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ARTICLES

Effects of the Discrimination of Sample Composition with the Use of Split Injection into Gas Chromatographic Capillary Columns

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Abstract—The manifestation of noticeable effects of the discrimination of sample composition upon split injection into short capillary columns with large diameters at small splitting ratios is discussed. They consist in the anomalously strong dependences of the peak areas of even volatile components on the injector temperature, the solvents used and, to a lesser extent, on the amounts of injected samples. It is proposed to consider the following criteria for assessing the degree of manifestation of these factors: (1) the dependence of the absolute peak areas of different analytes on the injector temperature and (2) the analogous dependence of the relative peak areas of the same components in different solvents. In this case, the relative peak areas of various components in the same solvents remained almost constant regardless of the injector temperature. The above effects complicate quantitative determinations based on the measurement of absolute peak areas (the method of internal normalization and the determination of distribution coefficients in partition chromatography). For these purposes, it is preferable to use standard capillary columns with split sample injection at a sufficiently high splitting ratio.

Keywords: gas chromatography, capillary columns, split sample injection, discrimination of sample composition, discrimination criteria, injector temperature effect

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An analysis of current literature on gas chromatography [1] showed that more than 95% of analytical problems are solved by this method using chromatographic capillary columns. Unlike packed columns, their use most often involves split sample injection when only a small portion of the sample arrives at the column. Effects of the discrimination of sample composition (or, in other words, the nonlinearity of splitting), which interfere with the results of quantitative determinations[1], have been known since the appearance of this injection technique. Most often, this is understood as a decrease in the peak areas of high-boiling components relative to the peak areas of low-boiling components, as shown schematically in Fig. 1. If the mass concentrations of homologues (for example, *n*-alkanes) in the injected sample are the same, their corresponding peak areas can decrease with the number of carbon atoms in the molecules. These effects are expressed to the greatest extent on the injection of samples with a syringe into a heated injector of a chromatograph in the determination of high-boiling analytes.

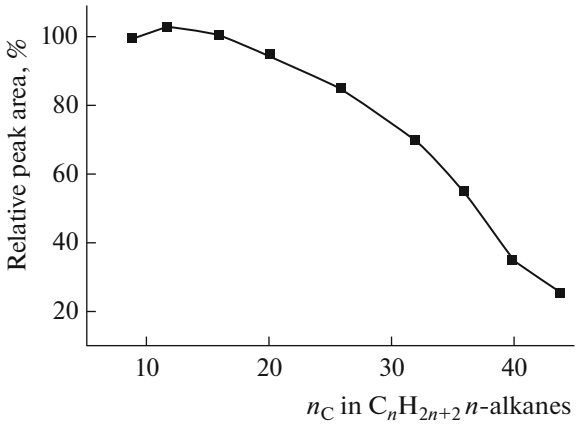

Fig. 1. Graphic illustration of a typical effect of discrimination of the peak areas of *n*-alkanes with different numbers of carbon atoms in a sample at their equal concentrations in the sample (the figure was not borrowed from any particular publication, but it tentatively combines data from different information sources).

[1] There are noticeable terminological differences in the literature: the discrimination of samples, sample components, sample compositions, and peak areas of various components and even the stage of injection itself and the nonlinearity of splitting are considered. In fact, all of them are correct, but we will use the terms *discrimination of sample composition* or *discrimination effects* in this paper.

If a chosen quantitative determination method (external standard, absolute calibration, internal standard, or standard addition) implies the preliminary calibration of an instrument with target analytes under the same conditions as those used for analysis, there is no need to take into account the effects of discrimination. It is likely that, for this reason, the above effects were not referred to in many manuals specifically devoted to work with capillary columns [2, 3] and in modern reference books [4]. However, there are tasks involving the measurement of absolute peak areas without preliminary calibration, in particular, quantitative analysis by an internal normalization method, which is widely used to present the results of the analysis of multicomponent samples. Another example is a so-called partition chromatographic method for the determination of the distribution coefficients of analytes from ratios between absolute peak areas obtained upon the injection of equal volumes of partially miscible solvents [5]. In such cases, the effects of discrimination play a significant role.

A considerable number of publications have been devoted to discussing the effects of discrimination since the beginning of the widespread use of capillary columns (late 1970s) [6–11]. At the same time, note that these effects are inadequately considered in Russian educational and scientific literature. They were considered only in the Russian editions of foreign publications [12, 13]. Briefly, such effects were mentioned in a manual by Tsarev et al. [14], and a monograph by Sakodynskii et al. [15] only noted that splitless sample injection into columns makes it possible to exclude them. A contemporary discussion of such effects is concentrated in practical user guides offered by various companies and available on the Internet (including so-called Troubleshooting Guides), for example [16]. At the same time, it is difficult to get a concept on the true scale of the effects of discrimination and their manifestations from the currently available literature.

Currently, the use of short capillary columns of large internal diameters with thick films of stationary phases (such as Megabore) is becoming increasingly popular. However, a number of unexpected anomalies appear in the properties of these columns. For example, the dependence of gas-chromatographic retention indices on the ratio between the amounts of target analytes and reference components differs from the similar dependence for conventional (Narrow bore type) capillary columns [17]. Another anomaly is the unexpectedly strongly pronounced manifestation of the effects of the discrimination of sample composition upon split sample injection into such columns at small split ratios considered in this paper. These effects are noticeable even with relatively low-boiling organic compounds, and they are responsible for the significant dependence of the results of gas-chromatographic analysis on such factors as the nature of the solvent, the split ratio, and the injector temperature. This work is devoted to the consideration of these issues.

EXPERIMENTAL

Preparation of solutions. The 100-μL portions of (a) toluene and 3-heptanone, (b) carbon tetrachloride and 1-pentanol, or (c) 3-heptanone and isopropylbenzene (all of chemically pure grade) were added to 5 mL of hexane or 2-propanol (chemically pure for chromatography) in a 10-mL penicillin vial. The resulting solutions were directly analyzed on a gas chromatograph. They were diluted by a factor of 400 with hexane or 2-propanol for gas chromatography–mass spectrometry (GC–MS) analysis.

Gas-chromatographic analysis. The gas-chromatographic analysis of the samples was carried out on a Kristall 5000.2 chromatograph with a flame ionization detector (FID) on a BPX-1 column 10 m long and 0.53 mm in internal diameter with a stationary phase film thickness of 2.65 μm. Column temperature, 70 or 80°C isotherm; carrier gas, nitrogen: (a) flow rate of 5.9 mL/min (linear velocity, 45.5 cm/s) and split ratio of 1 : 3 (mode A) and (b) flow rate of 5 mL/min (linear velocity, 43.2 cm/s) and split ratio of 1 : 6 (mode B). The injector contained a glass wool insert (~4 cm), and the injector temperature was varied in a range of 120–210°C with a step of 30°C.

An MSh-10 microsyringe was used for sample injection; the injected sample volume was varied from 0.5 to 2 μL, and two to five parallel injections of each particular sample were performed in each mode. To eliminate the human factor effect, the same analyst performed the injection of all of the samples. Additionally, we checked the capabilities of air bubble injection mentioned in the literature. In this method, the syringe after sampling was filled with ~2 μL of air so that the needle was empty at the moment of insertion into the heated injection port. However, it was found that this method does not eliminate the detected effects, but it only leads to a decrease in the reproducibility of the results. The injected amounts of all analytes at all split ratios were no greater than the mass overload limit of the column used (17 ± 4 μg).

GC–MS analysis. The GC–MS analysis was performed on a Shimadzu QP 2010 SE instrument with an Optima 5 MS column with a length of 30 m, an internal diameter of 0.32 mm, and a stationary phase film thickness of 0.25 μm. Detection mode: 70-eV electron ionization; the measurement of total ion current chromatograms. Column temperature, 80°C isotherm; carrier gas, helium: flow rate of 1.84 mL/min (linear velocity, 49 cm/s) (mode C). The injector temperature was varied in a range of 120–210°C with a step of 30°C. The injected sample volume was 1 μL.

Processing of the results. Excel (Microsoft Office 2010) was used for the statistical processing of peak areas and the calculation of ratios between them, and

Table 1. Variations in the absolute peak areas of toluene (c = 16.7 mg/mL) and 3-heptanone (c = 15.7 mg/mL) on the injection of their solutions in hexane and 2-propanol at different injector temperatures (separation mode A; split ratio, 1 : 3)

Analyte	Solvent	$S \pm s(S) \times 10^3$ (s_r), mV ms				S^{210}/S^{120}
		120°C	150°C	180°C	210°C	
Toluene	Hexane	311.5 ± 16.4 (0.052)	325.2 ± 8.4 (0.026)	360.3 ± 11.2 (0.031)	393.8 ± 29.1 (0.074)	1.26
	2-Propanol	225.6 ± 2.7 (0.012)	298.1 ± 28.0 (0.093)	367.3 ± 14.2 (0.039)	465.6 ± 29.1 (0.062)	2.06
3-Heptanone	Hexane	203.4 ± 9.6 (0.047)	219.9 ± 7.5 (0.034)	243.9 ± 5.4 (0.022)	270.8 ± 16.0 (0.059)	1.33
	2-Propanol	136.7 ± 6.2 (0.046)	188.9 ± 19.4 (0.103)	240.5 ± 7.3 (0.030)	309.3 ± 15.3 (0.049)	2.26

the Origin software (version 4.1) was used for calculating the parameters of regression equations and constructing the plots.

RESULTS AND DISCUSSION

It is reasonable to start a discussion of discrimination effects on injection into gas-chromatographic capillary columns with an example illustrating particular experimental data. Table 1 compares the absolute peak areas of toluene and 3-heptanone upon the injection of their solutions with equal mass–volume concentrations in hexane and 2-propanol in mode A (a short capillary column with a large diameter and a thick stationary phase film at a split ratio of 1 : 3).

In the consideration of the above data, it should be primarily noted that these data clearly depend on the injector temperature: when it was increased from 120 to 210°C, the peak areas of toluene and 3-heptanone for the solutions of these analytes in hexane or 2-propanol (S^{210}/S^{120} ratios) monotonically increased by factors of 1.26 and 1.33 or 2.06 and 2.26, respectively. This effect is well known, and it was discussed by Jennings [12]; however, as noted above, it is of interest to evaluate the real features and scales of its manifestation. Note that all of the injector temperatures were higher than the boiling points of the selected solvents (68.7°C for hexane and 82.3°C for 2-propanol). Usually, it is believed that these dependences are due to the evaporation of most of the samples upon their injection at higher temperatures. However, the monitoring of the residual volumes of solvents remaining in a syringe after injecting 1 μL of solutions showed that they were almost independent of the solvent and the injector temperature and close to the technical characteristics of MSh-1 syringes (a needle volume of ~0.7 μL). Thus, a significant increase in the absolute peak areas was determined by a change in the operation mode of the sample splitter. This effect is also difficult to describe because its manifestations can be markedly different depending on the design of the sample splitter (the model of a chromatograph).

For a clearer representation of the observed variations in the composition of samples arrived at a chromatographic column upon split injection under different conditions, it is reasonable to supplement the consideration of the dependencies of absolute peak areas with an analysis of relative values, primarily, the dependence of the ratio between peak areas of the same component in different solvents on the injector temperature. To standardize this operation, we will consider the ratios of analyte peak areas in a less volatile solvent to the values in a more volatile solvent; that is, the values of S_i(2-propanol)/S_i(hexane) in our case. Table 2 summarizes the average values of these ratios for toluene and 3-heptanone, which monotonically increased by a factor of 1.6–1.7 as the injector temperature was increased from 120 to 210°C. Thus, at a relatively low injector temperature, the amounts of analytes arrived at the chromatographic column with the use of an even slightly less volatile solvent were smaller than those with the use of a more volatile solvent. However, as the temperature was increased, the situation unexpectedly changed to the very opposite: the injection of solutions with equal analyte concentrations in less volatile 2-propanol led to larger peak areas than those upon injecting the solutions in hexane.

A third criterion for identifying and controlling the effects of discrimination, which is based on an assessment of the dependence of ratios between the peak areas of different components in different solvents on the injection temperature, is also possible. As in the previous case, in order to standardize this operation, we will consider a ratio between the peak areas of a less volatile component (3-heptanone, T_b = 147°C) and a more volatile component (toluene, T_b = 110.6°C). Table 3 summarizes these ratios calculated according to the data given in Table 1.

Table 2. Average values of variations in ratios between the peak areas of toluene (c = 16.7 mg/mL) and 3-heptanone (c = 15.7 mg/mL) in 2-propanol and hexane at different injector temperatures of the evaporator (separation mode A; split ratio, 1 : 3)

Analyte	Injector temperature, °C				$S_{rel}{}^{210}/S_{rel}{}^{120}$
	120	150	180	210	
Toluene	0.72	0.92	1.02	1.18	1.64
3-Heptanone	0.67	0.86	0.99	1.14	1.70

Table 3. Average values of variations in ratios between the peak areas (S_1/S_2) of 3-heptanone (c = 15.7 mg/mL) and toluene (c = 16.7 mg/mL) in hexane and 2-propanol at different injector temperatures (separation mode A; split ratio, 1 : 3)

Solvent	Injector temperature, °C				Average value
	120	150	180	210	
Hexane	0.65	0.68	0.68	0.69	0.68 ± 0.02
2-Propanol	0.61	0.63	0.65	0.66	0.64 ± 0.02

This form of data presentation naturally reflects the absence of the temperature dependence of relative concentrations of different components that enter the column as a result of injecting samples in different solvents. The average values of ratios between the peak areas of 3-heptanone and toluene upon the injection of their solutions in hexane and 2-propanol did not differ from each other within two standard deviations. The difference of these values from unity is due to a lower concentration of 3-heptanone compared with that of toluene (16.7 and 15.7 mg/mL, respectively) and a lower FID sensitivity to the oxygen-containing compound than that to hydrocarbons.

Thus, to characterize the effects of discrimination, it is reasonable to use the following criteria for evaluating the influence of the injector temperature on the results of determinations rather than the dependence of the peak areas of homologues on their volatility (the number of carbon atoms in the molecules), which is shown in Fig. 1:

(1) the dependence of the absolute peak areas of different analytes (including volatile compounds) on the injector temperature;

(2) the dependence of the relative peak areas of the same component in different solvents on the injector temperature; and

(3) the dependence of the relative peak areas of different components in the same solvents on the injector temperature.

In this case, only the first two criteria illustrate the actual effects of discrimination, whereas the third is chosen to confirm the absence of any regular variations.

The clearly pronounced dependence of the absolute and relative peak areas of volatile compounds on the injector temperature is a rather unexpected fact, which requires additional confirmation. For this reason, information given in Table 1 is reproduced in Table 4 with the use of two other compounds (carbon tetrachloride and 1-pentanol) as examples. Due to the significantly lower sensitivity of a FID to CCl_4, the chosen concentrations of the components in a sample were different by a factor of ~30, which did not affect the results obtained. As in the previous case, the S^{210}/S^{120} ratios were much higher than unity, and they were greater for a less volatile solvent (2-propanol) than for hexane (2.4–2.8 vs. 1.4). Table 5 summarizes ratios between the peak areas of these components in different solvents; they were as high as 1.8–2.0, which are higher than analogous ratios in Table 2. The ratios between the peak areas of different components in the same solvents (criterion 3) also did not differ from each other within two standard deviations (Table 6).

Thus, the observed anomalous dependences of the absolute and relative peak areas of volatile components are not related to the chemical nature of analytes, but they are determined by other factors. To confirm them at the next step, it is reasonable to choose other solvents and to vary split ratios on injecting samples into the column. Toluene was chosen as a model analyte; Table 7 summarizes the results. In addition to the S^{210}/S^{120} ratio, the S^{150}/S^{120} and S^{180}/S^{150} ratios are no less informative. As with other solvents, an increase in the temperature with the use of chloroform and acetonitrile led to an increase in the absolute peak areas; however, this increase was 1.4–1.9 for the former ratio (higher for more polar acetonitrile) at a split ratio of 1 : 3, but it was much lower (1.0–1.2) at a split ratio of 1 : 6 (separation mode B). This fact confirmed that all of the effects observed were caused by the discrimination of sample composition in a split injector, and they were most pronounced at low split ratios, that is, in operations with short (like Megabore) capillary columns of large diameters.

To confirm the dependence of the effects of sample composition discrimination on the split ratio, we performed analogous experiments on a GC–MS instrument with a standard capillary column 30 m in length

Table 4. Variations in the absolute peak areas of carbon tetrachloride ($c \approx 91.5$ mg/mL) and 1-pentanol ($c \approx 3.1$ mg/mL) on the injection of their solutions in hexane and 2-propanol at different injector temperatures (separation mode A; split ratio, 1 : 3)

Analyte	Solvent	$S \pm s(S) \times 10^3$ (s_r), mV ms				S^{210}/S^{120}
		120°C	150°C	180°C	210°C	
CCl_4	Hexane	95.7 ± 0.0 (0.00)	113.1 ± 0.8 (0.007)	131.5 ± 5.0 (0.038)	132.7 ± 2.2 (0.017)	1.39
	2-Propanol	75.4 ± 1.0 (0.013)	107.1 ± 3.9 (0.036)	151.2 ± 6.2 (0.041)	183.3 ± 6.7 (0.036)	2.43
1-Pentanol	Hexane	38.7 ± 0.1 (0.003)	47.1 ± 0.8 (0.017)	55.6 ± 2.6 (0.047)	54.0 ± 2.6 (0.048)	1.40
	2-Propanol	25.4 ± 0.5 (0.018)	36.6 ± 2.1 (0.058)	54.8 ± 0.8 (0.014)	72.2 ± 2.3 (0.032)	2.84

Table 5. Average values of variations in ratios between the peak areas of carbon tetrachloride ($c \approx 91.5$ mg/mL) and 1-pentanol ($c \approx 3.1$ mg/mL) in 2-propanol and hexane at different injector temperatures (separation mode A; split ratio, 1 : 3)

Analyte	Injector temperature, °C				$S_{rel}^{210}/S_{rel}^{120}$
	120	150	180	210	
CCl_4	0.79	0.95	1.15	1.38	1.75
1-Pentanol	0.66	0.78	0.99	1.34	2.03

Table 6. Average values of ratios between the peak areas of 1-pentanol ($c \approx 3.1$ mg/mL) and carbon tetrachloride ($c \approx 91.5$ mg/mL) in hexane and 2-propanol at different injector temperatures (separation mode A; split ratio, 1 : 3)

Solvent	Injector temperature, °C				Average value
	120	150	180	210	
Hexane	0.40	0.42	0.42	0.41	0.41 ± 0.01
2-Propanol	0.34	0.34	0.36	0.39	0.36 ± 0.02

and 0.32 mm in internal diameter with a stationary-phase film thickness of a 0.25 μm (separation mode C; split ratio, 1 : 10) using much more dilute solutions of 3-heptanone and isopropylbenzene in hexane and 2-propanol as examples (Table 8). As in all of the examples discussed above, an increase in the absolute peak areas was observed as the injector temperature of the GC–MS instrument was increased from 120 to 210°C; however, it was much smaller than that at lower split ratios: the values of S^{180}/S^{150} were only 1.02–1.06. It can be assumed that a further increase in the split ratio flow will lead to even greater leveling of the effects of discrimination.

Thus, the clearly pronounced effects of discrimination were most pronounced at small split ratios on the injection of samples into short capillary columns of large diameters. The manifestation of these effects includes the dependence of the absolute and relative peak areas of relatively low-boiling compounds on the nature of the solvent, the split ratio, and the injector temperature.

A greater or smaller effect of changes in separation conditions on recorded peak areas is well known in chromatography. Thus, it was shown that the results of quantitative determinations by an internal normalization method depend on the temperature conditions of a chromatographic column (isothermal or temperature-programming) [18, 19], but such variations are incomparably smaller than the effects of discrimination described in this work. Therefore, with the use of short capillary columns with large diameters at small split ratios, the internal normalization method should be applied with extreme caution because the results can strongly depend on factors such as the nature and temperature of the injector. In any case, the accuracy of the resulting estimates will be low.

A partition chromatographic method [5] should be noted as another example of the principal undesirability of applying short capillary columns at low split ratios because it is most easily to use the ratios of peak areas for estimating the partition coefficients (K_p) of analytes in heterophase systems of liquids sparingly soluble in one another:

$$K_p = c_1/c_2 \approx S_1/S_2. \quad (1)$$

To eliminate possible errors, the most reliable values of partition coefficients in the hexane–acetonitrile [20], hexane–nitromethane [21], hexane–2,2,2-trifluoroethanol [22], perfluorodecalin–acetonitrile [23], etc., systems were determined using packed gas-chromatographic columns (with splitless sample injection) to remove the effects of discrimination [18, 19]. The possibilities of determining K_p with the use of capillary columns require verification in each specific case.

Another important practical issue is the manifestation of the effects of discrimination upon varying the sample injection volumes. Table 9 compares variations in the mean absolute values of the peak areas of carbon tetrachloride and 1-pentanol in 2-propanol and hexane for 0.5- and 2.0-μL samples (the same MSh-10 microsyringe was used) in the above range of injector temperatures (from 120 to 210°C; separation mode A; split ratio, 1 : 3). The data of Table 9 can be considered together with the data given in Table 4 for the same analytes at a sample volume of 1 μL.

Table 10 presents the temperature dependence of the relative peak areas of the same components in different solvents at different equal injected sample vol-

Table 7. Average values of variations in the absolute peak areas of toluene ($c = 16.7$ mg/mL) (average values upon the injection of solutions in chloroform and acetonitrile at different injector temperatures, separation modes A and B)

Solvent	Split ratio	$S \times 10^3$, mV ms				S^{150}/S^{120}	S^{180}/S^{150}
		120°C	150°C	180°C	210°C		
Chloroform	3 : 1	326.4	444.2	520.5	600.9	1.36	1.17
	6 : 1	143.3	145.6	–	–	1.02	–
Acetonitrile	3 : 1	310.1	593.2	768.2	850.4	1.91	1.30
	6 : 1	110.7	127.5	129.1	126.2	1.15	1.01

Table 8. Average values of variations in the absolute peak areas of 3-heptanone s ($c \approx 39.3$ μg/mL) and isopropylbenzene ($c \approx 41.4$ μg/mL) upon the injection of their solutions in hexane and 2-propanol at different injector temperatures from 120 to 210°C (separation mode C; split ratio, 1 : 10)

Analyte	Solvent	$S \times 10^3$, mV ms				S^{180}/S^{150}
		120°C	150°C	180°C	210°C	
3-Heptanone	Hexane	126.4	122.6	128.0	151.6	1.04
	2-Propanol	–	80.0	81.4	90.0	1.02
Isopropylbenzene	Hexane	179.8	174.4	185.0	227.2	1.06
	2-Propanol	–	144.4	147.0	159.3	1.02

Table 9. Average values of variations in the absolute peak areas of carbon tetrachloride ($c \approx 91.5$ mg/mL) and 1-pentanol ($c \approx 3.1$ mg/mL) in 2-propanol and hexane upon varying their injected volumes at different injector temperatures (separation mode A; split ratio, 1 : 3)

Analyte	Solvent	$S \times 10^3$, mV ms							
		120°C		150°C		180°C		210°C	
		0.5	2.0	0.5	2.0	0.5	2.0	0.5	2.0
CCl_4	Hexane	43.0	246.1	44.5	298.8	52.6	342.6	52.6	338.4
	2-Propanol	34.1	160.0	43.6	275.9	54.1	345.7	60.4	375.5
1-Pentanol	Hexane	17.6	99.1	18.5	121.5	22.5	140.0	22.1	139.3
	2-Propanol	14.0	50.8	17.8	88.6	23.3	125.1	28.0	149.2

Table 10. Temperature variations in the relative peak areas of carbon tetrachloride and 1-pentanol in hexane and 2-propanol at various equal volumes of injected samples (in accordance with the data given in Table 9)

Analyte (sample volume)	Injector temperature, °C			
	120	150	180	210
CCl_4 (0.5 μL)	1.26	1.02	0.97	0.87
CCl_4 (2.0 μL)	1.54	1.08	0.99	0.90
1-Pentanol (0.5 μL)	1.26	1.04	0.96	0.79
1-Pentanol (2.0 μL)	1.95	1.37	1.12	0.93

umes (criterion 2) for samples of different volumes. Injection at low injector temperatures with the use of a higher boiling polar solvent (2-propanol) was characterized by the greatest differences. In this case, as previously, criterion 3 regularly confirmed the absence of dependence of the relative peak areas of different components in the same solvents on the injector temperature.

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