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Optimization of coal tar gas chromatography conditions using probabilistic-deterministic design of experiment

The development of physicochemical methods for the analysis of objects of complex composition requires the application of methods of mathematical experiment design. This article investigates the possibility of using probabilistic-deterministic design of experiment (PDDoE) for obtaining a mathematical model of the chromatographic separation process of coal tar hydrogenation products on an Agilent 7890A device with an Rxi-5ms column. It is shown that the relationship between the column heating rate and the carrier gas pressure with the values averaged for the entire chromatogram can be established with a high accuracy. It is noted that the accuracy of modeling the individual characteristics of the mixture components' peaks is less, but remains sufficient for many practical needs. Nonlinear multiple correlation coefficients (NMC) for the dependence of the average retention time and average intensity on the considered factors are more than 0.99; they are more than 0.98 for the average peak width. NMC for the dependence of the resolution with the relation to the peaks of naphthalene and 2-ethylphenol is more than 0.8 at a significant level that sufficient for practice. The quality of the mathematical model was checked by triple registration of the chromatogram at the values of the column heating rate and carrier gas pressure that were not used in the training experiment. The measurement results are excellent squared with those calculated using the obtained generalized equations. The PDDoE method can be recommended as a method for mathematical design of an optimization experiment in gas chromatography.

Keywords: gas chromatography, design of experiment, coal tar, GC-MS, PDDoE, optimization, retention time, peak width and height.

Introduction

Gas chromatography (GC) is one of the most effective methods being used to separate complex mixtures of substances. The separation quality depends on a number of the experiment parameters, including device settings [1]. Most gas chromatography devices allow one to set two parameters of the chromatographic separation process, namely the flow rate (pressure) of the carrier gas and the column heating rate. The influence of each of these two factors on the retention time of substances is qualitatively predictable based on general laws, specifically the relative retention time decreases with increasing gas pressure and temperature. Column efficiency is not linearly dependent on gas flow rate and temperature, and is unique to each column. Thus, controlling the temperature and gas flow rate allows to control the chromatogram quality and the analysis rate. Considering the unique characteristics of chromatography devices and analytes, it seems impossible to predict the retention time of a particular component and the resolution capability of the method in the case of a given object by using the fundamental laws. On the other hand, empirical formulas, that link instrument settings to chromatogram characteristics, can be obtained relatively easily. These parameters have a combined effect on the results; therefore, it is considered effective to use mathematical experiment design to optimize them [2].

The authors of a number of works achieved a significant improvement in the characteristics of the developed methods by applying traditional methods of experiment design to the chromatography process or to sample preparation. In [3], the authors optimize the sample preparation of biological fluids for the determination of formaldehyde using mathematical design of the experiment. In most works, conditions optimization of a gas chromatography is carried out by the empirical selection of parameters until satisfactory results are achieved. The low efficiency of this method compared to design of experiment has been repeatedly discussed in various sources. Publications [4–5] show that the optimization of GC parameters can significantly improve the components separation, and, as a consequence, reduce the limit of detection and determination limit, as well as simplify their identification.

Analysis of the literature indicates that probabilistic-deterministic design of experiment [6], that is being used successfully in the study of chemical-technological processes [7, 8], can be also used in the development of methods of physical and chemical analyses [9, 10]. It seems interesting to investigate the possibility of using PDDoE to optimize the conditions of a gas chromatography.

Coal tar is a valuable source of a number of organic compounds. An international group of researchers, including professor M.I. Baikenov and his employees who conducted the research on the production of liquid fuels from light oil and other fractions of coal tar [8, 11, 12]. These studies require systematic control of the qualitative and quantitative composition of the reaction mixtures by gas chromatography – mass spectrometry (GC-MS).

The aims of the study are as follows:

1) Obtaining mathematical models linking the carrier gas pressure and the column heating rate with the average values of the retention time, height, and width of the main peaks in the chromatogram.

2) Verification of the mathematical model in a control experiment.

3) Obtaining a mathematical model for the resolution of closely spaced peaks, for example, naphthalene and 4-ethylphenol.

Experimental

A solution of a light fraction of coal tar in chloroform was used as a test mixture. An Agilent 7890A gas chromatography device with an Agilent 5975C mass selective detector has applied. 0.01 g of the sample was dissolved in the solvent, so the volume of the solution was 10 ml. The solution was filtered and injected into the column using an autosampler. The analysis was carried out under the following conditions: column type was Rxi-5ms, column length was 30 m; column diameter was 0.25 mm; column adsorbent thickness was 0.25 μm, evaporator temperature was 250 °C; thermostat temperature was 60-250°C; carrier gas was helium; sample volume was 0.2 μl with a 1:1 sample separation. The heating rate of the thermostat and the pressure of the carrier gas were set according to the design of a four-factor experiment with three levels of variation, and then chromatograms were recorded. The positions of two factors in the design of experiment were left vacant. The structure of the PDDoE design and the mathematical processing of the results of its application, as well as calculations based on the obtained empirical equations, were carried out using the previously developed program “PDDoE” (Auth. Sert. RK No. 26 dated 01.10.2018).

As a matter of convenience, peaks with high intensity corresponding to the highest content of the substance in the mixture were selected for the study. The primary processing of the results was carried out automatically using the standard program “GC-MS Data Analysis”, containing a database of mass spectra of nearly 1,000,000 compounds.

Considering the high reproducibility of the GC method and the unique features of the PDDoE method, it is possible to avoid the errors of a singular measurement [9], so the optimization experiment was carried out in one repetition. The chromatogram obtained under the conditions determined by the PDDoE method was recorded three times to assess the performance and quality of the model.

Results and Discussion

Table 1 illustrates the design of a four-factor experiment for the optimization of the GC conditions with three levels of factors variation, as well as some results of its application. The rate of column temperature rise and the pressure of the carrier gas were selected as variable factors. The positions of two factors were left vacant.

Table 1

Design and results of the optimization experiment

No.	ΔT, $^{\circ}C$/min	P, psi	Vac. 1	Vac. 2	$\overline{t_R}$, min	$\overline{\omega}$, min	$\overline{I}*10^{-4}$
1	1	2	1	1	84.93	0.389	300.9
2	1	5	2	2	81.71	0.334	272.7
3	1	10	3	3	77.44	0.338	190.45
4	6	2	2	3	21.51	0.0945	1390.9
5	6	5	3	1	20.71	0.0936	1236.4
6	6	10	1	2	19.83	0.0845	884.54
7	12	2	3	2	12.8	0.06	1754.5
8	12	5	1	3	12.27	0.06	1777.3
9	12	10	2	1	11.6	0.06	1413.6

Here, ΔT°C/min is column heating rate; P, psi is a carrier gas pressure; Vac. 1, Vac. 2 are values of vacant factors, $\overline{t_R}$, min is an average retention time, $\overline{\omega}$, min is an average peak width, $\overline{I}*10^{-4}$ is an average intensity over 11 peaks.

The main goal of the optimization experiment was to achieve a balance between the resolution and the duration of the chromatogram registration process. In Figure 1 it can be seen that changing the conditions process significantly affects the chromatogram.

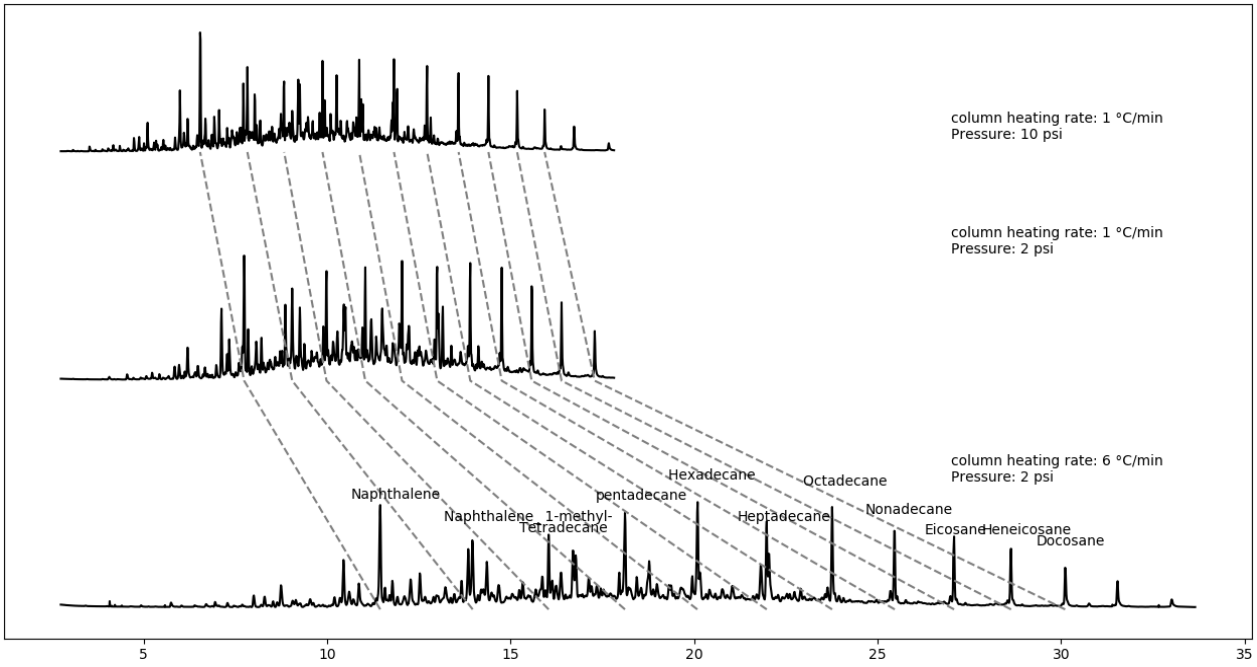

Figure 1. Influence of helium pressure and column heating rate on chromatogram quality

The figure perfectly illustrates that there is the general tendency of the process acceleration with increasing pressure and, more specifically, increasing heating rate, and an increase in resolution with decreasing carrier gas pressure. The data in Table 1 were processed using PDDoE to establish a quantitative relationship between gas pressure, heating rate, and some parameters of the chromatogram. Since three levels of factors variation create only three points for approximating the partial dependence, the list of used approximating functions was limited to linear and intrinsically linear ones. Figure 2 shows the dependence of the average retention time on significant parameters. Analysis of the curves clearly demonstrates that the average distance between the peaks decreases rapidly with an increase of the heating rate and slightly decreases with an increase of the carrier consumption. The dependences on the vacant factors are expressed by straight lines that practically coincide with the line of average values, which indicates the minimal influence of unaccounted and random factors on the experiment result.

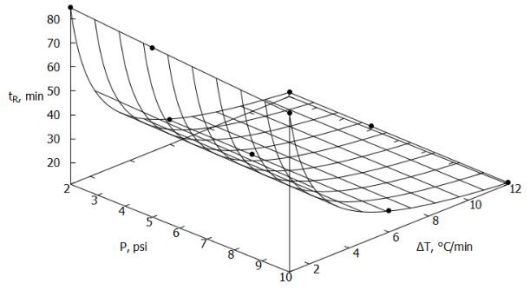

Figure 2. Dependence of the average retention time on heating rate and helium pressure

Generalized equation (1) describes the dependence of the average retention time on the considered factors:

$$\overline{t_R} = 81.26 \times \Delta T^{-0.7631} \times \frac{1}{0.03421 + 0.0004116 \times P} / 27.3804,\ R = 0.9917,\ t_R = 146.9447. \quad (1)$$

The dependences of the average width of the peaks in the chromatogram on the considered parameters (Fig. 3) also turned out to be decreasing. The heating rate plays a dominant role, as in the case of the average retention time.

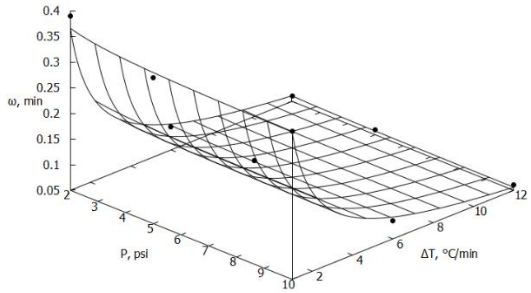

Figure 3. Dependence of the average width of the peak on heating rate and helium pressure

Generalized equation (2) describes the dependence of the average retention time on the considered factors:

$$\overline{\omega} = 0.3478 \times \Delta T^{-0.7219} \times (0.117 + \frac{0.0255}{P}) / 0.1234,\ R = 0.9857,\ t_R = 85.0297. \quad (2)$$

The partial dependences of the average peak height on the conditions of chromatographic separation, presented in Fig. 4, allow us to conclude that the relationship between the width and height of the peaks is ambiguous. The average height logically increases with an increase of the heating rate, but decreases with an increase of the carrier gas pressure, more than the average width.

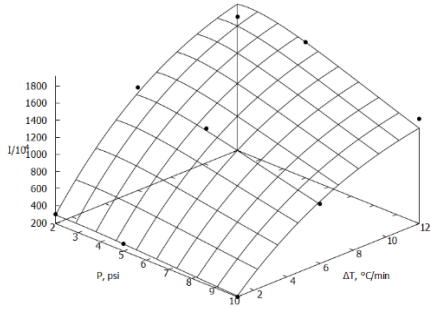

Figure 4. Dependence of the average height of the peak on heating rate and helium pressure

Generalized equation (3) describes the dependence of the average retention time on the considered factors:

$$\bar{I} \times 10^{-4} = 264.9 e^{-0.05799 \Delta T} \times \Delta T^{1.014} \times 925.8 e^{-0.09389 P} \times P^{0.2335} / 778.2956,\ R = 0.9928,\ t_R = 169.4889. \quad (3)$$

For multicomponent systems, as a rule, it is not possible to select the conditions for a chromatogram registration that are equally suitable for a clear separation of all components. At the same time, the obtained mathematical model (equations 1–3) is applicable for an optimization of the general qualitative and semi-quantitative analysis.

Based on the recorded chromatograms, a model can be built for any other measurement result (for example, for the resolution with a relation to certain signals) without repeated measurements. This point is the undoubted advantage of the PDDoE in comparison to other methods of mathematical experiment design.

For mathematical models of the resolution with a relation to a particular pair of peaks, a slight decrease in accuracy is observed, which is most likely associated with the variance in determining the width of the peaks. For example, the dependence of the resolution (R_S) of the peaks of naphthalene and 4-ethylphenol on the considered parameters is described with the help of the equation (4):

$$R_S = (0.083 + 0.2346 / P) \times (0.1364 + 0.08223 / \Delta T) / 0.1577 \text{ , } R = 0.8003, t_R = 5.4526. \quad (4)$$

The experimental value of the resolution for these peaks was obtained according to the generally accepted formula $R_S = \frac{2d}{\omega_1 + \omega_2}$, in which d is a distance between the tops of the peaks, ω is a width of the peak.

Figure 5 allows to see that individual experimental points are located at a relatively large distance from the approximated surface.

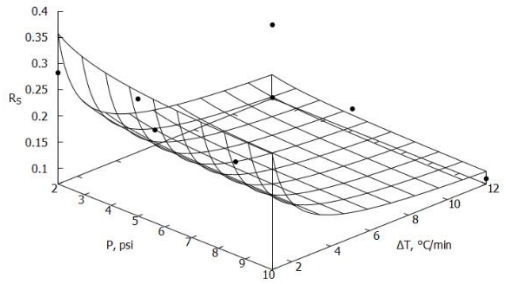

Figure 5. Dependence of the resolution (R_S) of the peaks of naphthalene and 4-ethylphenol on heating rate and helium pressure

The calculation of the maximum achievable value of the resolution of the indicated peaks leads to a value of 0.3575 at P = 2 psi ΔT = 1 °C/min.

Experimental verification of the obtained dependencies was carried out by triple registration of the chromatogram at a pressure of 3 psi and a heating rate of 2 °C/min. Considering the Student's coefficient for three measurements and a probability of 0.95, equal to 4.3, the results are represented in Table 2.

Table 2

Results of the experimental verification of the model

Y	Y_{calc}	Y_{exper}
$\bar{t}_R$	49.5026	49.55±1.89
$\bar{\omega}$	0.2145	0.2164±0.0085
$\bar{I}$	549.75	549.01±19.11
R_S	0.2082	0.2185±0.0833

The result of the control experiment shows that the mathematical model is adequate and the assessment of its accuracy is correct. The accuracy of the generalized equations generally correlates with the reproducibility of the quantities.

Conclusions

Summarizing all of the results, we can conclude that probabilistic-deterministic design of experiment can be successfully used to optimize the conditions for gas chromatography of complex mixtures. When using the method, it should be considered that the averaged parameters of the chromatogram are explained by

generalized equations with an accuracy higher than 0.98, while for individual characteristics (the height of one peak, the resolution of 2 peaks, the retention time of the component, etc.), the accuracy of the models turns out to be noticeably lower due to the worse experimental reproducibility of these values. In general, PDDoE can be recommended for carrying out an optimization of the experiment in gas chromatography.

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Эксперименттің ықтималды детерминистік жоспарлауын қолданумен көмір шайырының газ хроматографиясы жағдайларын оңтайландыру

Құрамы күрделі объектілерді талдаудың физика-химиялық әдістерін әзірлеу үшін экспериментті математикалық жоспарлау әдістерін қолдануды талап етеді. Мақалада Rxi-5ms бағаны бар Agilent 7890A аспабында таскөмір шайырын гидрогенизациялау өнімдерін хроматографиялық бөлу үдерісінің математикалық моделін алу үшін эксперименттің ықтималды-детерминистік жоспарлауды (ЭЫДЖ) қолдану мүмкіндігі зерттелген. Бағанның қыздыру жылдамдығы мен тасымалдаушы газ қысымының барлық хроматограмма үшін орташа мәндерімен байланысын жоғары дәлдікпен орнатуға болатындығы көрсетілген. Қоспаның құрамдас бөліктерінің шығындарының жеке сипаттамаларын модельдеудің дәлдігі аз, бірақ көптеген практикалық қажеттіліктер үшін жеткілікті болып табылады. Орташа ұстау уақыты мен орташа қарқындылықтың қарастырылатын факторларға тәуелділігі үшін сызықтық емес көпше корреляция коэффициенттері (СККК) 0,99-дан асты, шыңның орташа ені үшін

ол 0,98-ді құрады. Нафталин мен 2-этилфенол шыңдарына қатысты айыру қабілетінің тәуелділігі үшін СККК практика үшін маңыздылық деңгейі жеткілікті жағдайында 0.8-ден асты. Математикалық модельдің сапасы оқыту экспериментінде қолданылмаған бағанның қыздыру жылдамдығы мен тасымалдаушы газдың қысымы мәндерінде хроматограмманы үш рет тіркеу жолымен тексерілді. Алынған жалпыланған теңдеулермен есептелген нәтижелер өлшеу нәтижелерімен жақсы үйлеседі. Газ хроматографиясында оңтайландырылған экспериментті математикалық жоспарлаудың әдісі ретінде ЭЫДЖ әдісін ұсынуға болады.

Кілт сөздер: газ хроматографиясы, экспериментті жоспарлау, көмір шайыры, МС-ГХ, экспериментті ықтималды-детерминистік жоспарлау, оңтайландыру, айыру уақыты, шыңның биіктігі мен ені.

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Оптимизация условий газовой хроматографии каменноугольной смолы с применением вероятностно-детерминированного планирования эксперимента

Разработка физико-химических методов анализа объектов сложного состава требует применения методов математического планирования эксперимента. В статье исследована возможность использования вероятностно-детерминированного планирования эксперимента (ВДПЭ) для получения математической модели процесса хроматографического разделения продуктов гидрирования каменноугольной смолы на приборе Agilent 7890A с колонкой Rxi-5ms. Показано, что взаимосвязь скорости нагревания колонки и давления газа-носителя с величинами, усредненными для всей хроматограммы, может быть установлена с высокой точностью. Отмечено, что точность моделирования индивидуальных характеристик пиков компонентов смеси меньше, однако остается достаточной для многих практических нужд. Коэффициенты нелинейной множественной корреляции (КНМК) для зависимости среднего времени удерживания и средней интенсивности от рассматриваемых факторов превысили 0,99, для средней ширины пика составили более 0,98. КНМК для зависимости разрешающей способности по отношению к пикам нафталина и 2-этилфенола превысили 0,8 при достаточном для практики уровне значимости. Качество математической модели проверено трёхкратной регистрацией хроматограммы при значениях скорости нагревания колонки и давления газа-носителя, не использовавшихся в обучающем эксперименте. Результаты измерений отлично согласуются с вычисленными по полученным обобщённым уравнениям. Метод ВДПЭ может быть рекомендован в математическом планировании оптимизационного эксперимента в газовой хроматографии.

Ключевые слова: газовая хроматография, планирование эксперимента, каменноугольная смола, ГХ-МС, ВДПЭ, оптимизация, время удерживания, высота и ширина пика.

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