Chemistry, Physics and Technology of Surface. 2024. V. 15. N 4. P. 500-506

PACS: 82.00.00; 82.75.Z; 82.39.Wj; 82.80.Bg doi: 10.15407/hftp15.04.500

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NEW SORBENTS FOR DETERMINING THE QUALITY OF ALCOHOLIC BEVERAGES BY CHROMATOGRAPHIC ANALYSIS

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A new universal gas-chromatographic method of identification of toxic impurities is proposed in order to improve the quality indicators of alcoholic beverages. Application of chromatographic methods in wine making is characterized by some peculiarities, which is stipulated from one hand by substance characteristics as they are and from the other by changes in chromatographic methods possibilities. The method allows to determine the quality and chemical composition of the alcoholic beverages, which to some extent determines the possibility of regulating its quality on a scientific basis. Modification of the methods presented in the work is based on utilization of packed and capillary-packed columns. They are mainly usable for quantitative analysis, are stable, characterized with good reproducibility and can be used as long as a year and more. Several immobile liquid phases – PEG-300, PEG-400, PEG-20000, SE-30 and polymeric sorbent – Poropak-Q, Separon-CDA – were tested in order to determine the optimum conditions for chromatographic separation. To achieve this goal, a combined chromatographic packed column (Poropak-Q+SE-30) based on the principles of adsorption and distribution chromatography was created. Chromatography of a twelve-component 0.1 % graded mixture (acetone, acetic aldehyde, butanone-2, methanol, propanol-2, ethanol, butanol-2, propanol-1, isobutanol, butanol-1, crotonaldehyde, isopentanol) was carried out. The analyses were performed in both isothermal and temperature-programmed modes.

The chromatographic method developed by combining air-adsorption and distribution chromatography (combined column) provides the possibility of effective identification and maximum separation of harmful micro-impurities in alcoholic beverages.

***Keywords**: alcoholic beverages, gas-chromatography, combined column, toxic impurities*

INTRODUCTION

Improvement of quality indicators of alcoholic beverages on the basis of specification of appropriate technological processes remains one of the actual tasks. Therefore, the peculiarities of chromatographic analysis of harmful impurities in alcoholic beverages are still relevant today. Chromatographic methods of research open a unique opportunity to determine the relationship between the quality of the beverage and its chemical composition, which to some extent gives rise to the possibility of regulating its quality on a scientific basis. As a result of these studies, the understanding of the composition of alcoholic beverages at different process stages is expanding while at the same time gaining experience in the use of chromatography for the separation of complex systems [1–4].

The volatile components of alcoholic beverages consist of a wide range of compounds, including acids, alcohols, aldehydes and other aromatic compounds in trace amounts. Gas chromatography (GC) is a powerful tool for analysing alcoholic beverages. Minimal sample preparation is usually required because the samples are in a liquid state in an alcohol or alcohol-water matrix. Flavour compounds tend to be volatile in nature, which fulfils one of the basic requirements of GC. General purpose detectors such as a flame ionisation detector (FID) or more informative detectors such as a catarometer, mass selective detector (MSD) can be used. In addition, the ability to automate the analysis makes GC a very practical tool in a quality assurance and quality control environment [5, 6].

During impurities partition, overlapping peaks (in particular, methanol, ethanol, acetaldehyde, *etc*.) are often observed in the chromatogram. The reason for this phenomenon is that the ethanol content of an alcoholic beverage is usually quite high, and the corresponding peak in the chromatogram overlaps the peaks of its previous and subsequent

components. The analytical mixture contains substances with boiling points close to each other. In addition, depending on the selectivity of the liquid phase, even substances with significantly different boiling points can be initiated as a single peak. Therefore, when performing air chromatographic analysis, it is necessary to use several such phases, which allow maximum separation of the components of the objects of study due to the different selectivity of the phases for different compounds [7–10].

To improve the quality of alcoholic beverages, a new universal air gas-chromatographic method for the identification of toxic impurities is proposed.

The modification of the methods presented in this work is based on the use of packed and capillary packed columns. They are particularly reliable for quantitative analysis, stable, have good reproducibility and work up to a year and more.

MATERIALS AND METHODS

Several stationary liquid phases – PEG-300, PEG-400, PEG-20000, CE-30 and polymeric sorbents – Poropak-K, Separon-CDA – were tested in order to determine the optimal conditions for chromatographic separation.

The studies were carried out on a gas chromatograph Chrom-4 (Czech Republic), which was modernized: the chromatograph is connected to a personal computer via a multimeter AX-18B with a USB port and a corresponding computer program allowing to process experimental data in Excel format. Flame ionization detector and thermal conductivity detector (catarometers) were used. Different solid carriers (Chromaton N-AW, Chromosorb W and Celite-545) as well as different carrier gases (N_2, Ar) were tested to determine the optimum conditions for chromatographic separation. The studies were carried out at different chromatographic column temperatures and at different carrier gas velocities. Packed columns of different lengths (0.5, 2.4, 3, 3.5, 3.7, 4 m) were prepared. Accordingly, a combined packed column was prepared and tested, the ratio of liquid phase and polymer sorbent was also varied.

The separation ability of the columns was tested on the example of artificial graded mixtures containing harmful micro-impurities of alcoholic beverages. The analysis was carried out both in isothermal and in temperature programming regimes.

A 12-component (acetone, acetic aldehyde, butanone-2, methanol, propanol-2, ethanol, butanol-2, propanol-1, isobutanol, butanol-1, croton aldehyde, iso-pentanol) graded mixture (0.1 %) was prepared and chromatographically analyzed.

RESULTS AND DISCUSSION

The study of the efficiency of the prepared columns showed that a wide range of identification of harmful micro-impurities and the best separation were obtained on the stationary liquid phase SE-30 (column length 3.5 m) and on the polymeric sorbent – Poropak-Q (column length 0.5 m). The advantage of these phases is that they separate a part of volatile substances, which are eluted to ethyl alcohol (methanol, acetic aldehyde) (Table 1).

Table 1. Retention times of harmful micro-impurities in a graduated mixture on liquid phase SE-30 (column length 3.5 m) and on polymeric sorbent – Poropak-Q (column length 0.5 m)

Harmful micro-impurities	**Retention time, minute**	
	Liquid phase - ***SE-30***	Polymeric sorbent – ***Poropak-Q***
Acetic aldehyde	1.14	0.06
Methanol		0.13
Ethanol	1.32	
Acetone		0.41
Propanol-2	1.58	
Propanol-1	2.15	1.20
Butanon-2	2.35	2.08
Butanol-2	2.45	
Iso-butanol	3.08	2.26
Crotonaldehyde		2.47
Butanol-1	3.58	3.33

As can be seen from the Table 1, the separation of the eleven-component mixture is improved on the polymer sorbent (Poropak-Q), in particular, isobutanol-crotonic aldehyde pair is separated and acetic aldehyde peak is identified, which is not observed on the stationary liquid phase (SE-30). However, it should be noted that ethanol, acetone and propanol-2 are identified as a single peak on the polymer sorbent, while ethanol and acetone are identified on the liquid phase.

A chromatographic method based on the combination of gas-adsorption and partition chromatography (combined column) was developed for effective identification and maximum separation of harmful micro-impurities contained in alcoholic beverages.

The combined column consisted of a fixed liquid phase (SE-30) and a polymer sorbent (Poropak-Q). The length of the column was 4 metres. The separation of a twelve-component graded mixture of harmful micro-impurities contained in alcoholic beverages was carried out under the selected optimal conditions of analysis (Fig. 1).

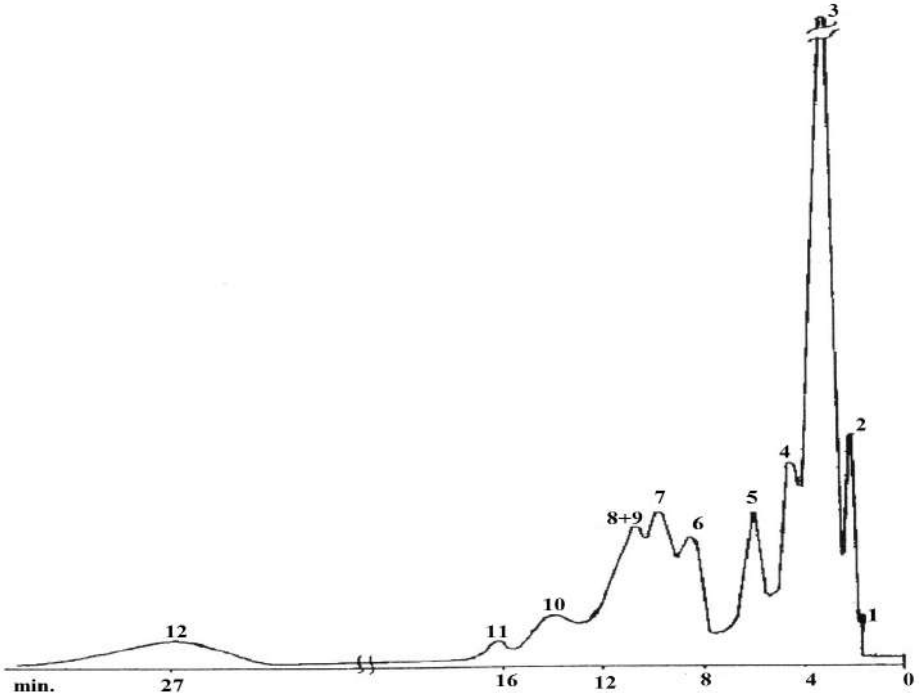

Fig. 1. Chromatogram of separation of the graded mixture containing harmful micro-impurities found in alcoholic beverages: combined column, column length 4 m. Graduated mixture: *1* – acetaldehyde; *2* – methanol; *3* – ethanol; *4* – propanol-2; *5* – propanol-1; *6* – butanone-2; *7* – acetone; *8* – butanol-2; *9* – iso-butanol; *10* – crotonaldehyde; *11* – butanol-1; *12* – iso-pentanol

As can be seen from the chromatogram, the order of elution of the components on the column changes. On the fixed liquid phase (SE-30) and on the polymeric sorbent (Poropak-Q) acetone elutes together with ethanol, while on the combined column it moves to the 7th position and is registered as a separate peak, which is probably due to the features of the polymeric sorbent (Poropak-Q).

Factory produced cognac spirit (Brandy spirit) (Fig. 2), mulberry (Fig. 3 *a*) and grape vodka (Fig. 3 *b*) were investigated on selected sorbents [fixed liquid phase (SE-30) and polymeric sorbent (Poropak-Q)] and on a combination column, under the set of optimum conditions used.

The method of direct introduction of the alcoholic beverage into the chromatographic column was used in this work, since this method provides an accurate representation of the quantitative and qualitative content of substances in the sample under study (Figs. 2 and 3). Quantitative calculation of peaks on the chromatogram was carried out using the planimetric method.

Table 2 presents the volumetric concentrations of harmful micro-impurities in alcoholic beverages on the combined column for graduated mixture and test samples.

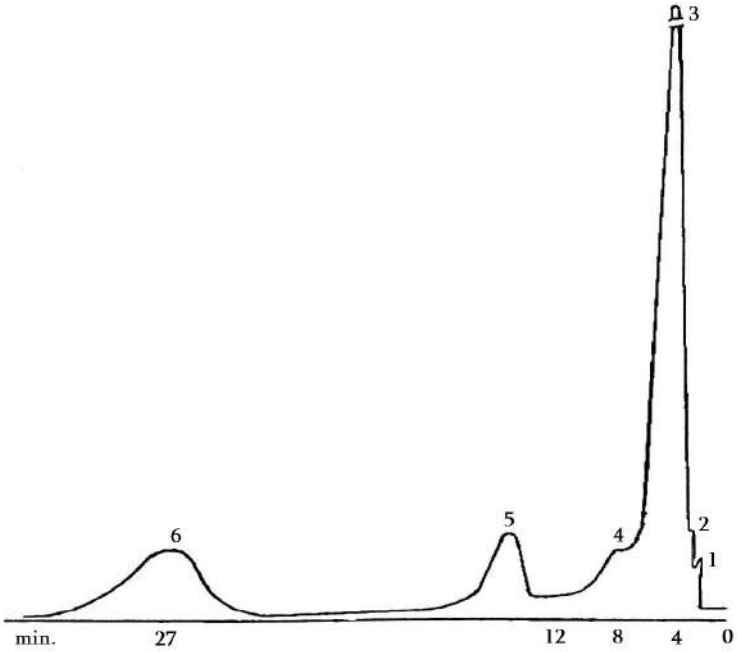

Fig. 2. Chromatogram of identification of harmful micro-impurities contained in factory-produced cognac alcohol (combined column: *1* – acetaldehyde, *2* – methanol, *3* – ethanol, *4* – propanol-1, *5* – iso-butanol, *6* – iso-pentanol)

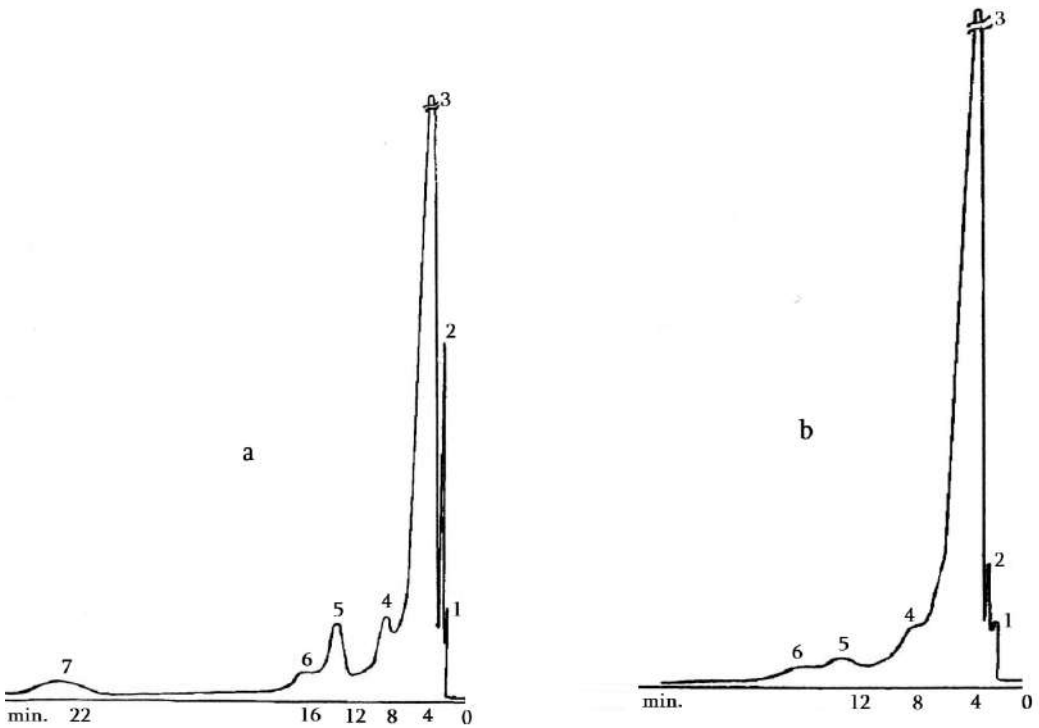

Fig. 3. Chromatogram of identification of harmful micro-impurities contained in mulberry (*a*) and grape (*b*) vodkas (combined column: *1* – acetaldehyde, *2* – methanol, *3* – ethanol, *4* – propanol-1, *5* – acetic acid, *6* – iso-butanol, *7* – iso-pentanol)

Table 2. Volumetric concentrations of harmful micro-impurities in the tested samples and in the graded mixture

Harmful micro-impurities	Volumetric concentrations			
	Graduated mixture	***Brandy spirit***	***Mulberry vodka***	***Grape vodka***
Acetic aldehyde	0.38	0.70	0.40	0.49
Methanol	2.75	1.63	6.41	1.99
Ethanol	53.0	70.44	77.54	89.93
Propanol-2	7.10	-	-	-
Propanol-1	6.03	5.62	6.70	5.08
Butanon-2	5.86	-	-	-
Acetone	8.83	-	-	-
Butanol-2	8.76	-	***Acetic acid*** 5.23	***Acetic acid*** 1.87
Iso-butanol		6.26	1.79	0.62
Crotonaldehyde	2.91	-	-	-
Butanol-1	0.58	-	-	-
Iso-pentanol	3.77	15.34	1.92	-

The Table 2 shows that it is very important to choose an effective column, selective sorbent and optimal conditions. In particular, in the graduated mixture, butanol-2 and isobutanol are registered as one peak, it was found that mulberry and grape vodka contain acetic acid instead of butanol-2 and it elutes instead of butanol-2.

Wines and alcoholic beverages produced, processed or transported in contact with plastics (tanks, pipes, pump casings, plastic containers ...) can be contaminated with organic compounds from the phthalates group. It is for this reason that the demand for analyses of phthalates in wines and alcoholic beverages has gradually increased in recent years [11]. Phthalates are widely used as additives in the production of plastic materials as well as in some food packaging materials. Some of these compounds are considered as potent endocrine destroyers, which has recently led to changes in regulations regarding their use in food contact materials. The critical standards for dibutylphthalate in alcoholic beverages are 0.01–2.20 mg/kg [12].

The paper presents the identification of dibutylphthalate in three different cognac alcohols on the liquid phase SE-30, applied to a solid carrier, Chromaton N-AW, column length 3 m. The volume fraction of dibutylphthalate in cognac alcohol was determined by experimental data, which are presented in Table 3.

Table 3. Volumetric concentrations of dibutylphthalate in three different cognac alcohol

Dibutylphthalate	**Volumetric concentrations in different cognac alcohol, %**		
	#1	***#2***	***#3***
	9.02	7.24	4.80

CONCLUSION

The carried out work presents the characteristics of the packed chromatography column, providing: optimally possible identification of toxic micro-impurities, as well as the conditions of research and chromatographic data processing technique; comparative analysis of the efficiency of packed chromatographic columns in the analysis of toxic micro-impurities by gas-adsorption chromatography method.

The chromatography method developed by combining gas-adsorption and distribution chromatography (combined column) provides the possibility of effective identification and maximum separation of harmful micro impurities in alcoholic beverages.

Absolute calibration and internal standard methods were mainly used in the presented work.

Нові сорбенти для визначення якості алкогольних напоїв методом хроматографічного аналізу

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Запропоновано новий універсальний газохроматографічний метод ідентифікації токсичних домішок з метою покращення якісних показників лікеро-горілчаних виробів. Застосування хроматографічних методів у виноробстві характеризується деякими особливостями, які зумовлені, з одного боку, властивостями субстанцій як вони є, а з іншого – змінами у можливостях хроматографічних методів. Спосіб дозволяє визначити якість і хімічний склад алкогольної продукції, що певною мірою визначає можливість регулювання її якості на науковій основі. Модифікація представлених у роботі методів базується на використанні насадкових і капілярно-насадкових колонок. Вони в основному використовуються для кількісного аналізу, стабільні, характеризуються хорошою відтворюваністю і можуть використовуватися протягом року і більше. Для визначення оптимальних умов хроматографічного розділення досліджено декілька нерухомих рідких фаз – ПЕГ-300, ПЕГ-400, ПЕГ-20000, СЕ-30 та полімерний сорбент – Поропак-Q, Сепарон-ЦДА. Для досягнення поставленої мети була створена комбінована хроматографічна насадкова колонка (Poropak-Q+SE-30) на основі принципів адсорбційної та розподільчої хроматографії. Проведено хроматографію дванадцятикомпонентної 0.1 % градаційної суміші (ацетон, оцтовий альдегід, бутанон-2, метанол, пропанол-2, етанол, бутанол-2, пропанол-1, ізобутанол, бутанол-1, кротоновий альдегід, ізопентанол). Аналіз проводили як в ізотермічному, так і в температурно-програмованому режимах. Хроматографічний метод, розроблений шляхом поєднання повітряно-адсорбційної та розподільної хроматографії (комбінована колонка), забезпечує можливість ефективної ідентифікації та максимального відділення шкідливих мікродомішок в алкогольних напоях.

***Ключові слова**: алкогольні напої, газова хроматографія, комбінована колонка, токсичні домішки*

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Received 10.06.2024, accepted 25.11.2024