified as liquid-gas chromatography (LGC).

Even the initial reports on the frontal version of LGC appreciated the practical prospects of its applications in the determination of gaseous substances dissolved in water[1,2] and components that are able to produce gaseous products via decomposition.[3] The combination of the LGC frontal version as a method of gaseous component extraction from a liquid sample with traditional gas chromatography (GC) allowed us to conceptualize a new approach to determining gases dissolved in a liquid.[4] Analyzed gaseous components extracted from a liquid sample by

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filtering it through a LGC column are directed by gas carrier flow from the LGC to the GC column where separation and detection take place.

Experimental evidence of the possibility of realizing the LGC process was in advance of its theoretical prediction.[5] Giddings and Myers believe that a number of objective reasons is evidence for this new version of liquid chromatography (LC). Therefore, four possible advantages of LGC for light nonpolar gases analysis are noted, especially with aqueous or other polar mobile phases. The first consists of the strong retention of dissolved gases during their filtration through the LGC column, so that retention volumes may easily exceed 10 interstitial volumes of the column for most gases. This is due to the preferential distribution of gas molecules in the stationary gas phase, which prevents the study of cryogenic conditions or special sorbents for retention of low molecular weight compounds.

The second advantage Giddings and Myers see is the relatively large difference among the distribution coefficients for some significant gas pairs. For instance, nitrogen and oxygen differ in distribution coefficients by almost twofold. This creates the necessary prerequisite for their fast separation.

The third advantage is found in the simple analytical procedure of immediately injecting the sample containing dissolved gases into the chromatographic column.

The fourth advantage is connected with the extremely high rate of diffusional mass exchange in the stationary gas phase. It is approximately 10^4 higher here than the rates observed in liquids. As for the mobile phase, in which the diffusion rate is many times lower, a hydrodynamic agitation takes place. Giddings and Myers[5] feel that these considerations make the new LC the performance leader.

The abilities of LGC, like those of chromatographic methods in which the stationary phase is in the liquid state, are determined mainly by the physicochemical properties of the solid support of the stationary gas phase (SGP). In principle, the existence of the SGP is possible at any hydrophobic porous support while using a nonwetting surface mobile liquid phase (MLP). Capillary pressure arises in the pores of the nonwettable support. The pressure prevents the pores from filling up with liquid so long as the pressure of the liquid does not surpass the sum value of the capillary pressure and the pressure of the gas in the pore space. Correspondingly, one can write the general condition of LGC realization as

$$P_1 < P_c + P_g \tag{1}$$

where P_1 is the pressure of the MLP at the chromatographic column inlet, P_c is the capillary pressure in the pores retaining the SGP, and P_g is the pressure in the pore space.

The value of capillary pressure is connected with pore radius by[6]

$$P_c = \frac{2\sigma \cos \theta}{r} \tag{2}$$

where σ is the surface tension of the liquid at the border with the gas, θ is the contact angle between the solid support and the liquid phase, which has a negative value for nonwettable supports, and r is the pore radius.

Depending on the radius of individual pores and their size uniformity, one can conditionally divide SGP supports into two types. Relating to the first type are microporous materials with pores that are uniform in size for which the condition

$$P_c = \frac{(2\sigma \cos \theta)}{r_{\max}} + P_v \tag{3}$$

is satisfied (for all pressure ranges within which the LGC process is realized), where $r_{\max}$ is the maximum pore radius in the support and P_v is the saturated vapor pressure for any given temperature.

In order to meet this first condition, the volume of the SGP in the chromatographic column remains constant and is equal to all volumes of the support pore space independent of whether or not the eluent is saturated by the gas. When the gas phase is absent, the liquid is prevented from penetrating the solid support pores by capillary and saturated vapor pressures, the total value of which surpasses the pressure of the filtering liquid. Thus, we may avoid preliminary gas phase setting in solid support pores, which involves blowing the gas through the column. In the ultimate case of an absence of the dissolved in MLP gases, and eluent vapor serves as the SGP and liquid-vapor chromatography is realized.[7]

The LGC process is also possible when the gas content in the sample surpasses its solubility at a certain temperature and pressure. Redundant gas passes into the pore space and undertakes the role of the SGP.

When using water and aqueous solutions as the MLP, condition (3) is satisfied by a series of sorbents widely used in LC and GC: Porapacks Q and P, 100 series nonpolar Chromasorbs, and fine-porous silica gels with grafted alkyl groups used in reversed-phase adsorption LC. For support of this type the SGP volume amounts to about half the interstitial volume of a column. Retention parameters for such supports within experimental error do not depend on whether the filtering liquid is degassed or is saturated with the gas. This makes solid support of this type suitable both for the frontal LGC version, with the goal of joint extraction of dissolved gases, and for the eluent version, where the aim of the process is the separation of dissolved gases.

Nonwettable by the MLP, porous materials with larger average pore radii and greater pore size dispersion can be classified as a second type of support. An example of this support is porous PTFE. The upper limit of the radii of pores able to retain the SGP will change depending on the experimental conditions:

$$r_{\lim} < \frac{2\sigma \cos\theta}{P_1 - P_g} \qquad (4)$$

where $r_{\lim}$ is the radii limit of pores retaining the SGP under liquid P_1 and gas P_g pressures.

The limiting radii of pores retaining the SGP will change depending on the concentration of dissolved gases in the liquid phase. Therefore, in the case of the second type of support a constant SGP total volume within the chromatographic column can be ensured only by providing preliminary saturation of the MLP by the gas playing the role of the SGP which is under column outlet pressure. Moreover, the $r_{\lim}$ value is different for the same support along the column (this takes into account the pressure drop of the liquid in it). Correspondingly, the fractional volume occupied by the SGP in the column increases in the direction of MLP flow. Unlike the first type of solid support, a transition from gas-saturated to degassed eluent leads in the second type to a multiple decrease in the

TABLE 1

Ratios of Retention Volumes of Gases Dissolved in Water to Interstitial Volume of LGC Column (V_r/V_0) with Different Supports and Properties of These Supports

Support	Type	S (m^2/g)	$\bar{r}$ (nm)	$\cos\theta$	V_r/V_0			
					1[a]		2[a]	
					O_2	N_2	O_2	N_2
Porapack QS	1	750	3.7	−0.28	20	41	17	35
Silasorb C (LC)	1	350	2.5	−0.28	20	40	17	35
Polysorb-1	1	250	6.6	−0.15	19	35	16	31
Chromosorb-101	2	50	180	−0.15	17	32	2.1	2.9
Polychrom-1	2	3.0	140	−0.31	9.3	14.1	2.9	4.3
PTFE	2	0.5	840	−0.31	7.6	11.8	2.1	3.8
SKT carbon	—	1000	2.0	0.57	3.0	5.8	1.8	3.0

Note: S = specific surface. $\bar{r}$ = average pore radius, θ = equilibrium contact angle.[a] (1) eluent is saturated by helium: (2) eluent is degassed.

SGP volume and correspondingly in the retention volumes of dissolved gases (see Table 1). Instability of the retention parameters in the second type of solid support makes them unfit for the eluent LGC version, but does not exclude their possible use in the frontal version of LGC process realization.[1-4]

Experimental verification of the performance of the eluent version was carried out using the example of the separation of gases dissolved in water. The dependence of HETP on the eluent flow rate has the same pattern as for traditional kinds of LC. Simultaneously, LGC performance is higher, effective HETP values are three to four times lower than in traditional LC versions, and absolute HETP values amount to 1 to 2 mm at supports with 150 to 200 μm particles and an elution rate up to 3 cm/s. This provides for the rapid separation of most dissolved gases in short LGC columns, and with low input pressures of the eluent.[8]

At the same time, the prospects for using the eluent LGC version in the analysis of dissolved gases, despite the high separation ability of the new version of LC, are far from obvious. This is because of an absence of highly sensitive detectors for the direct determination of dissolved gases in the eluent. The universal refractometer, for instance, is able to detect gases dissolved in water only at the level of 10^{-4} to 10^{-3} mol/dm^3. This and the strong retention of dissolved gases in LGC columns using the first type of solid sorbents makes more rational the joint extraction of dissolved gases by filtration through the LGC column (frontal version) with subsequent GC determination of extracted gases.[9]

Analysis includes four general stages:

1. The withdrawal of analyzed components from the LGC column, usually accomplished by the carrier gas flow.
2. Analyzed sample filtration through LGC column until the less-retained component overflows or up to equilibrium saturation of SGP by analyzed components.
3. Removal of the residual liquid sample from LGC column by the carrier gas flow and simultanious transfer of gas phase with analyzed gaseous components extracted from the sample into the gas chromatograph.
4. GC determination of components extracted by means of the LGC column.

Of the two regimes of gaseous components extraction—equilibrium saturation of SGP and filtration until breakthrough—preference should be given to the latter because its results do not depend on influential factors (temperature, sample composition), if one chooses the sample volume, taking into account oscillations of these factors and the number of theoretical plates in the concentrating LGC column.

On the basis of gas-solid chromatography (GSC) and LGC synthesis were elaborated various modifications of extant chromatographs and "Aqua" unit for laboratory and automatic continuous analysis of dissolved gases.[10] The elementary analysis of dissolved gases in the frontal LGC version is presented in Figure 1. The liquid sample is drawn into the sampling loop (1), the injec-

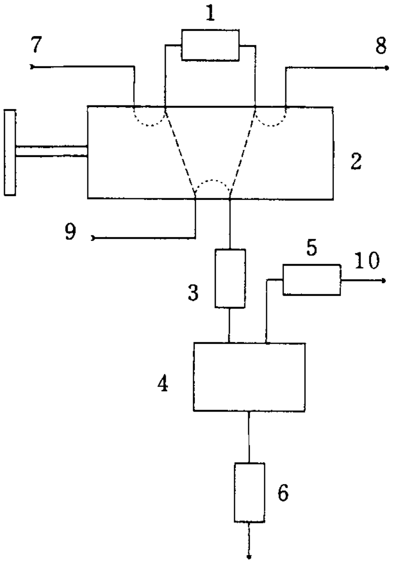

FIGURE 1. The scheme of dissolved gases analysis by means of LGC: (1) sampling loop; (2) injection valve; (3) LGC column; (4) collector; (5) desiccator; (6) valve; (7, 8) sample inlet and outlet; (9, 10) carrier gas inlet and outlet.

tion valve (2) is switched to the position, which is marked by dashed lines, and the sample is forced through the LGC column by carrier gas flow (3). The filtrate remains in the collector (4) when eliminated gases are directed using gas-carrier flow into the chromatograph via the desiccator (5). After the chromatogram is obtained the filtrate is eliminated as waste through the valve (6).

When using helium as a carrier gas and a common thermal conductivity detector, this analytical scheme allows the determination of O_2, N_2, and CO_2 dissolved in water with detection limits of 0.5, 0.2, and 20 $\mu g/dm^3$ respectively. The methodical possibilities of the LGC are not confined to the scheme presented in Figure 1. Detection limits for dissolved gases can be lowered significantly when all the gas from the column is removed before a liquid sample is filtered through the LGC column using solid support of the first type and by transfer of extracted gases from the LGC column to the chromatograph, not by carrier gas but by aqueous vapor flow with subsequent absorption.[11,12] The operations mentioned are aimed at reducing to minimum the dilution of the high concentration zone of analyzed gaseous components by carrier gas. The zone is formed in the LGC column after sample filtration. The operations are also aimed at providing a compact injection of this high concentration zone into the chromatograph.

The analytical possibilities provided by LGC are not confined to the determination of gaseous components in aqueous solutions. This method can also be the basis for the determination of dissolved substances which are able to produce gaseous compounds as a result of chemical transformation. As an example, the authors cite the determination of hydrogen peroxide[3] and of carbonates dissolved in aqueous solutions. Additionally, an inversion of hydrophobic supports wettability achieved by the dilution of polar liquids (alcohols, acetone), with water and gained by this sharp rise in dissolved gases distribution coefficients allows the use of the LGC method to determine gaseous micro-admixtures, not only in aqueous solutions, but in polar solvents.[13]

All of the above is classified as the LGC method, in which retention of substances is determined only by their distribution in the liquid-gas system. We must assume *a priori* that adsorption of extracted substances at the surface of the support exerts no substantial influence on their retention in the chromatographic column. This assumption is indisputable only for supports with low specific surface and for most low boiling point substances. For the first type of solid supports it is necessary to take into account the possible adsorption from the SGP at the surface of the support. It is impossible to exclude adsorption from MLP. The contribution made by different processes can be estimated via the retention of substances based on the additive equilibrium retention theory.[14] In accordance with this theory, the retention volume of a component in a real polyphase chromatographic system is equal to the sum of partial retention volumes attributed to adsorption and component distribution between phases. In relation to the considered system liquid (mobile phase)–gas (stationary phase)–solid support, the following expression[15] must be valid:

$$V_r = KV_g + KK_{gs}S_{gs} + K_{ls}S_{ls} \qquad (5)$$

where V_r is adjusted retention volume (in cubic centimeters), K is the coefficient of the component distribution between SGP and MLP, V_g is the SGP volume in the column (in cubic centimeters), K_{gs} is the coefficient of adsorption at the boundary between SGP and the solid support (in cubic centimeters per square meter), S_{gs} is the area of the solid support contacting the SGP (in square meters), K_{ls} is the coefficient of adsorption at the boundary between the MLP and the solid support (in cubic centimeters per square meter), and S_{ls} is the area of the solid support contacting the MLP (in square meters).

The first term on the right side of (5) displays the contribution of the component distribution between SGP and MLP and corresponds to the LGC process. The second term takes into account adsorption at the surface of the solid support from the SGP, and the third term displays adsorption at the surface of the solid support from the liquid phase and corresponds to the process of liquid adsorption chromatography. The values contained in the expression (5) can be obtained experimentally,[15] with the exception of K_{ls}. While filtering a liquid through the first type of solid support the SGP inevitably exists in the support, and realizing the liquid adsorption chromatography process becomes impossible in the pure aspect. The K_{gs} value may be obtained from component retention volumes resulting from gas phase saturation by aqueous vapor.[15]

As follows from the data in Table 2, adsorption from the gas phase on the surface of the support makes an appreciable contribution to retention even for so-called regular gases. As for the components adsorbed from the aqueous phase, it can be neglected proceeding from the satisfactory agreement between V_r and the sum of partial retention volumes attributed to the distribution in the liquid-gas system and adsorption from the gas phase. This conclusion corresponds to the following theoretical premises. First, the interphase surface area SGP-solid support (S_{gs}) is manifold greater than the area of MLP-solid support contact (S_{ls}) because the gas phase is located in the finest pores of the sorbent. These fine pores determine the support area. Second, the coefficient of adsorption from the gas phase (K_{gs}) is also manifold greater than the coefficient of adsorption from the liquid phase, K_{ls}. As for the presence of filtering liquid (H_2O) vapor in the SGP, the vapor exerts no significant effect on the adsorption of nonpolar substances for styrene and divinylbenzene copolymers, and other hydrophobic (or, more precisely, nonwettable by water) sorbents display extremely weak adsorption ability for aqueous vapor.[16]

Taking into account that when filtering the liquid phase through a nonwettable fine-porous sorbent, the absorption of volatile substances takes place via the gas phase. This chromatographic process is called liquid-gas-solid chromatography (LGSC).[10] LGSC is significant conceptually for the elucidation of the retention mechanism in liquid adsorption chromatography and of the concentration of volatile organic substances (VOS) from aqueous solution on hydrophobic sorbents. For VOS with a boiling point higher than 250 to 300 K one can neglect the contribution of distribution in the liquid-gas system to retention. In order to approximately evaluate VOS retention volumes for aqueous solutions, the expression

$$V_r = K \cdot K_{gs} \cdot S_s \cdot M \qquad (6)$$

is useful, where S_s is specific surface of the sorbent (m^2/g) and M is the mass of the sorbent (g).

TABLE 2
Contribution of Various Processes to Component Retention from Aqueous Solutions of Porapack QS (20°C)

Component	K	K_{gs}	Column vol (cm^3)	Partial retention		V_r (cm^3)
				$K \times U_g$ (cm^3)	$K \times K_{gs} \times S_{gs}$ (cm^3)	
Nitrogen	65	0.00065	3.8	72	33	112
Oxygen	32	0.00065	3.8	35	16	54
Xenon	10	0.016	3.8	11	126	120
Butane	6.7	6.9	0.05	0.27	460	450
Hexane	20	22	0.05	0.8	4350	4500
CCl_4	0.97	35	0.05	< 0.1	340	360
Benzene	0.20	38	0.05	< 0.1	75	79
$CHCl_3$	0.11	14	0.05	< 0.1	15	16
Acetone	0.0017	3.3	3.8	< 0.1	4.4	4.0
Ethanol	0.00014	14	3.8	< 0.1	0.24	< 0.1

Because $(K \times K_{gs} \times S_s)$ is the component specific volume retained from the liquid phase (V_l) and $(K_{gs} \times S_s)$ is a specific volume retained from the gas phase (V_g), the validity of expressions (5) and (6) and of considerations of the LGSC process can be checked by correlating K and volume ratios. Table 3 confirms that the LGSC process model is correct.

The concept of the retention of volatile substances from aqueous solutions at the expense of their adsorption on the interphase boundary water–sorbent[16-18] is the most widely employed. Practical recommendations concerning VOS adsorption isolation in analytical practice are based on this concept. In particular, preliminary wetting of the hydrophobic sorbent by an organic solvent was recognized as necessary to increase the contact surface of the sorbent with solution.[19,20] However, because adsorption of dissolved VOS proceeds not from the liquid but from the gas phase during filtration through a nonwettable sorbent, sorbent prewetting gives no positive effect, and VOS extraction efficiency slightly deteriorates in comparison to sorbent purge via gas before sample filtration. This is proved experimentally (see Table 4). The HETP value in the case of the sorbent prewetting by organic solvents is significantly higher in comparison to gas purging. This means that the volume of the liquid sample that can be passed through the LGSC column until the extracted admixture breaks through to the filtrate is smaller with sorbent prewetting, and the concentration coefficient is ultimately smaller.

The range of LGSC applications in concentrations of dissolved volatile substances is substantially wider than that of LGC. Components for which $K \times K_{gs} \times S_s > 1$ have practically significant retention in LGSC. Hence, the VOS concentration from aqueous solutions on nonpolar sorbents is the rule rather than the exception. The same conclusion can be drawn when analyzing heat data on the absorption of volatile substances in the gas phase on polymeric sorbents. These heat data are greater than those of the dissolution of substances in aqueous solutions.[21] An exception is substances that are most polar, such as light alcohols and amines with $K \ll 0.01$.

The limitations of the LGC method can be expanded via the salting out effect and via transformation of analyzed components to the less polar derivatives (hydrogenation, etherification). Moreover, the cited transformations are realized, in some cases, immediately within the LGC column during filtration of the sample through it. For instance, hydrogenation of nonsaturated hydrocarbons dissolved in water to corresponding alcanes which have much greater K values allows a several-fold decrease of the detection limits of the components. The LGC column is packed by Polysorb impregnated with a hydrogenation catalyst, preliminarily purged by hydrogen, and the aqueous sample is passed through the column with subsequent GC determination of formed alcanes.

Unlike concentration via the LGC mechanism, extracted from the liquid sample gaseous components can be displaced from

TABLE 3
Comparison of Specific Volumes Retained from Liquid (V_l) and Gas Phases of Hydrophobic Sorbents

		Porapack QS		Polsorb-1		Chromosorb-101	
Component	K	V_l (cm^3/g)	V_l/V_g	V_l (cm^3/g)	V_l/V_g	V_l (cm^3/g)	V_l/V_g
CCl_4	0.84	11100	0.80	3030	0.82	3100	0.78
Benzene	0.20	4400	0.19	2790	0.19	1380	0.18
$CHCl_3$	0.11	1660	0.12	681	0.11	2670	0.12
Ethylacetate	0.0048	183	0.0045	46	0.0049	—	—
Acetone	0.0013	11.6	0.0014	—	—	—	—

TABLE 4
Influence of Sorbent Pretreatment on Efficiency of VOC Extraction from Aqueous Solutions

Treatment before sample filtration	Component	Porapack QS V_r (cm^3)	Porapack QS HETP (mm)	Polysorb-1 V_r (cm^3)	Polysorb-1 HETP (mm)
Acetone rinse	Benzene	230 ± 11	2.6 ± 0.3	89 ± 4	8.6 ± 0.9
	Bichlorethane	70 ± 3	3.2 ± 0.3	53 ± 6	9.2 ± 0.9
Helium purge at 200°C	Benzene	255 ± 12	1.0 ± 0.1	100 ± 5	5.2 ± 0.5
	Dichlorethane	75 ± 4	1.2 ± 0.1	46 ± 6	5.0 ± 0.5

Note: Column 4.5 × 0.3 cm, solution flow rate 2 cm^3 / min, components content 20 mg / dm^3.

the concentrating column not at an ambient temperature only. In the case of the concentration of less volatile admixtures by the LGSC mechanism, desorption of the gaseous components is carried out by extraction with an organic solvent or by thermodesorption into the inert gas atmosphere after removing water from the concentrating LGSC column. Thermodesorption is less universal, but it allows a decrease in detection limit by approximately two orders of magnitude. The main characteristics of the methods of determination for volatile substances dissolved in water are presented in Table 5.

Realization of a chromatographic process in the liquid-gas system is also possible without solid support.[22,23] The principle is analogous to liquid-liquid centrifugal chromatography,[24] the difference being that the one of the phases is a gas phase. The development of centrifugal chromatography opens up new, insufficiently studied opportunities. It is evident, however, that due to the technical complexity, realizing this chromatographic pro-

TABLE 5
Characteristics of Gas Chromatographic Determinant Ion Methods for Gaseous and Highly Volatile Admixtures in Water with Use of LGSC Preconcentration

Analyzed component	Sample vol (cm^3)	Column vol (cm^3)	Desorbent / temp (°C)	Relative error (%)	Duration (min)	Detection limit (μg / dm^3)
Hydrogen	10	2.0	Ar / 20	3.6	3	0.05
	100	15	Ar / 20		8	0.006
Oxygen	10	15	He / 20	4.2	4	4.0
	100	15	He / 20		9	0.5
CO_2	10	15	He / 20	4.5	5	25
Hexane	30	0.05	Acetone	4.9	9	0.3
			He / 190	6.1	11	0.02
Benzene	30	0.5	Acetone	5.6	9	2.0
			He / 190	6.8	11	0.03
Dichlorethane	20	1.0	Acetone	5.0	7	1.0
			He / 190	6.6	9	0.1

Detectors: FID and TCD with detection limits for propane 2.3 × 10^{-11} g / s and 5 × 10^{-4} vol %, respectively. LGSC concentration conditions: t = 20°C; sorbent, Polysorb-1; sample filtration rate, 15 cm^3 / min for gas extraction and 5 cm^3 / min for VOS extraction.

cess can be justified only when an identical result cannot be obtained using traditional methods.

Liquid-gas chromatography has much in common with the headspace analysis (HSA) method.[25] Both methods are based on the distribution of analyzed components in the liquid-gas system and subsequent analysis of the gas phase. Some specialists in the HSA field thus consider the frontal version of LGC to be a dynamic version of HSA with stationary gas phase.[26] Therefore, a comparison of different HSA and LGC versions discussed in Reference 26 showed that by efficient extraction of volatile substances from the liquid phase, LGC corresponds to the very effective multistage dynamic gas extraction (MDGE), in which each barbotage stage functions as a peculiar theoretical plate in a chromatographic sense. At the same time, technical difficulties arising from realizing MDGE make LGC the preferential method, even for the analysis of weak-adsorbed light gases.

The known principles of LGC and LGSC allows us to find the optimal conditions for concentrating volatile micro-admixtures from aqueous solutions and from polar liquids for their subsequent analytical determination. The LGC method has found application in the nuclear and heat power industries for the express analytical control of dissolved gases in technological aqueous media.[3,27,28]

REFERENCES

1. Moskvin, L.N.; Gorshkov, A.I.; Gumerov, M.F., *Dokl. Akad. Nauk SSSR*. **1982**, *265*, 378.
2. Moskvin, L.N.; Gorshkov, A.I.; Gumerov, M.F., *Zh. Fiz. Khim*. **1983**, *57*, p. 1979.
3. Moskvin, L.N.; Gumerov, M.F.; Gorshkov, A.I., *Teploenergetika*. **1980**, *10*, 25.
4. Moskvin, L.N.; Gumerov, M.F.; Gorshkov, A.I., USSR Patent 1033874, 1983.
5. Giddings, J.C.; Myers, M.N., *J. High Resol. Chromatogr*. **1983**, *6*, 381.
6. Adamson, A.W., *Physical Chemistry of Surfaces*; Wiley: New York, 1976.
7. Gumerov, M.F.; Rodinkov, O.V.; Moskvin, L.N.; Gorshkov, A.I., *Zh, Fiz. Khim*. **1988**, *62*, 2249.
8. Gumerov, M.F.; Rodinkov, O.V.; Moskvin, L.N., *Zh. Fiz. Khim*. **1990**, *64*, 501.
9. Gorshkov, A.I.; Gumerov, M.F.; Leont' eva, E.I.; Moskvin, L.N., *Zh. Anal. Khim*. **1986**, *41*, 145.
10. Moskvin, L.N.; Tsaritsyna, L.G., *Metody Razdeleniya i Kontsentrirovaniya v Analiticheskoi Khimii*; Khimiya: Leningrad, 1991.
11. Gumerov, M.F.; Rodinkov, O.V., USSR Patent 1563396, 1991.
12. Gumerov, M.F.; Rodinkov, O.V., USSR Patent 1459450, 1990.
13. Rodinkov, O.V.; Gumerov, M.F., USSR Patent 1545767, 1991.
14. Berezkin, V.G.; Pakhomov, V.P.; Fateeva, V.M. et al., *Dokl. Akad. Nauk SSSR*. **1968**, *180*, 1135.
15. Rodinkov, O.V.; Gumerov, M.F.; Moskvin, L.N., *Zh. Fiz. Khim*. **1989**, *63*, 3128.
16. Kiselev, A.V.; Poshkus, D.V.; Yashin, Ya.I., *Molekulyarnye Osnovy Adsorbtsionnoi Khromatografii*; Khimiya: Moscow, 1986.
17. Byerman, K., *Organic Trace Analysis*, Ellis Horwood: Chichester, 1979.
18. Dressler, M. *J. Chromatogr*. **1979**, *165*, 1677.
19. Liska, I.; Krupcik, J.; Leciercq, P.A., *J. High Resol. Chromatogr*. **1989**, *12*, 577.
20. Namiesnik, J.; Gorecki, T.; Biziuk, M.; Torres, L., *Anal. Chim. Acta*. **1990**, *237*, 1.
21. Sakodynsky, K.I.; Panina, K.I., *Polimernye Sorbenty v Molekulyarnoi Khromatografii*, Khimiya: Moscow, 1990.
22. Japanese Patent 60-46383, 1986.
23. Japanese Patent 62-14781, 1988.
24. Ito, Y.; Conway, W.D., *Anal. Chem*. **1984**, *56*, 354A.
25. Ioffe, B.V.; Vitenberg, A.G., *Head-Space Analysis and Related Methods in Gas Chromatography*; Wiley: New York, 1984.
26. Marinichev, A.N.; Vitenberg, A.G.; Bureiko, A.S., *J. Chromatogr*., **1991**, *600*, 251.
27. Yefimiov, A.A.; Kritsky, V.G.; Moskvin, L.N., *Teploenergetika*. **1988**, *4*, 37.
28. Moskvin, L.N.; Gumerov, M.F.; Yefimiov, A.A. et al., in *Metody Khimicheskogo i Radiokhimicheskogo Kontrolya v Yadernoi Energetike*; L.N. Moskvin, Ed.; Energoatomizdat: Moscow, 1989.