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ARTICLES

Magnetic Sorbents Based on Hydrophobized Silicas: Influence of Structural Matrix Parameters on Magnetic and Sorption Properties

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Abstract—The magnetic and sorption properties and structural characteristics of hydrophobized silicas (CMS-C_{16}) modified with magnetite nanoparticles (MNPs) are studied. The structural characteristics of CMS when modified with MNPs, established by low-temperature nitrogen adsorption, practically do not change, and the sorption and magnetic properties depend to the greatest extent on the size of the sorbent particles. The dependence of the efficiency of extraction of some organic compounds on magnetic sorbents on the size of sorbate molecules is found. The magnetic sorbent was used for the sample preparation using the QuEChERS method for determining the active ingredients of drugs and their metabolites in animal kidneys using liquid chromatography—mass spectrometry.

Keywords: sorption, chemically modified silica, magnetite nanoparticles, magnetic sorbents

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Sorption extraction of various compounds is an effective method of sample preparation in analytical practice. Currently, new sorption materials have been obtained, and the technology of the sorption process is being changed. One of developing areas is the production and use of magnetic nanomaterials, mainly magnetite (Fe_3O_4) and magnetic sorbents based on it. A large number of magnetic sorbents have been synthesized, mainly magnetic nanoparticles (MNP) with various inorganic or organic compounds with a "core—shell" structure immobilized on their surface [1—3].

Of particular interest are magnetic nanocomposite sorbents, which can be synthesized by relatively simple methods: by encapsulating MNP in the initial matrix or by forming MNP on the surface of a sorbent. Magnetic sorbents combine the sorption properties of source materials with the ability of separating the sorbent from the matrix solution using a magnet. Depending on the type of the main matrix, which occupies most of the volume of the nanocomposite material, carbon-containing [4] or organopolymer magnetic sorbents, e.g., based on hyper-cross-linked polystyrene [5], are used.

A method has been developed for producing magnetic sorbents based on silicas chemically modified with hexadecyl groups (CMS-C_{16}). These are commercially available sorbents effectively extracting many organic compounds [6]. A distinctive feature of these sorption materials is the presence of samples with a wide range of matrix structural parameters: pore diameter, specific surface area, particle size. The use of magnetic sorbents is promising to simplify the determination of toxicants, drugs or pollutants in complex matrices based on the ability of the control of the movement of sorbents in two-phase systems using an external constant magnetic field [7—11].

The aim of this work was to study the effect of the structural characteristics of the silica matrix on the magnetic and sorption properties of the resulting magnetic sorbents in relation to various organic compounds, and also to establish a possibility of using these sorbents to determine the active ingredients of drugs and their metabolites in the animal kidneys.

EXPERIMENTAL

Reagents and equipment. Silicas chemically modified with hexadecyl groups (ZAO BioKhimMak ST, Russia) and magnetic sorbents obtained on their basis according to the procedure described in [6] were used as sorbents.

We used alcoholic solutions of pyrene and naphthalene (0.25 mg/mL, Sigma—Aldrich, United States), and an aqueous solution of the Sunset Yellow FCF dye (1 g/L, Sigma—Aldrich, United States). Solutions of the following standards in methanol with

Table 1. Characteristics of the initial and resulting magnetic sorbents

Sorbent	S_{sp}, m^2/g	V_{pore}, cm^3/g	d_{pore}, nm
CMS-C_{16}-130, particle size 7 μm	198	0.58	11.3
CMS-C_{16}-130/Fe_3O_4	183	0.52	11.4
CMS-C_{16}-100, particle size 100–200 μm	198	0.47	9.4
CMS-C_{16}-100/Fe_3O_4	191	0.45	9.4

a concentration of 1 mg/mL were also used: diflubenzuron (98%, TRC, Canada), deltamethrin (99.7%, Dr. Ehrenstorfer, Germany), piperonyl butoxide (95.8%, LGC, UK), 4-chlorophenylurea (98%, TRC, Canada), diflubenzoron-D4 (99%, Pharmaffiliates, India), deltamethrin-D5 (98%, TRC, Canada), piperonyl butoxide-D9 (96%, TRC, Canada).

The absorbances of solutions were recorded on an SF-103 spectrophotometer (Akvilon, Russia). The pH values of solutions were monitored using an Expert 001 pH potentiometer (Econix-Expert, Russia). Magnetic solid-phase extraction was carried out on an Ekros-6500 electromechanical shaker (Ekroskhim, Russia). The magnetic sorbent was separated from the solution using an Nd–Fe–B magnet (20 × 20 × 20 mm). The specific surface area and characteristics of the porous structure of the samples were determined by low-temperature nitrogen adsorption on an ASAP 2010 N automatic sorptometer (Micromeritics, United States). An LCMS-8050 liquid gas chromatograph–mass spectrometer (Shimadzu Corporation, Japan) was used in this work.

Sorption procedure in the static mode. A solution of a test substance was put into graduated 15-mL test tubes and the mixture was diluted with water to 10 mL. The absorbance of the solution before sorption was measured. Then a sorbent sample (0.07 g) was placed in the resulting solution. Before adding to the solution, the sorbent sample was treated with a small amount of ethanol (3–4 portions of 50 μL). The test tubes were shaken on a vibration mixer for the time necessary to establish a sorption equilibrium. After this, the sorbent was separated from the solution by decantation (in the case of magnetic sorbents, using a magnet). The distribution of analytes was controlled by determining equilibrium concentration in the aqueous phase using a spectrophotometric method. The concentrations on the sorbent were calculated from the difference between the initial and equilibrium concentrations in the aqueous phase.

Previously, we developed a method for modifying silica-based sorbents by the sorption of MNP from methanol [6]. Under the selected conditions, magnetic sorbents based on hydrophobized silicas were obtained: CMS-C_{16}-100/Fe_3O_4 (particle size 100–200 μm) and CMS-C_{16}-130/Fe_3O_4 (particle size 7 μm) with different structural parameters (Table 1).

RESULTS AND DISCUSSION

Properties of the resulting sorbents. The synthesized sorbents are superparamagnetic. The saturation magnetization of the sorbents obtained under identical conditions with a magnetite–sorbent mass ratio (1 : 4) was 0.8 emu/g for coarse fraction sorbents and 5.7 emu/g for fine-grained sorbent. It was found that, at a ratio in the range 1 : 30–1 : 5, the MNP content was significantly lower, and the sorbents had less pronounced magnetic properties, which made phase separation difficult.

The magnetic properties of the sorbents depend on the magnetite content in the sorbent phase. It was found that, with an increase in the pore diameter (from 10 to 50 nm) of the initial hexadecyl silicas, the iron content decreased slightly (from 0.49 to 0.43%), which is apparently associated with a decrease in the specific surface area of the matrix [12]. For the fine fraction of the sorbent CMS-C_{16}-130/Fe_3O_4, the iron content was 1.5%, i.e. three times higher. The presence of iron on the surface of silica sorbents was confirmed by energy-dispersive X-ray spectroscopy data; for one of the samples of the CMS-C_{16}-100/Fe_3O_4 sorbent it was 0.45 wt % (0.19 at %).

Using the method of low-temperature nitrogen adsorption at 77 K on an ASAP 2010 N installation, porous structure was studied and the specific surface area of the initial and magnetic sorbents was determined. Modification with magnetite practically did not lead to a change in the total surface area and specific pore volume for the coarse fraction the CMS-C_{16}-100/Fe_3O_4 sorbent; for the fine-grained CMS-C_{16}-130/Fe_3O_4 sorbent ,these values decreased slightly (Table 1). It is likely that magnetite nanoparticles are sorbed only on the outer surface of the granules. In this case, the MNP content and saturation magnetization are higher for a finely dispersed sorbent. This is explained by the higher sorption capacity of a finely dispersed sorbent due to the 15–30 times higher value of S_{sp} (m^2/g) of the outer surface of its granules compared to the coarse sorbent fraction (the ratio of S_{sp} of sorbents of coarse and fine fractions is proportional to the ratio of the radii of granules).

From a comparison of electron microphotographs (Fig. 1), one can see that MNP on the surface of the sorbent are present as agglomerates, because, taking

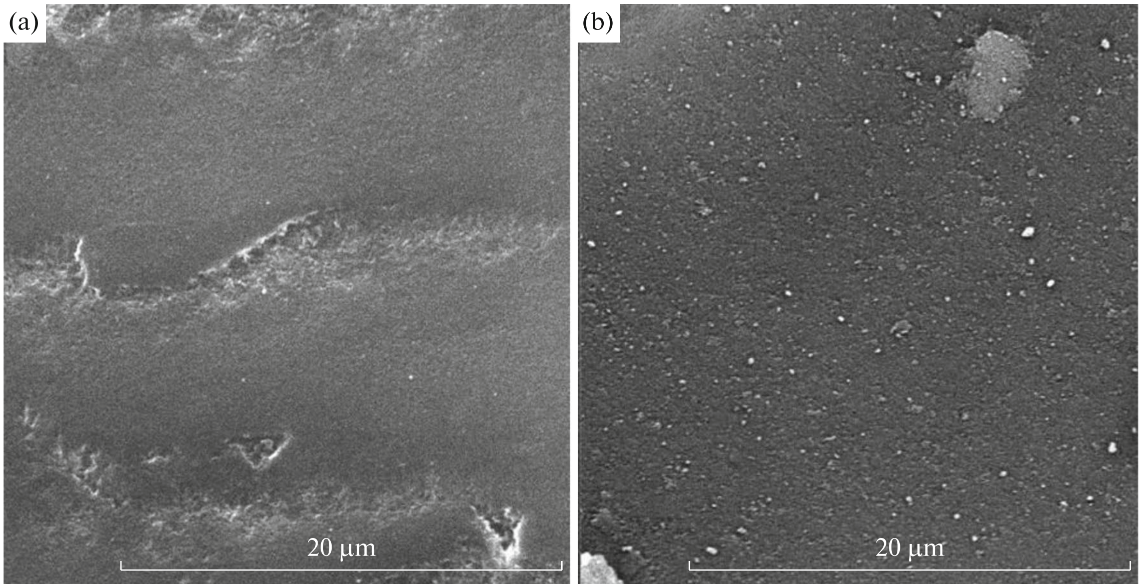

Fig. 1. Electron microphotographs of (a) CMS-C$_{16}$-100 and (b) CMS-C$_{16}$-100/Fe$_3$O$_4$.

into account the scale of the image, the particle size is at least 1 μm.

Thus, the structural parameters of hydrophobized silicas practically do not change when they are modified with magnetite, and the MNP content depends to a greater extent on the particle size of the initial sorbents.

Sorption properties of magnetic sorbents. A distinctive feature of almost all magnetic sorbents is their limited use in the region pH < 2, because magnetite begins to dissolve under these conditions. In [12], we found that magnetic hydrophobized silicas are stable in the pH range 3–7, which creates certain restrictions in using them for the sorption preconcentration of various analytes. The sorption capacities of CMS-C$_{16}$/Fe$_3$O$_4$ in relation to food dyes, phenols, and some PAH were compared. The determination of these compounds, which differ in molecular size and hydrophobicity, is an important environmental challenge.

It was found in [12] that the sorption of the Sunset Yellow (SY) food dye as an ion pair with cetyltrimethylammonium bromide (CTAB) on magnetic sorbents is slower and less efficient compared to the initial sorbents. Among the coarse-fraction sorbents, CMS-C$_{16}$-100/Fe$_3$O$_4$ turned out to be the most effective; therefore, it was chosen for the further research. In addition, CMS-C$_{16}$-100/Fe$_3$O$_4$ is closest in structural parameters to the finely dispersed CMS-C$_{16}$-130/Fe$_3$O$_4$ sorbent, which makes it possible to study the dependence of sorption on the particle size of the sorbent. It was found that particle size significantly affects the sorption of SY (Fig. 2). As one can see in the figure, sorption on CMS-C$_{16}$-130/Fe$_3$O$_4$ is faster and more efficient than on CMS-C$_{16}$-100/Fe$_3$O$_4$; however, in this case, the recovery of the dye on the magnetic sorbent is lower than that on the initial one. Below are the recoveries (R, %) of SY on (a) non-magnetic and (b) magnetic sorbents (m_c = 0.07 g, c_{cr} = 0.01 g/L, $c_{CTAB} = 4.6 \times 10^{-4}$ M, V = 10.0 mL, t = 60 min):

CMS-C$_{16}$-130		CMS-C$_{16}$-100	
90 (a)	75 (b)	90 (a)	65 (b)

One possible explanation for this effect is the large size of the SY molecule (the projection area of the SY molecule is 1.8 nm^2, and its ion pair with CTAB is even

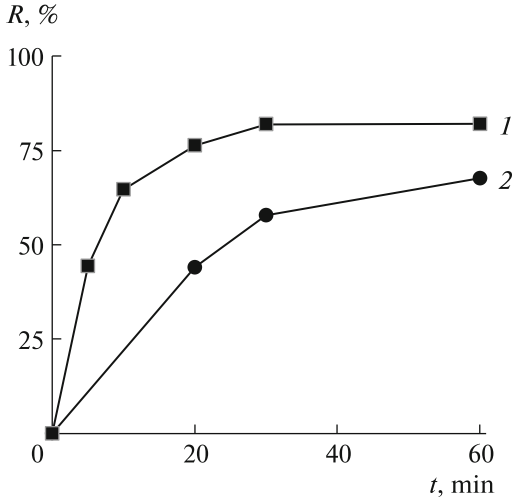

Fig. 2. Dependence of the recovery of the "Sunset Yellow" dye on magnetic sorbents CMS-C$_{16}$-130/Fe$_3$O$_4$ (*1*) and CMS-C$_{16}$-100/Fe$_3$O$_4$ (*2*) on the time of phase contact. $V_{aq.p.}$ = 5 mL, $m_{sorbent}$ = 0.05 g.

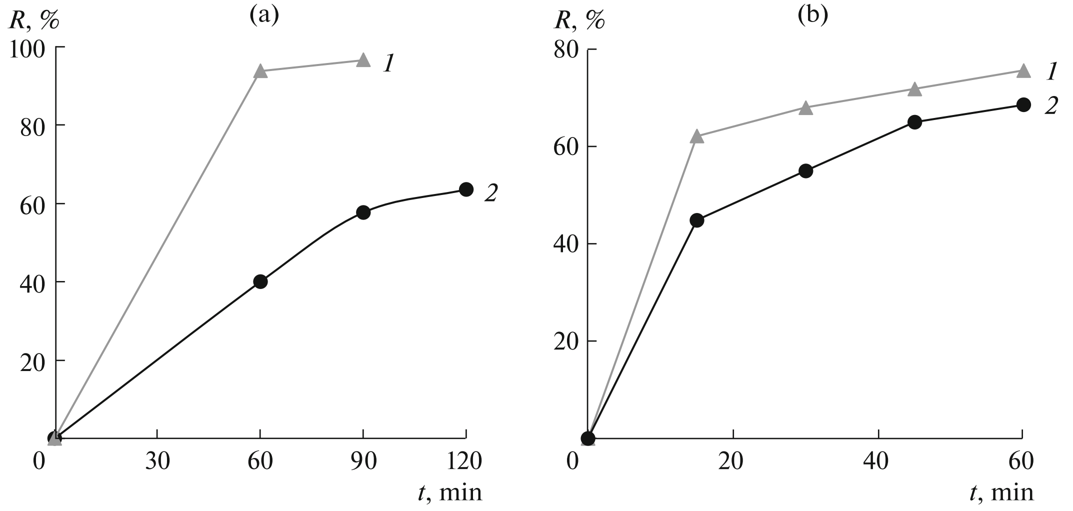

Fig. 3. Dependence of PAH sorption on the time of phase contact on sorbents CMS-C_{16}-100 (*1*) and CMS-C_{16}-100/Fe_3O_4 (*2*). (a) Pyrene: $m_{\text{sorbent}} = 10$ mg, 20% aqueous–alcoholic solution of pyrene ($c = 1.25$ μg/mL, $V = 10$ mL, $\lambda = 335$ nm). (b) Naphthalene: $m_{\text{sorbent}} = 20$ mg, 1% aqueous–alcoholic solution of naphthalene. $c = 5 \times 10^{-5}$ M, $V = 10$ mL, $\lambda = 275$ nm.

larger). To test this assumption, we studied the sorption of pyrene and naphthalene, whose molecular sizes are different (the projection area of pyrene and naphthalene molecules is 2.0 and 1.4 nm^2, respectively) on CMS-C_{16}-100 and CMS-C_{16}-100/Fe_3O_4. The sorption of pyrene on a magnetic sorbent is less efficient compared to the initial one (Fig. 3). Compared to pyrene, the difference in the sorption recovery of naphthalene on these sorbents is insignificant, which is probably due to the almost twofold smaller size of the naphthalene molecule.

The assumption that sorption depends on the size of the sorbate molecules is also confirmed by the results of studying the sorption capacity of magnetic sorbents in relation to phenol and its chlorine and nitro derivatives, the projection areas of the molecules of which are 0.2–0.7 nm^2. It was found that the sorption capacity of the magnetic sorbent does not differ from that of the initial one [13].

Thus, the structural characteristics of CMS modified with MNP, determined by the method of low-temperature nitrogen adsorption, practically do not change; therefore, the sorption capacity of magnetic sorbents is preserved in relation to small molecules (the projection area of the sorbates is less than 1 nm^2). A decrease in the sorption capacity of magnetic sorbents for larger molecules may be due to the partial blocking of the sorbent pores by magnetite nanoparticles.

Determination of deltamethrin (DM), piperonyl butoxide (PBO), diflubenzuron (DFB) and 4-chlorophenylurea (4-CPU) in animal kidneys. Hydrophobized silicas are used not only to extract the analyte being determined, but also to purify the sample from accompanying non-polar compounds using the QuEChERS method, while the analyte component remains in the organic phase [14, 15]. Thus, it is possible to determine the active ingredients of drugs in animal organs and tissues [10, 16, 17].

We studied a possibility of using the magnetic sorbent CMS-C_{16}-100/Fe_3O_4 for the determination of medicinal substances (MS) according to the procedure [18], which uses the Chromabond C_{18} sorbent. Table 2 presents the characteristics of the sorbents used.

To determine drugs in the kidneys of animals, 1.0 g of a pre-crushed kidney sample was placed in a 15-mL polypropylene test tube and extraction was carried out with 2 mL of acetonitrile. The extract was separated by decantation. A 0.1-g portion of a sorbent was added to the resulting solution, and the analytes to be determined remained in the acetonitrile extract, while the

Table 2. Characteristics of hydrophobized silica sorbents used in the QuEChERS method

Characteristic	Chromabond C_{18}	CMS-C_{16}-100/Fe_3O_4
S_{sp}, m^2/g	500	191
Pore size, nm	6.0	9.4
ω(C), %	14–15	16.5
ω(Fe), %	–	0.45

Table 3. Equations for calibration dependences of chromatographic peak area on the concentration (ng/g) of a medicinal substance in the kidneys

Active substance	The most intense MRM transition Q1/Q3	Calibration equation	Linearity range, ng/g	R^2
Diflubenzuron (DFB)	311.00 > 158.10 (+)	$y = 0.22x + 0.30$	10–500	0.992
Deltamethrin (DM)	523.20 > 280.90 (+)	$y = 0.03x + 0.03$	10–500	0.995
Piperonyl butoxide (PBO)	356.20 > 149.10 (+)	$y = 0.06x + 0.004$	1–50	0.995
4-Chlorophenylurea (4-CPU)*	169.00 > 126.00 (–)	$y = 1850.x + 2680$	10–500	0.987

* Calibration dependence was obtained without using an internal standard.

Table 4. Results (ng/g) of the simultaneous determination of diflubenzuron (DFB), deltamethrin (DM), piperonyl butoxide (PBO), 4-chlorophenylurea (4-CPU) in the kidneys of animals ($n = 3$, $P = 0.95$)

Compound	Found (added)		
DFB	52 ± 4 (50)	104 ± 6 (100)	192 ± 11 (200)
DM	51 ± 3 (50)	105 ± 6 (100)	190 ± 10 (200)
4-CPU*	53 ± 4 (50)	102 ± 7 (100)	195 ± 10 (200)
PBO	5.2 ± 0.5 (5)	10.7 ± 0.9 (10)	19 ± 3 (20)

*Determination without using internal standard.
In determining the active substances without introducing them into the initial matrix, the determined concentrations in the matrix were below the lower limit of quantification: 1 ng/mL for PBO, 10 ng/mL for DM, DFB, 4-CPU.

interfering matrix components (e.g., fats) were retained on the sorbent. Next, the sorbent was separated from the solution by centrifugation, the magnetic sorbent was separated by magnetic separation, and the supernatant was filtered into a vial through a syringe membrane filter. The resulting sample was used for an HPLC–MS/MS analysis. The conditions were as follows: ZORBAX Eclipse Plus C18 column (2.1 × 50 mm, 5 μm); pre-column ZORBAX Eclipse Plus C18 (2.1 × 12.5 mm, 5 μm); mobile phase A—deionized water; mobile phase B—a 5 mM solution of ammonium formate in methanol. Gradient program was as follows: 0–0.5 min—50% B; 0.5–10 min—100% B, 10–13 min—100% B, 13–13.05 min—0% B, 13.05–19 min—0% B. Injected volume was 5 μL, column temperature was 30°C, flow rate was 0.3 mL/min.

To construct calibration graphs using the reference sorbent Chromabond C_{18}, standard MS solutions were added to kidney samples. The calibration dependences of the chromatographic peak area on the MS concentration were linear in the ranges 10–500 ng/g (DFB, DM, 4-CPU) and 1–50 ng/g (PBO). The equations of the calibration graphs are given in Table 3.

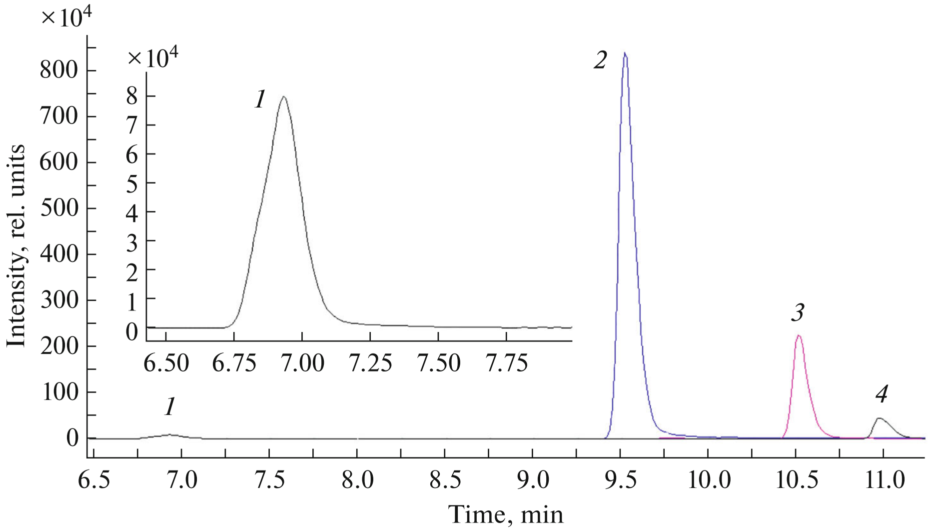

Fig. 4. Chromatogram of medicinal substances using CMS-C_{16}-100/Fe_3O_4 at the sample preparation stage: (*1*) 4-chlorophenylurea (500 ng/g), (*2*) diflubenzuron (500 ng/g), (*3*) piperonyl butoxide (50 ng/g), and (*4*) deltamethrin (500 ng/g).

Artificial mixtures of MS added to kidney samples were analyzed using the magnetic sorbent CMS-C_{16}-100/Fe_3O_4 for the purification of extracts. Concentrations were calculated using the resulting calibration graphs. The results are presented in Table 4. A chromatogram of a mixture of the studied MS using the CMS-C_{16}-100/Fe_3O_4 sorbent is shown in Fig. 4.

The data obtained indicate a possibility of using a magnetic sorbent in this method as an alternative to Chromabond-C_{18} without losing the efficiency of substance extraction. At the same time, the sample preparation stage is simplified and accelerated, because in the case of Chromabond-C_{18}, centrifugation for 15 min at 4500 rpm is used to separate the sorbent, while in using a magnetic sorbent, phase separation occurs within 1 min and no special equipment is required.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

REFERENCES

1. Chen, J. and Zhu, X., *Food Chem.*, 2016, vol. 200, p. 10. https://doi.org/10.1016/j.foodchem.2016.01.002
2. Roto, R. and Yusran Kuncaka, A., *Appl. Surf. Sci.*, 2016, vol. 377, p. 30. https://doi.org/10.1016/j.apsusc.2016.03.099
3. Liu, J., Su, Z., Xu, Q., Shi, Y., Wu, D., Li, L., Wu, Y., and Li, G., *Food Chem.*, 2023, vol. 399, p. 133843. https://doi.org/10.1016/j.foodchem.2022.133843
4. Grazhulene, S.S., Zolotareva, N.I., Red'kin, A.N., Shilkina, N.N., Mitina, A.A., and Kolesnikova, A.M., *Russ. J. Appl. Chem.*, 2018, vol. 91, no. 11, p. 1849. https://doi.org/10.1134/S0044461818110154
5. Tolmacheva, V.V., Apyari, V.V., Furletov, A.A., Dmitrienko, S.G., and Zolotov, Yu.A., *Talanta*, 2016, vol. 152, p. 203. https://doi.org/10.1016/j.talanta.2016.02.010
6. Karsakova, Yu.V. and Tikhomirova, T.I., *Sorbtsionnye Khromatogr. Protsessy*, 2018, vol. 18. C. 845. https://doi.org/10.17308/sorpchrom.2018.18/612
7. Varela-Martínez, D.A., González-Salámo, J., González-Curbelo, M.Á., and Hernández-Borges, J.Ch., in *Liquid-Phase Extraction*, Poole, C.F., Ed., Amsterdam: Elsevier, 2020, p. 399 https://doi.org/10.1016/b978-0-12-816911-7.00014-1
8. Chen, M., Chen, L., Pan, L., Liu, R., Guo, J., Fan, M., Wang, X., Liu, H., and Liu, S., *J. Chromatogr. A*, 2022, vol. 1668, p. 462913. https://doi.org/10.1016/j.chroma.2022.462913
9. Xiong, X., Li, D., Du, Z., Xiong, C., and Jiang, H., *J. Chromatogr. A*, 2020, vol. 1622, p. 461137. https://doi.org/10.1016/j.chroma.2020.461137
10. Islas, G., Ibarra, I.S., Hernandez, P., Miranda, J.M., and Cepeda, A., *Int. J. Anal. Chem.*, 2017, vol. 2017, p. 8215271. https://doi.org/10.1155/2017/8215271
11. Hubetska, T.S., Kobylinska, N.G., and Menendez, J.R.G., *J. Agric. Food Chem.*, 2020, vol. 68, p. 13550. / https://doi.org/10.1021/acs.jafc.0c00601
12. Karsakova, Yu.V., Tikhomirova, T.I., and Tsizin, G.I., *Moscow Univ. Chem. Bull.*, 2020, vol. 75, p. 293. https://doi.org/10.3103/S0027131420050041
13. Karsakova, Yu.V., Frolova, A.I., Tikhomirova, T.I., and Tsizin, G.I., *J. Anal. Chem.*, 2022, vol. 77, p. 1540. https://doi.org/10.1134/S1061934822100070
14. Perestrelo, R., Silva, P., Porto-Figueira, P., Pereira, JA.M., Silva, C., Medina, S., and Câmara, J.S., *Anal. Chim. Acta*, 2019, vol. 1070, p. 1. https://doi.org/10.1016/j.aca.2019.02.036
15. Xu, J., Yang, M., Wang, Y., Yang, Y., Tu, F., Yi, J., and Chen, D., *J. Food Compos. Anal.*, 2021, vol. 103, p. 104120. https://doi.org/10.1016/j.jfca.2021.104120
16. Xu, X., Xu, X., Han, M., Qiu, S., and Hou, X., *Food Chem.*, 2018, vol. 276, p. 419. https://doi.org/10.1016/j.foodchem.2018.10.051
17. Chen, D., Xu, Q., Lu, Y., Mao, Y., Yang, Y., Tu, F., and Yang, Z., *J. Food Compos. Anal.*, 2021, vol. 101, p. 103965. https://doi.org/10.1016/j.jfca.2021.103965
18. Goncharova, E.N., Karsakova, Yu.V., Bryskina, D.E., Kozlov, S.V., Usha, B.V., Selimov, R.N., and Komarov, A.A., *Mater. IX Vseros. konf. s mezhdunar. uchastiem "Mass-spektrometriya i ee prikladnye problemy"* (Mater. IX All-Russ. Conf. on Mass Spectrometry and Its Applied Problems), Moscow, 2021, p. 128. https://doi.org/10.1016/j.foodchem.2016.01.002

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