Проведені дослідження з визначення питомої сорбційної ємності активованого вугілля марки БАУ-А та пористих полімерів типу полісорб-1, полісорб-10 та тенакс GC з використанням газової хроматографії. Це дало змогу прогнозувати їх експлуатаційні характеристики та можливості використання в адсорбційних системах вловлювання ароматичних речовин під час концентрування соків та екстрактів

Ключові слова: газова хроматографія, ізотерма адсорбції, адсорбційна ємність, адсорбент, ароматична речовина

Проведены исследования по определению удельной сорбционной емкости активированного угля марки БАУ-А и пористых полимеров типа полисорб-1, полисорб-10 и тенакс GC с использованием метода газовой хроматографии. Это позволяет прогнозировать их эксплуатационные характеристики и возможности использования в адсорбционных системах улавливания ароматических веществ во время концентрирования соков и экстрактов

Ключевые слова: газовая хроматография, изотерма адсорбции, адсорбционная емкость, адсорбент, ароматическое вещество

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THE USE OF GAS CHROMATOGRAPHY IN DETERMINING THE SORPTION CAPACITY OF THE ADSORBENT

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1. Intoduction

One of the priority sectors in food industry is the production of concentrates of aromatic plant material. The use of concentrates is predetermined by the need to provide a high degree of readiness of the manufactured foodstaffs, save packaging and transportation efforts, and ensure a sustainable range of products all year round.

Despite the use of modern technology to provide concentration and low temperature of the process, many aromatics, or aromatic compounds (ACs), of juices and extracts are lost in the juice vapour, which degrades the quality of the finished product. Thus, saving an aromatic component in a concentrate is a topical problem for the industry in Ukraine and other countries.

Europe and the USA use the notion of *FTNJ* (*From the Named Juice*) (natural flavor from the named juice) or *"back flavor"*, i. e. a set of ACs obtained from distillates of raw materials of the same name. Such flavourings are used to rearomatize fruit juices, extracts, and concentrate bases, i.e. return the ACs extracted or separated from the same type of product [1].

Advanced producers of juice concentrates and extracts have proposed technological methods to trap aromatic components that are based on the processes of distillation and condensation (the equipment of such companies as *Khranmash* and *Yednist'* (*Unity*)), absorption by solvents or inert gases (the *Termovak* plant), and adsorption. Since AC production involves the processes of condensation, extraction and absorption, it is characterized by significant shortcomings: high costs of cooling, solvents, and low concentration of ACs. The latter can be increased via the solvent stripping, although it is accompanied by additional costs and some loss in ACs).

An industrially efficient, yet insufficiently studied, method to trap low-concentration volatile ACs is adsorption. The method of AC trapping by the activated carbon adsorbent directly from the juice vapour was proposed by Gross. The adsorbent is placed in perforated cylinders embedded in pipelines for juice vapours. The adsorbent saturation usually takes up to 15–20 hours [2]. Researchers have suggested that the degree of concentration might be increased and, consequently, AC loss reduced due to the AC trapping by a sorbent with subsequent desorption via heat treatment at 170 °C. A 2–3 mm diatomite preliminarily covered with polymethylfenylsiloxane [3], XAD-7HP [4], is used as a sorbent.

Therefore, the introduction of the adsorption method in the technology allows enterprises to efficiently recycle plant material and obtain their natural AC concentrates.

2. Literature review and problem statement

An important parameter of adsorption properties and performance of the adsorbent to be used in a batch adsorber is its sorption capacity. Adsorption capacity is determined by the specific substances and is expressed in units of mass or volume that is best kept by the adsorbent under certain conditions. Thus, the adsorbent amount required to trap the AC is calculated for specified temperature and pressure provided there is no loss in the latter.

There is not yet any methodology to determine the sorption capacities of adsorbents that are used to extract ACs from water vapour.

The capacity of each adsorbent is primarily measured by means of static methods of constructing adsorption isotherms, in particular, the weight method (based on the adsorbent weight gain after adsorption) or the volume method (based on the adsorbate amount reduction in the vapour phase after adsorption). At present, there exist automatic electronic devices to measure this characteristic of adsorbents. For example, the *TriStar 3020* analyzer calculates the surface area and porosity by the isotherm of the low-temperature sorption of nitrogen vapour [5].

One known method consists in plotting the isotherm of water vapour adsorption in the desiccator placed in a thermostat, where the water vapour pressure is provided by saturated salt solutions or solutions of different concentrations of sulfuric acid [6].

Besides the above static methods, dynamic methods are also commonly used to measure the sorption capacity of the adsorbent in the process of a constant flow of the adsorbate passing through it [7, 8]. The authors of [9] have proposed an equipment to determine adsorption isotherms by zeolites of ethanol vapours while they are constantly passing through of the adsorbent layer at certain temperature and pressure. Unlike static ones, dynamic methods allow evaluating the adsorption properties of the adsorbents that are specified in calculating industrial adsorbers for drying or cleaning vapours from impurities.

The gas chromatography method is promising in plotting adsorption isotherms [10, 11]. Measurements are made as follows: a chromatographic column is filled with an adsorbent and thermostated; then the column is slowly purged with a mixture of an adsorbate gas and a carrier gas (such as nitrogen, helium, or hydrogen); at a certain temperature the adsorbent traps the adsorbate while leaving out the carrier gas. As a result, a partial pressure of the substance in the mixture decreases, whereas the detector records its quantity and the peak – adsorption. After an even saturation at a fixed concentration of an adsorbtive in the working mixture the sample is heated. This results in separation of the adsorptive (thermal desorption); the quantity of the latter is recorded at the peak – desorption. The areas of the peaks of adsorption and desorption are proportional to the amount of the substance adsorbed on the surface of the adsorbent [11]. Other studies [12] were aimed at determining the sorption capacities of adsorbents for nitrogen at a temperature of liquid nitrogen, argon at 77 K, CO^2 at 273 or 293 K, and other components. Experimental facilities are modified to determine adsorption capacities for more volatiles by means of blowing the carrier gas through the equipment [13, 14].

Given the drawbacks of both static and dynamic methods, the gas chromatography method is used to determine the sorption capacities of adsorbents. The choice of the method is determined by the following advantages:

– the possibility to specify the necessary conditions for the system "AC-adsorbent", i. e. the temperature and flow rate corresponding to the real conditions of evaporation of juices and extracts;

– the possibility to plot adsorption isotherms for volatile ACs whose concentrations in juice vapours and extracts are small;

– high rate and accuracy of the analysis findings;

– minor cost of the experiment.

3. The purpose and objectives of the study

The purpose of the study was to determine the sorption capacities of adsorbents (capable of trapping ACs) for camphor and isoamylol by means of the gas chromatography method.

To achieve the goal we had to solve the following tasks:

– to determine the terms for experimental studies in measuring the adsorption capacities of adsorbents for ACs;

– to plot the camphor adsorption isotherm and the isoamylol isotherm for the selected adsorbents under prescribed conditions;

– to calculate the sorption capacities of the adsorbents and make recommendations on the use of the obtained data in the calculation of adsorbers to trap ACs.

4. Materials and methods of the use of gas chromatography in determining the sorption capacities of adsorbents

Previous studies [15] allowed selecting adsorbents capable to trap ACs from water vapour of juices and extracts, such as activated carbon BAC and porous polymers of the polysorb and tenax types. Physical and chemical properties of the selected adsorbents are given in Table 1.

The experiments were conducted on the gas chromatograph Selmikhrom-2003 (Ukraine) equipped with a flame ionization detector. Nitrogen is used as the carrier gas, whereas such ACs as camphor (with a molecular weight of 152.2 g/mol) and isoamylol (with a molecular weight of 88 g/mol) serve as adsorbates.

Table 1

Physical and chemical properties of adsorbents capable of trapping ACs

Adsorbent		Specific surface, m^2/g	Average pore diameter, nm	Bulk density, g/cm^3	Temperature limit, °C	Composition
activated carbon BAC-A		700–800	≤200	0.161	300	carbon form (87–97 %)
Porous polymeric sorbents	tenax GC	19–30	140	0.181	350	poly (2.6-diphenyl) phenylenoxide
	polysorb-1	300–350	13	0.152	250	styrene copolymer (60 %) with divinylbenzene (40 %)
	polysorb-10	300–350	20	0.162	250	polydivinylbenzene

The methods described in [16] allowed creating the trace curves of camphor and isoamylol at the moment of their passing through the packed column that is filled with polysorb-1, polysorb-10, tenax-GC, and activated carbon BAC-A. The curve points were used to calculate the values of the substance concentration in the gaseous environment C, μ/ml, and the corresponding amount of the adsorbed matter a, μ/ml.

5. Findings on the adsorbent sorption capacity obtained with the use of gas chromatography

Fig. 1–4 show the isotherms of monomolecular adsorption of isoamylol and camphor on the surface of adsorbents such as polysorb-1, polysorb-10, tenax-GC, and activated carbon BAC-A.

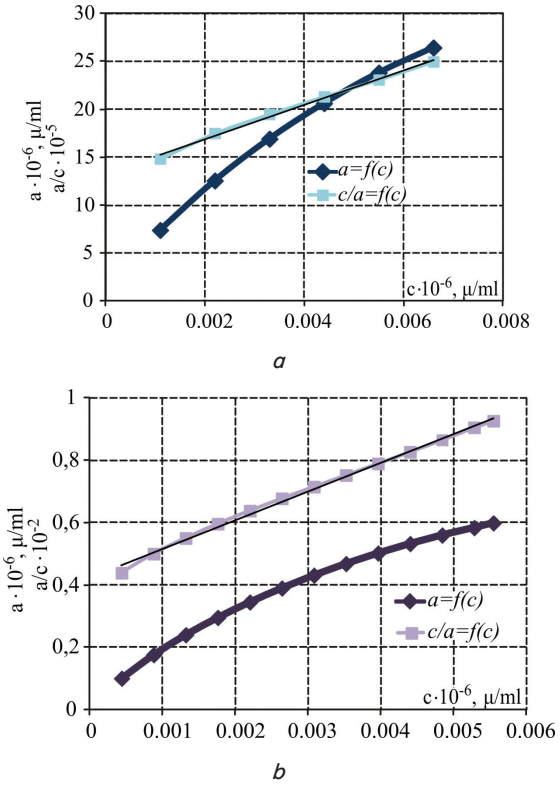

Fig. 1. Adsorption isotherms for polysorb-1: *a* – isoamylol and *b* – camphor

The above isotherms were used to impart specificity to the Langmuir monomolecular adsorption for the amount of AC of up to 0.1 mg.

The adsorption isotherm is described by the Langmuir equation (11) as follows:

$$a = a_0 \cdot \frac{c}{K_1 + c} = a_0 \cdot \frac{p}{K_1 + p}, \quad (11)$$

where a_0 is the monolayer capacity, p is the partial pressure of the adsorbate, c is the adsorbate concentration in the vapour phase, and K_1 is a constant that depends on the temperature and kind of the adsorbent and a constant value for the pair adsorbent-adsorbate that is numerically equal to the adsorbate concentration that engages half of the active centres of the adsorbent.

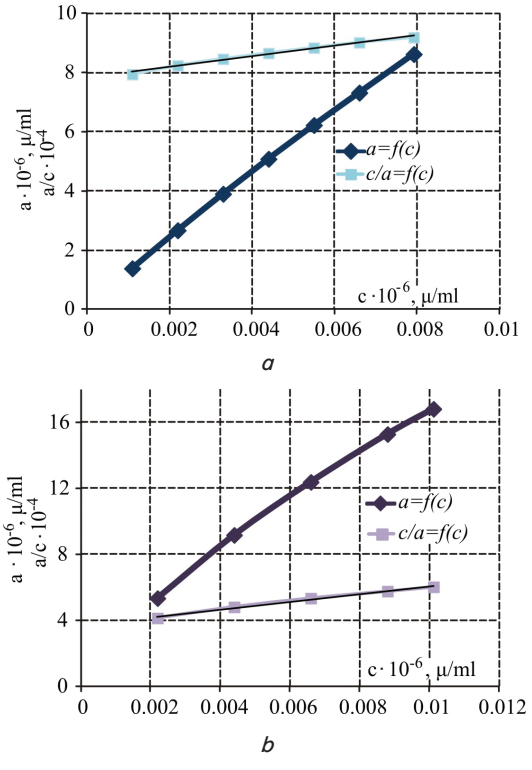

Fig. 2. Adsorption isotherms for polysorb-10: *a* – isoamylol and *b* – camphor

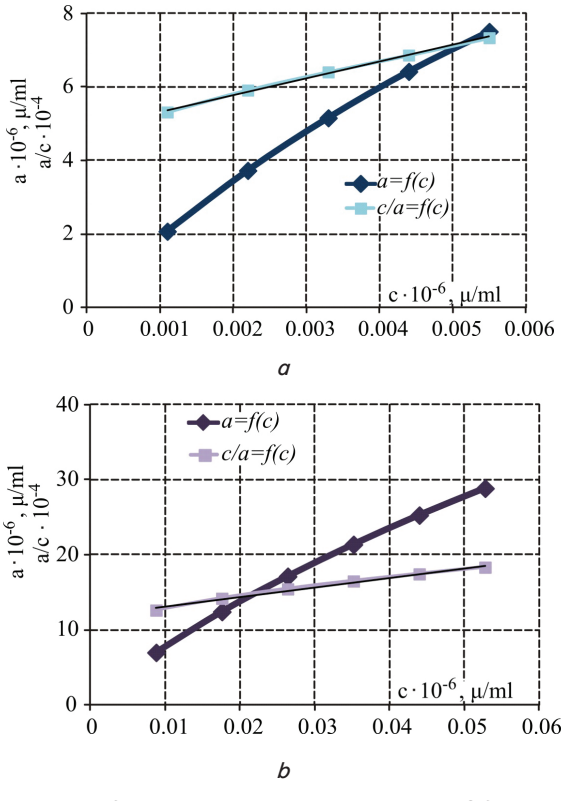

Fig. 3. Adsorption isotherms for tenax GC: *a* – isoamylol and *b* – camphor

The graphic solution of the Langmuir equation (11) by converting the adsorption isotherm a=f(c) into the straight line c/a=f(c) has given the cotangent of the tilt angle that is equal to the adsorbent monolayer capacity for ACs.

Calculations of the specific adsorption capacities of adsorbents are given in Table 3.

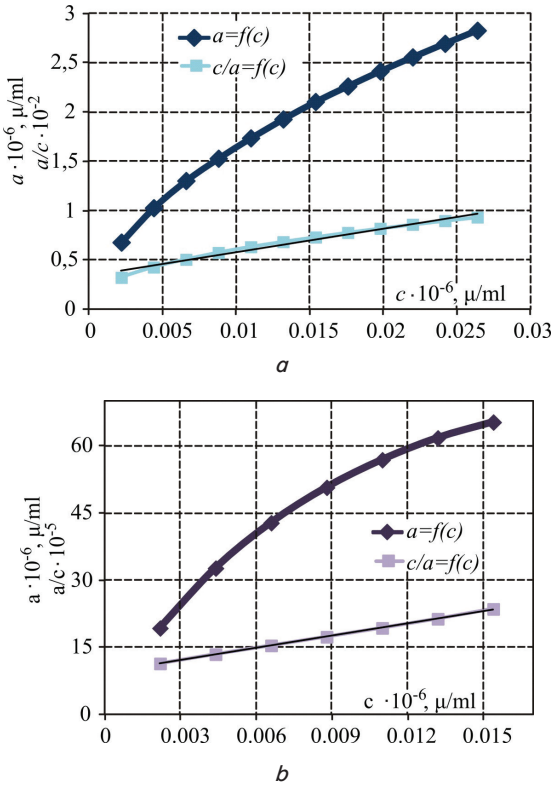

Fig. 4. Adsorption isotherms for activated carbon BAC-A: *a* — isoamylol and *b* — camphor

Table 3

The specific adsorption capacities of adsorbents

Adsorbent	Bulk density, g/cm³	Adsorbate	Monolayer specific capacity	
			×10⁻⁶ mmol/cm³	mg/g
polysorb-1	0.152	isoamylol	55.60	29.26
		camphor	1.04	1.04
polysorb-10	0.162	isoamylol	55.60	27.46
		camphor	42.46	39.89
tenax GC	0.181	isoamylol	22.00	9.72
		camphor	78.34	65.88
BAC-A	0.161	isoamylol	3.96	1.97
		camphor	109.45	103.47

The relative error in the measurement and calculation of the specific adsorption capacities of adsorbents was no more than 2.5–2.8 %.

The obtained data reveal differences in the effect of camphor and isoamylol on the specific sorption capacities of the adsorbents, which is due to differences in the interaction "adsorbent-adsorbate", as well as the size and polarity of camphor and isoamylol molecules.

6. Discussion of the findings on the use of gas chromatography in determining the sorption capacity of the adsorbent

Analyzing the findings we should emphasize the benefits of using gas chromatography to determine the sorption capacities of adsorbents. They are as follows:

– the method is accurate and reliable, as evidenced by high sensitivity of the chromatograph detector;

– the research does not require any bulky equipment as it employs only the classic gas chromatograph equipped with an analytical chromatographic column of 10–20 cm and an automatic registering device – computer or recorder;

– the research/experiment conditions are flexible, i. e. there is possibility to change the temperature of adsorption, the adsorbent, as well as the adsorbate and its concentration in the vapour phase.

The research disadvantages include:

– the complexity of calculations for plotting the adsorption isotherms;

– the complexity of studying the adsorption of ACs at high boiling points because of "smearing" in the desorption curve.

The obtained data on the sorption capacities of adsorbents for isoamylol and camphor have practical use in the calculation of the optimal amount of the adsorbent for adsorption of ACs from extracts and juices. For example, the concentration of 100 kg peppermint extract involves evaporation of 80–90 g of aromatic components in the juice vapour. The trapping of ACs requires 77 kg of polysorb-1 or 0.773 kg of activated carbon BAC-A. In addition, the amounts of ACs can be optimized depending on the fractional composition of the AC of juice or extract and considering the selectivity of adsorbents.

The use of gas chromatography also provides data on the selectivity of adsorbents. Polisorb-1 has the highest specific capacity for the low-molecular AC of isoamylol (29.26 mg/g) rather than camphor (1.04 mg/g). Tenax GC and activated carbon are more selective to camphor (65.88 and 103.47 mg/g, respectively) than to isoamylol (9.72 and 1.97 mg/g, respectively).

Further studies that can be aimed at enhancing the range of adsorbents and ACs are likely to offer options for the latter use in adsorption systems in food industry.

7. Conclusions

1. We have determined the conditions of experimental studies in the adsorption capacities of adsorbents for ACs, namely: the adsorption temperature (in the column thermostat) of 100 °C and the sensitivity of the flame ionization detector of $10 \cdot 10^{-10}$.

2. The trace curves obtained with the use of gas chromatography were used to plot the isotherms of camphor and isoamylol adsorption by activated carbon BAC-A, polysorb-1, polysorb-10, and tenax GC. The resulting isotherms are characteristic of the Langmuir monomolecular adsorption provided isoamylol and camphor concentration in the vapour phase is up to 0.1 mg/l. This allowed calculating the monolayer capacity of each adsorbent.

3. The obtained adsorption isotherms were used to determine the adsorption capacities for camphor and isoamylol of such adsorbents as polysorb-1, polysorb-10, tenax, and activated carbon BAC-A. These adsorbents have the following

capacities: polysorb-1 – 1.04 and 29.26 mg/g, polysorb-10 – 39.89 and 27.46 mg/g, tenax – 65.88 and 9.72 mg/g, and activated carbon BAC-A – 103.47 and 1.97 mg/g, respectively. These findings demonstrate the ability of the adsorbents to trap the above components in the vapour phase, as well as reveal the selectivity of adsorbents to ACs from different chemical classes. Thus, polisorb-1 is selective to isoamylol, whereas tenax and BAC-A are selective to camphor. Consequently, the studies have shown the possibility of using gas chromatography to determine the adsorption characteristics of adsorbents. The findings are important for calculating adsorbers that are capable to trap ACs.

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