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REVIEWS

ORDERED MESOPOROUS SILICA IN MODERN VERSIONS OF SOLID-PHASE EXTRACTION

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Abstract. The review systematizes information on nanostructured materials used in solid-phase extraction **(SPE)** and its modern versions. The main attention is paid to the consideration of nanostructured analogues of MCM-41 and SBA-15 both in classical SPE and in modern versions of solid-phase microextraction, microextraction by matrix solid-phase dispersion, dispersive solid-phase extraction, and magnetic SPE. The use of silicas with a hexagonal and cubic mesophase structure makes it possible to significantly increase the completeness of analyte extraction, improve the metrological characteristics of determining both metal ions and biologically active substances in complex multicomponent matrices of real objects of analysis. An abnormally high surface area (up to 1000 m^2/g and more), adjustable mesopore size, ease of modification by grafting functional groups allow to significantly increase the selectivity of solid-phase materials compared to traditionally used silica gels and polymer ion exchangers. The advantages of ordered silicas when used at the stage of extraction and concentration of analytes in solid-phase extraction options, as well as chromatographic separation of substances similar in nature, make it possible to expand the range of linearity of the analytical signal response of the analysis methods used, and the detection limits of ions and molecules can be reduced to the level of ng/mL, ng/g.

Keywords: *ordered mesoporous silicas, MCM-41, SBA-15, sample preparation, solid-phase extraction, dispersive solid-phase extraction*

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Recently, there has been a tendency to miniaturize sample preparation and reduce the duration of analysis. Along with the traditionally used liquid-liquid and solid-phase extraction (**SPE**), new sample preparation options are widely used in the determination of ions and molecules in multicomponent matrices. Among them are solid-phase microextraction, dispersive SPE, matrix solid-phase dispersion, etc., which are discussed in several reviews [1–5].

Modern variants of solid-phase extraction using classical sorbents have become the most widespread [1]. Traditionally, normal-phase silicones (silica gels) [6], as well as modified reverse-phase sorbents with grafted groups C8 and C18 [7] and polymer materials [8] are used. It is noted in [2] that the development of sample preparation methods is associated with the expansion of the range of sorbents, including new materials based on silicon oxide, which can increase the degree of analyte extraction or increase the efficiency of their concentration. The emergence of new classes of silica with an ordered nanostructure suggests an increase in the availability of sorption centers for analytes, the proportion of the used capacity of the sorption layer at the time of flow termination [9]. This is especially necessary when implementing SPE under dynamic conditions in order to achieve maximum efficiency values for the sorption concentration of *CE* [10, 11].

Taking into account the physical meaning of *CE*, increasing the efficiency of sorption concentration is important for increasing the analytical signal by concentrating the analyte per unit time [10]. Significantly lower limitations in the kinetics of ion and molecular sorption, noted in [9, 12–14], suggest an increase in the full utilization of the sorption layer capacity of ordered mesoporous silica. In this case, an increase in the efficiency of sorption concentration is associated with an increase in the ratio of the amount of sorbed substance «before the slip» to the amount of the component entering the layer [9]. It was shown in [9] that with dynamic sorption concentration of phosphatidylcholine, the efficiency (*CE* value) is several times higher when using nanostructured silica compared with silica gel. The disordered structure and uneven distribution of sorption centers on the pore surface of classical sorbents lead to a significant blurring of the output curves, which makes it impossible to achieve high concentration efficiency [9].

The peculiarities of sorbent synthesis determine the primary role in the formation of their structure and degree of order. In addition, the properties of solid-phase materials used at the stages of extraction, concentration and separation of substances can vary significantly depending on the development (specific area) of the surface, porosity and pore size distribution. The influence of synthesis conditions on the structure of silica is considered in detail in the literature [15–20]. Special attention was paid to the use of ordered silicones in solid-phase extraction in [21]. However, the issues of choosing sorbents for SPE are not sufficiently considered, including taking into account the role of the ordering of silicones, as well as the advantages provided by nanostructured materials.

The novelty of silica-ordered compounds complicates the choice of a criterion for comparing sorbents used at the stage of component concentration. In general, concentration is characterized by a concentration coefficient, which is defined as the ratio of the concentrations of a component in the initial solution and in the concentrate. However, in works on the use of ordered materials, this value is practically not given. The metrological characteristics of determining a component in a certain matrix are usually indicated [22–26]. In some works [22, 23, 27], the Enrichment Factor (***EF***) has been calculated. In this case, the complexity of comparing sorbents remains, since *EF* is provided only for the most «effective» sorbent [22, 23, 27]. The «most effective» material is understood to be the material whose use makes it possible to achieve the largest chromatographic peak area of the component being determined [22, 23] or the maximum degree of extraction [24–26].

Most frequently the nature of changes in analytical parameters when using ordered mesoporous silicones in SPE is not given in the literature, but only at the qualitative level, changes in the properties of sorbents are considered as a result of varying the nature of the matrix, modifiers, and functional grafted groups.

The purpose of this review is to discuss the peculiarities of changing the sorption properties of nanostructured silicones, as well as to identify their advantages for the implementation of modern solid-phase extraction options.

SYNTHESIS OF ORDERED SILICONES

Ordered mesoporous silica is obtained by the sol-gel template method (Fig. 1) [28, 29]. Alkoxysilanes, colloidal solutions of SiO_2, and sodium silicates are used as sources of silicon oxide. There are known works on the synthesis of ordered silica based on quartz [30], sand [31], rice husk ash [32] and other agricultural waste [33]. The use of such sources of silicon oxide significantly increases the environmental friendliness of synthesis, and in some cases makes it possible to organize waste-free production [34]. Surfactants of various natures are used as a template. The most commonly used are cetyltrimethylammonium bromide [15] and polyethylene oxide-polypropylene oxide-polyethylene oxide block copolymers (Pluronic P123, Pluronic F127) [17, 35]. By varying the synthesis conditions, it is possible to control the structure of silica (cubic, hexagonal, layered), the size of pores and particles, the surface area, the density of surface silanol groups, etc. Ionic liquids [36, 37], fatty acids [38], phospholipids [39, 40], et al are used as alternative templates. In some cases, synthesis is carried out on mixed micelles [41–43].

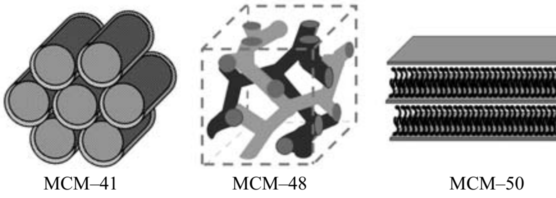

Fig. 1. Structure of some ordered mesoporous silica

One of the first papers devoted to the synthesis of silica with a controlled pore size was presented in 1990. Kuroda et al. [44]. The material was obtained by the ion exchange method from kanemite polysilicate in the presence of alkyltrimethylammonium salts with different hydrocarbon chain lengths. Later, the authors were able to obtain more ordered silica FSM-16 [28].

Nanostructured silica aroused particular interest after the publications of a group of scientists from Mobil Oil Corporation [15]. By varying the conditions, silicones with hexagonal (MCM-41), cubic (MCM-48), and layered (MCM-50) structures were obtained (Fig. 2). The pore size was 1.5–10 nm, depending on the chain length of the structure-guiding component. The first ordered mesoporous silica was obtained in the presence of ionnogenic surfactants (templates) interacting with silicate due to electrostatic forces. According to the proposed mechanism of silica formation, silicate ions condensed on already organized micelles [29]. However, it was later shown that such materials are formed as a result of more complex processes [45].

Scientists from other groups have obtained new ordered mesoporous silicones with a cubic mesophase structure (MSM-48, KIT-6) [15, 20]. In the mid-90s, a nonionic synthesis pathway was proposed [17]. Mesoporous silica MSU-1, MSU-2, and MSU-3 were obtained on the basis of polyethylene oxide surfactants [46]. In the presence of neutral diamines with a hydrocarbon chain length from 8 to 12 carbon atoms, ordered MSU-V silicones were synthesized [47]. The idea of using nonionic block copolymers as templates led to the appearance of SBA (Santa Barbara Amorphous) series materials with a bimodal system of micro- and mesopores [17, 35], the size of which exceeded the size of MCM-41 and MSM-48 mesopores.

Further development of methods for the synthesis of ordered materials is associated with the introduction

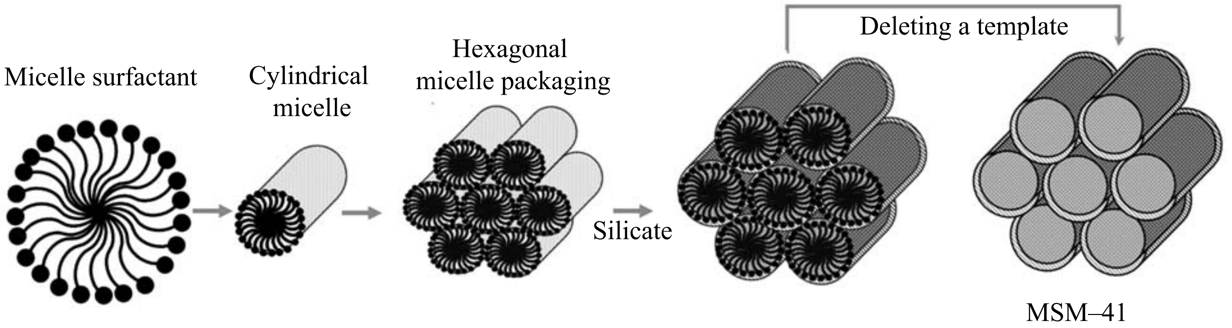

Fig. 2. Scheme of synthesis of ordered mesoporous silica (using the example of MCM-41)

of various additives into the reaction medium [48–50]. The presence of alkanols (for example, butanol-1) in the reaction mixture during the synthesis of ordered silicones can lead to the transition of the hexagonal structure of silica into a cubic one with a significant change in the distribution and specific density of sorption centers on the surface, their solvation, and, as a result, the sorption properties of silica as a whole. The sorbents synthesized in this way are classified as analogues of KIT-6 silica [48].

An important task to ensure high sorption capacity, high rate of sorption and desorption of analytes is to vary the size of mesopores while maintaining an ordered structure [51]. The mesopore dimension factor is regulated by the nature of the template, the conditions of silica synthesis, as well as additives that affect both the structure formation of the template and the formation of the silica matrix with the participation of precursors [52]. In particular, for MSM-41 analogues, the mesopore size can vary from 2 to 10 nm when using ionogenic alkylamines R-N$(CH_3)_3$X with the number of carbon atoms in the aliphatic part from 12 to 22 [13] (R = $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, etc.; X is the halide or hydroxide anion). Nonionic surfactants (for example, Pluronic P123 and Pluronic F127 block copolymers) are used to synthesize SBA-15 analogues with a pore size from 4 to 30 nm [17]. The change in the size of silica mesopores can be realized by using substances that affect the size of template micelles [49]. The addition of 1,3,5-trimethylbenzene as a solvent made it possible to obtain a material of the MCF (Mesostructured Cellular Foam) type [50], which is a uniformly arranged spherical cell forming a continuous three-dimensional pore system with a size of more than 10 nm. Large pores, uniform in size, determine the prospects for the separation of large molecules on MCF-type materials. It should be noted that the size of the mesopores, as well as the width of the pore size distribution, are especially important for the kinetics of ion and molecular sorption, including under dynamic conditions. Therefore, these parameters must be controlled to increase the efficiency of sorption concentration and sorption chromatographic separation of analytes using these silicones.

One of the factors determining the efficiency of columns in chromatography and the efficiency of sorption concentration during solid-phase extraction is the fractional composition of the sorbent, which ensures a narrow size distribution of sorbent granules [53]. Pseudomorphic transformation of silica gel [54, 55] to obtain ordered analogues of MSM-41 is a common synthesis method that allows achieving high efficiency of sorption concentration at SPE, as well as reducing the height equivalent to the theoretical plate for the sorbent layer during sorption chromatographic separation of substances [56].

Martin and Galarnu et al. [56] noted that the control of porosity and morphology in the synthesis of ordered materials (for example, MSM-41) allows to improve chromatographic characteristics compared with classical commercial columns. A very large surface area (~1000 m^2/g) leads, on the one hand, to higher retention times (a larger number of theoretical plates in the absence of a more significant erosion of the sorption front and peak width compared to classical sorbents). On the other hand, as noted by the authors of [56], the ordered porosity increases the efficiency of the column for high flow rates compared to classical silica gel-based columns, providing higher and more uniform molecular diffusion. This makes it possible to separate connections much faster without significant loss of column efficiency.

During sorption sample preparation under SPE conditions, ordered silica exhibits chromatographic patterns similar to those associated with more homogeneous molecular diffusion. It can be assumed that a lower dispersion of the analyte mass transfer rate in the sorbent layer also leads to an increase in the ratio of the amount of the substance «before the slip» to the amount of the component entering the layer, and therefore suggests that there is an increase in the efficiency of *CE* sorption concentration [9].

Similarly to chromatography, sorption concentration of a micro component can be characterized by the number of theoretical plates in accordance with the model of the theory of equivalent theoretical plates applied to solid-phase extraction [57]. The number of theoretical plates (N) is estimated taking into account the relative volume of retention (V_R) and the standard deviation of the relative volume of the «slip» of the substance ($\sigma_{V/V0}$) on the output curve, corresponding to the relative concentration of c/c_0 = 0.159–0.500 and c/c_0 = 0.500–0.841:

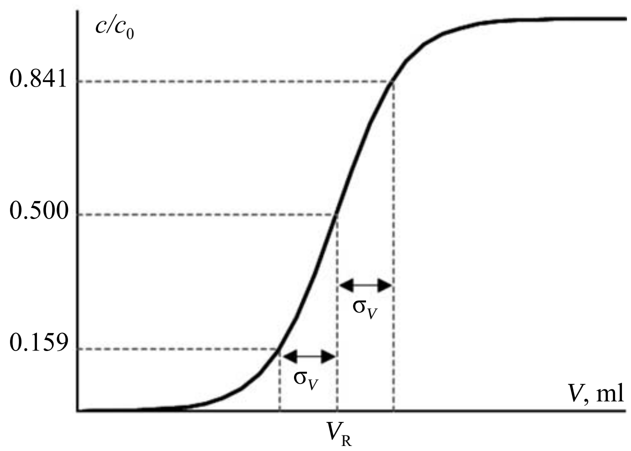

Fig. 3. A typical view of the output curve. V_R is the retention volume, σ_V is the standard deviation of the retention volume of the substance during its movement in the sorbent

$$N = V_R\,(V_R - \sigma_V)/\sigma_V^2.$$

The blurring of the output curve is related to the level of overshoot (Fig. 3), therefore, it directly affects the efficiency of the sorption concentration of *CE* [9].

However, Galarnu et al. [58] showed that the resistance to mass transfer is closely related to the size and shape of mesopores. Significant deviations of the mesopore diameter from the average value can lead to a decrease in *chromatographic* efficiency. This is often observed for classical silicones with a wide pore size distribution. Also, a decrease in the availability of sorption centers with a decrease in the size of mesopores leads to lower values of the number of theoretical plates of the sorption layer. In this context, spherical sorbent granules with large pores, narrow pore size distribution, and cubic symmetry (a highly connected pore network, as for MSM-48) may be the most suitable stationary phase for rapid separation processes in HPLC [58] and for concentrating analytes under dynamic conditions at SPE.

Modification of the surface by organic and inorganic reagents is one of the directions of variation in the sorption properties of silica. The most well-known and traditional approach to the modification of silica gels, which has become widespread, is the grafting of groups of octyl-, dodecyl-, hexadecyl- or octadecylsilanes, which make it possible to obtain reverse-phase silica C8, C12, C16 and C18. Silicones with grafted functional (amino-, cyano-, diol, etc.) groups have also become widespread, including in SPE. By their properties, such sorbents are often considered for variants of normal-phase processes in which the sorbent is more polar than the solvent. Similar grafting approaches for nonpolar and functionalized silanes are also used for ordered silicones (analogues of MSM-41, SBA-15, etc.) [59–63]. Modification of silicones, taking into account the variation of their sorption properties and use in various SPE variants, is carried out by encapsulation, impregnation [64, 65] and chemical grafting of functional groups [59, 66–73]. The modification of ordered silica by organic reagents is considered in detail in [74]. Currently, the field of modification of ordered silica by metal ions for the creation of complexing sorbents is actively developing [27, 75–77]. In some cases, silica is used at the sample preparation stage without first removing the template from the mesopores [78–80].

CLASSICAL SOLID-PHASE EXTRACTION USING NANOSTRUCTURED SILICA

A number of features of nanostructured silica distinguish them from traditionally used sorbents, in particular, analogues of MSM-41 and SBA-15 in SPE processes. In [21], the authors pay attention to a large surface area of up to 1000 m^2/g and a pore volume of more than 0.7–1.0 cm^3/g. In addition to the size of the specific surface area, it is necessary to take into account the polarity of the surface and the nature of the sorption centers. The sorption properties of solid-phase materials can also vary significantly with varying structures. In [81], the sorption properties of SBA-15 and an analog with spherical granules (SM) were studied in relation to one of the hormones 17b -estradiol. It was found that when using unmodified silica SBA-15 and SM, the analyte recovery is 16 and 84%, respectively. A noticeable difference in sorption properties in this case is related to the nature of the sorption centers (silanol and siloxane groups). Using the ^{29}Si NMR method, the authors of [81] showed that isolated silanol groups predominate on the surface of SBA-15 (signal Q^3), while the most intense signal in SM analysis corresponds to surface siloxane groups (Q^4). The above example indicates that, depending on the conditions of synthesis and modification of silicones, the ratio of silanol and siloxane groups makes it possible to regulate the sorption properties of solid-phase materials with respect to polar and nonpolar sorbates. It is worth noting that the control scheme for the nature of sorption centers is simplified in the case of analogues MSM-41 and SBA-15 due to the ordering of their hexagonal structure.

Nanostructured silica is used as sorbents for SPE in the procedures of sample preparation and subsequent chromatographic determination of substances in extracts of food and pharmaceutical products [24, 81–86]. An important group of analytes are substances with anti-cancer activity. The authors of [83] demonstrated the possibility of isolating and purifying the natural isothiocyanate compound sulforaphane from broccoli extract by solid-phase extraction using silica of varying degrees of order. It is worth noting that SBA-15 silicas with an ordered mesoporous matrix can achieve the highest completeness of analyte extraction (up to 98%) compared with the traditionally used silica gel C18, zeolites ZSM-5, Y, L and sodalite (SOD) [83].

It was noted in [84] that mesoporous silica SBA-15 achieves a more complete extraction of analytes compared to silica gels with grafted groups of octadecylsilane C18 and mesoporous carbon during solid-phase extraction of triterpenoid saponins from the herbaceous plant Chinensis. It is worth pointing out that with a sorption capacity comparable to some other solid-phase materials, SBA-15 has a significant advantage associated with the possibility of repeated use. The authors of [84] noted that the reproducibility of the results of the determination of saponins during their solid-phase extraction on SBA-15 does not decrease after five cycles of use.

The consumption of sorbents used in the sorption extraction and concentration of target substances is also important. The most common use of SPE cartridges with a sorbent weight of 200 or 500 mg. The high distribution coefficients of analytes during sorption on ordered silicones (MSM-41, SBA-15, UVM-7, etc.) due to the large specific surface area, the peculiarities of the distribution of sorption centers and their solvation make it possible to use small sorbent masses (10–100 mg) in the SPE of analytes. In [26], the sorption properties of silica MCM-41 and UVM-7 during the release of phosphaditylcholine were studied. Silica UVM-7 with ordered bimodal porosity has maximum sorption capacity for phospholipid. The authors attribute the higher capacity of UVM-7 to a high density of free silanol groups and a specific surface area (S_{spec}= 1275 m^2/g) almost twice that of the MCM-41 analog (S_{spec}= 660 m^2/g). The noted features of silica [26] substantiate the prospects of choosing UVM-7 for solid-phase extraction of phospholipids from multicomponent matrices (including when analyzing human milk for phospholipid content). The use of ordered silica allows the determination of phosphaditylcholine at concentrations of 150–600 micrograms/ml with a detection limit of 3.5 micrograms/ml. An important advantage of cartridges filled with nanostructured UVM-7 analogues is the preservation of satisfactory reproducibility of phospholipid determination results after 15 cycles of sorbent use (the degree of extraction remained in the range of 94 ± 4%).

Just as for traditional silica gels, their modification by grafting functionalized silanes is essential when varying the sorption properties of ordered silica. A large number of papers (for example, [24, 85–86]) are devoted to the solid-phase extraction of various substances with mesoporous silica grafted with nonpolar octadecyl groups. Obviously, the modification of silica by C18 groups contributes to the implementation of the distributive mechanism of sorbate retention. At the same time, it is worth noting improvements in the kinetics of the extraction process due to the greater availability of ordered mesopores [12]. It was noted in [12] that for nanostructured MSM-41, the effective diffusion coefficients of flavonoids (for example, quercetin and +(-)—catechin) take 2–5 times higher values than for silica gels with a wide pore size distribution. Moreover, the lower dispersion of the sorbate mass transfer rates may be due to both the greater proportion of sorption centers on the highly developed (surface area S_{spec} = 1,000–1,250 m^2/g) mesoporous surface of MSM-41 involved in the retention of analytes, and the narrow pore size distribution for ordered silica.

The selectivity of sorbents can be increased by forming molecular imprints in the sorbent structure. The authors of [25] obtained the sorbent MCM-41 with molecular imprints of nonylphenol for its solid-phase extraction from textile samples. The use of a potential analyte (as a molecular fingerprint) in the synthesis of silica makes it possible to achieve a sorbate recovery rate of up to 92–95% and a relatively high selectivity coefficient (α = 2–3). As noted above, an increase in the efficiency of sorption concentration when using a nanostructured sorbent is important for increasing the analytical signal due to the concentration of the analyte per unit time. At the same time, the absence of experimental output curves and a number of concentration parameters does not allow estimating the *CE* parameter based on the literature data. The use of ordered silicones at the stages of sample preparation (with SPE) makes it possible at subsequent stages of determination to more significantly reduce the noise level of the analytical signal by removing impurities that interfere with the determination and expand the range of detectable concentrations of the target components. For example, the authors of [25] noted a linear response in the concentration range of 0.25–20 micrograms/ml when determining nonylphenol by HPLC with UV detection. At the same time, a higher analytical signal, provided the sorption concentration is more efficient, leads to an increase in the sensitivity coefficient and a decrease in the detection limit of the analyte to 0.12 micrograms/ml.

Under the conditions of solid-phase extraction using disordered sorbents, the low rate and completeness of analyte desorption are due to the kinetic features of the relatively slower analyte mass transfer process under dynamic conditions, the mechanism of analyte retention (with a higher binding energy to sorption centers), as well as the slow establishment of sorption (distributive) equilibrium. Silica-based SPE variants with a system of ordered mesopores are partially devoid of these disadvantages. Such nanostructured sorbents provide relatively faster mass transfer of sorbates and shorter equilibrium time (sometimes by more than an order of magnitude) [9] due to a more developed outer surface and accessible sorption centers on the surface of the mesopores.

MODERN VARIANTS OF SOLID-PHASE EXTRACTION

Solid-phase microextraction. An important feature of ordered silicones for use in modern solid-phase extraction options is the possibility of miniaturization of SPE cartridges due to a significantly more developed surface (proportional increase in sorption capacity) and a decrease in the contribution of kinetic limitations of analyte sorption (increase in sorption concentration efficiency under dynamic conditions). Solid-phase microextraction (**SPME**) refers to either a number of methods that use a small amount of sorbent (usually 10–50 mg) [87–89], or applying a sorbent to the surface of a fiber or a microsprice needle [79, 90–98]. The small amount of sorbent makes it possible to expand the capabilities of traditional cartridges for solid-phase extraction [99]. At the stages of sample preparation, various sorbent packaging options can be implemented. Solid-phase extraction with ordered silica in the tip of a dispenser (pipette-tip) has been successfully applied in the determination of endogenous peptides in human plasma [100] and estradiol in milk [87].

Another feature of solid-phase microextraction is continuous mixing, which makes it possible to increase the surface area of the sorbent in contact with the sample. This approach involves using a stirrer together with a sorbent inside a polypropylene membrane. The use of the SPE variant with mixing makes it possible to expand the range of linearity of calibration dependencies for the determination of substances (for example, phenolic compounds) by an order of magnitude compared with traditional sample preparation methods. In [101], the determination of the content of nitrosamines in cosmetics was implemented by the SPME method with mixing on SBA-15 doped with cerium, followed by GC–MS determination. By optimizing the amount of dopant, the mass of the sorbent, the type and volume of the eluent, the degree of extraction can be increased to 80–100% [101], the linearity range is extended to 10–1000 ng/ml, and the detection limits during sample preparation with solid-phase microextraction can be reduced to several ng/ml (2.7–3.4 ng/ml according to [101]). It is worth noting that the use of nanostructured silica makes it possible to achieve high completeness of extraction in a wider range of concentrations compared to carbon nanotubes and carboxene/polydimethylsiloxane (CAR/PDMS) fibers [101].

The use of silica in aqueous solutions is limited by the competitive sorption of water molecules [74]. At the same time, ordered silicones can be used in SPE variants both in nonpolar media and in aqueous solutions due to the peculiarities of matrix formation and the distribution of sorption centers on the surface and, as a result, higher hydrophobicity. The authors of [102, 103] demonstrated the possibility of determining phenolic compounds in water during their solid-phase microextraction with mixing on SBA-15 with various grafted organic groups. The concentration coefficients of phenolic compounds on ordered silica were 20–30.

In a number of works, SPME is understood as a sample preparation option based on the dependence of the sorption of substances on temperature [92–94, 104–105]. The method consists in adsorption of analytes on the sorbent surface followed by desorption at higher temperatures. One of the main advantages of this type of SPME is the absence of the need for quantitative extraction of target components from the sample. It is sufficient to perform a linear relationship between the amount of the analyte to be sorbed and its concentration in the analyzed sample. The authors of [105] noted that the advantages of the method include the cylindrical geometry of the fibers, which provides easy access of analytes to the surface of ordered silica, as well as the absence of the need for complete desorption of sorbates.

In solid-phase microextraction, as in classical SPE versions, the nanostructure of the sorbent, its specific surface area and the distribution of sorption centers over the surface (including inside the mesopores) play an important role. If the structure of a solid-phase material (including the degree of its ordering, the type of mesophase) determines the kinetic features of analyte sorption (contributes to a change in the efficiency of sorption concentration under dynamic conditions), then the specific surface area of silica affects the sorption capacity, the ability to vary the operating range of analyte concentrations.

It was noted above that it is not always correct to select a sorbent based only on the degree of extraction of the substances being determined. The authors of [92] considered the solid-phase microextraction of aliphatic amines from air and fungi while varying the structure and pore size of ordered silica. The surface area, according to the authors, is not always a factor determining the sorption properties of a solid-phase material. When using MCM-41 silica with a specific surface area of 1180 m^2/g, the degree of amine extraction reaches only 60%. At the same time, for analogues KIT-6 and SBA-15 (S_{spec}= 970 m^2/g and S_{spec}= 760 m^2/g, respectively), the degree of analyte extraction is close to 100%. The authors of [92] attribute the difference in the completeness of analyte extraction primarily to the pore size, which is about 8 nm for KIT-6 and SBA-15, while in the case of MCM-41 it is 4 nm. To achieve high values of the degree of extraction of the analyte, it is important that the inner surface of the sorbent is accessible to it. However, as noted above, the quantitative extraction of detectable substances in solid-phase microextraction is not a necessary condition. A more important property of sorbents, especially when it is necessary to determine substances in multicomponent matrices, is the selectivity of the sorbent. It was shown in [92] that when analyzing real objects, solid-phase materials with relatively wide mesopores (KIT-6 and SBA-15) with high sorption capacity (significant volume and diameter of mesopores) had low selectivity for extractable substances. On the contrary, the choice of MCM-41, taking into account the conditions of the implementation of SPME and the modification of the sorbent, makes it possible to extract mainly target substances from complex mixtures. In this case, the sieve effect of ordered sorbents is manifested when the size of the mesopores varies.

Similarly to the peculiarities of the use of sorbents in classical SPE variants, modified ordered silicones have become widespread in SPE. SBA-15-C8 has been successfully used as a sorbent in solid-phase microextraction in the determination of polycyclic aromatic hydrocarbons [93, 94]. It was shown in [93] that 2–5 times more analyte is extracted on SBA-15 fiber with grafted C8 octyl groups compared with commercial polydimethylsiloxane.

Solid-phase microextraction is often used at the sample preparation stage followed by gas chromatographic determination of substances. In [95], aromatic hydrocarbons were determined with preliminary extraction on SBA-15-C8 by HPLC with UV detection. It is shown that after the sample preparation stage (in the solid-phase microextraction variant), a needle with the extracted analyte is placed in a static chamber for desorption, followed by the determination of the analyte by HPLC. In this case, 5 minutes in contact with the mobile phase in the injector is sufficient before introducing the sample to extract the analyte from the sorbent. The reduction in desorption time is due to the advantages of the ordered nanostructure of the sorbent, namely, the availability of the mesopore space for analytes.

The expansion of the SPME capabilities is an online sample preparation option with the connection of a tube filled with sorbent and the inclusion of a gas [54, 96] or liquid [97, 98, 106] chromatograph (in-tube solid phase extraction) into the system. In this type of sample preparation, the possibility of repeated use is important. It was shown in [97] that after more than 120 analyzes, the tube retains sorption properties with satisfactory metrological characteristics for determining analytes.

Matrix solid-phase dispersion. In most variants of solid-phase extraction, preliminary extraction of the substances to be determined with solvents is assumed [107]. This stage is not required in the matrix solid-phase dispersion method, which consists in the direct addition of a sorbent to a liquid or solid analyzed sample [108]. The sample is mixed and dispersed with the sorbent, and the substances are distributed into small sorbent particles. To extract the interfering components, the resulting mixture is transferred to a cartridge filled with the same or another sorbent. The analytes are desorbed with a suitable eluent for subsequent determination [109]. The undoubted advantage of microextraction by matrix solid-phase dispersion is the small mass of the test sample (about 20 mg), small volumes of solvent for eluting analytes (about 0.5 ml of 75% ethanol according to [88]), and the extraction time is 2–5 minutes. Compared with other SPE variants, this approach makes it possible to significantly reduce the duration of sample preparation, as well as the consumption of reagents, and significantly reduce the amount of the analyzed sample [4, 109].

Over the past ten years, nanostructured silicas have been widely used in microextraction options by matrix solid-phase dispersion. It is worth pointing out that the developed nanostructure of silica (analogues of MSM-41 and SBA-15) with a significant surface area and a narrow mesopore size distribution determines the advantages of these sorbents and the prospects for their use at the stages of sample preparation in the analysis of real objects of food, pharmaceutical, chemical industries and agricultural products. It was shown in [110] that the matrix solid-phase dispersion of analytes on MCM-41 and MCM-48 can be used to determine pesticides in fruit crops.

In a series of publications by Cao et al. [111–113], the determination of flavonoids in various sample preparation facilities using matrix solid-phase dispersion on mesoporous silica with cubic and hexagonal structures is considered. In [111], ordered silica with a cubic structure of the KIT-6 type was used as a sorbent for the determination of flavonoids in toothpaste and saliva. The degree of flavonoid extraction in these cases was more than 90%. The ordered structure of silica makes it possible to achieve higher degrees of extraction compared to normal-phase silica gel and reverse-phase sorbent with grafted C18 groups.

In the case of matrix solid-phase dispersion, the available outer and inner surface of the sorbent is the determining factor in increasing the completeness of analyte extraction. The sorption properties of ordered silicones with mesopores of 3–4 nm in size (MCM-41, MCM-48), as noted above, are determined primarily by the outer surface and weakly depend on the type of structure [110]. An increase in the pore size to 5–10 nm (SBA-15 and KIT-6) during the transition from hexagonal to cubic symmetry leads to noticeable differences in the sorption properties of ordered silicones [112]. In the considered SPE variant, it is assumed that substances are adsorbed mainly on the outer surface of MSM-41 and MSM-48. For SBA-15 and analogues with larger mesopores, analyte retention largely occurs at sorption centers inside the mesopores, which affects the sorption kinetics. In this case, it is important to take into account the desorption stage, which makes it possible to assess the completeness of analyte extraction, as well as the possibility of reuse of the sorbent.

It is also important to take into account the mechanism of retention of substances (adsorption, distribution, ion exchange, exclusion, etc.). Each of them can be implemented in the sorption of substances, taking into account the nature (polarity) of sorbates, its solubility in contacting phases, and the composition of the solvent. The authors of [88] showed that in the case of SBA-15, quantitative desorption of analytes is achieved (the recovery rate according to [88] was 96.8–104%) due to weak binding of analytes to a nanostructured dispersing material. At the same time, the extraction of substances by classical sorbents such as Florisil PR, alumina-B, AZO, and C18 is complicated by a low degree of desorption from the surface of traditionally used aluminum oxides and silica gel with grafted octadecyl groups [88].

Dispersion solid-phase extraction (dSPE). One of the requirements in solid-phase extraction for maintaining high concentration efficiency and extending the range of working concentrations of the analyte is uniform packing of the sorbent in the cartridge and uniform particle size distribution [114]. Failure to comply with these requirements complicates the diffusion of the sample components. The dispersion version of solid-phase extraction increases the contact area with the analytes by introducing the sorbent directly into the analyzed solution [3]. Compared with other SPE variants, this helps to reduce the required sample quantities, solvents, and sorbent weight and shorten the analysis time [114].

The method of dispersion solid-phase extraction was initially proposed only to purify the sample and eliminate the influence of the matrix [3]. In [115], dSPE is used for sample preparation in the extraction of tetracyclines from milk and surface waters, followed by determination by HPLC with diode-matrix detection.

Dispersion solid-phase extraction using ordered silica is also successfully used to determine polycyclic aromatic hydrocarbons in groundwater [116], phenolic compounds in strawberry fruits [117], polyphenols in juices and smoothies [114], manganese ions in water, hippuric and methylhippuric acids in human urine [89], etc. In [118], ketoconazole and voriconazole were determined in biological fluids during sample preparation using the DTE method on MCM-41, followed by HPLC–MS/MS determination. The use of nanostructured silica at the sample preparation stage with a relatively small sorbent mass ($m = 20$ mg) and solvent volume ($V = 200$ μl) makes it possible to expand the linearity range of the analytical signal at concentrations of ketoconazole and voriconazole in the range of 0.1–10 μg/l.

In the dispersion SPE variant, sorbents with grafted functional groups are used along with normal-phase silicones to increase selectivity and sorption capacity. In [116], SBA-15, modified with aminopropyl, phenyl, octyl, and octadecyl groups, is used in the dispersion microhardness phase extraction of polycyclic aromatic hydrocarbons from groundwater from monitoring wells at gas stations. The use of nanostructured sorbents SBA-15-C8 followed by GC–MS determination makes it possible to achieve minimally detectable analyte concentrations from 0.15 to 3.0 micrograms/l.

It was noted above that in SPE processes, both the size of the mesopores, the size of the specific surface area, and the structure (symmetry) of the sorbent can be essential. MSM-48 belongs to materials with cubic ($Ia\overline{3}d$) mesophase structure [119]. Along with MSM-41 and SBA-15 sorbents (with a hexagonal mesopore structure), MCM-48 analogues can be used in dSPE to extract toxic substances from water [120]. During sorption of hormone molecules (estriol, 17b -estradiol, estrone), as well as bisphenol A, inoculation of functional groups (amino –NH_2, phenyl –Ph, octadecyl –C18, aminopropyltrimethylsilyl –APTMS) leads to an increase in the completeness of extraction in the range MCM-48 < MCM-48-NH_2 < MCM-48-Ph < MCM-48-C18 < non-calcined MCM-48 < MCM-48-APTMS. When extracting less polar alkyl derivatives of phenol, there are no noticeable differences between the sorbents.

Nanostructured KIT-6 material (with a cubic structure) synthesized on the basis of the nonionic Pluronic P123 template is used in dispersion SPE. The KIT-6 sorbent, functionalized with amino groups, was used [89] for the extraction of hippuric and methylhippuric acids from human urine. An additional reduction in extraction time was achieved by the authors during ultrasonic treatment due to the acceleration of mass transfer and diffusion of analytes in sorbents. The relative recovery of analytes was 99.6–104.0% [89]. The open channels of KIT-6 mesoporous silica significantly reduce the resistance to sorbate mass transfer. The authors of [89] note a higher diffusion rate in KIT-6 pores compared to other ordered silicas (SBA-15 and MCM-41).

The characteristics of the matrix (wall thicknesses, distribution and nature of sorption centers) have a significant effect on the sorption properties of silica when used in dSPE variants. The authors of [114] synthesized mesoporous silica with worm-like pores (HMS) modified with octadecylsilane (C18). HMS-type silicas have thicker walls compared to SBA-15 and, accordingly, are more stable to aggressive media. The work [114] shows the applicability of HMS sorbents in dSPE variants for the extraction of a wide range of polyphenols (more than 20 compounds of various nature and structure) from fruit and vegetable juices and smoothies. The use of nanostructured silica with a large specific surface area of mesopores at the sample preparation stage in the UHPLC–MS method allowed the authors to carry out rapid determination of substances (in less than 10 minutes). The mesoporous structure of HMS provides a higher completeness of extraction of the R analyte (up to 99%) compared to commercially available amorphous silica gel C18 (for most analytes $R < 50\%$).

It was shown in [121] that in the classical version of solid-phase extraction of thyme analytes by ordered mesoporous silicones with grafted sulfogroups, a higher degree of extraction is achieved on SBA-15 particles of uniform size compared with HMS (hexagonal mesoporous silica with «worm-like» pores). The particles of the latter are close to a spherical shape, but differ markedly in the size of the granules, since under the conditions of HMS synthesis it is not always possible to synthesize materials with a narrow particle size distribution. In the case of dSPE, on the contrary, an increase in the completeness of extraction is observed during the transition from SBA-

15 ($S_{\text{ud}} = 560$ m^2/g) to ordered silica HMS with a larger specific surface area ($S_{\text{ud}} = 710$ m^2/g).

One of the promising directions for expanding the possibilities of dispersion SPE options is the modification of ordered silica with ionic liquids. In the work of Si et al. [122], the use of ordered mesoporous silica functionalized with an imidazolic ionic liquid in the determination of indole derivatives of aliphatic acids in ginseng was demonstrated in dSPE. This modification of the ordered material contributes to a more complete extraction of nitrogen-containing heterocyclic analytes compared with the initial silica and commercial sorbents, including silica gel, C18, SCX, MCX, NH_2, AL_2O_3 [122]. The range of linearity (0.05–22.5 ng/g) and detection limits (3–8 ng/kg) are noteworthy, while maintaining the metrological characteristics of determining target substances after five sorption — desorption cycles.

To increase the selectivity (specificity) of sorbents in SPE variants, they often resort to the immobilization of modifiers (for example, cyclodextrins). [117] describes the use of hybrid mesoporous silica with large pores functionalized with β-cyclodextrin for the dispersion solid-phase extraction of polyphenols from the fruits of the strawberry tree. The authors point out the advantages of the dSPE variant compared to classical SPE, including through the use of β-cyclodextrin-functionalized mesoporous silica. Sample preparation with the specified sorbent makes it possible to significantly increase the degree of extraction of the determined compounds (up to 73–102%) from complex matrices [118].

A special case of dispersion SPE is the QuEChERS method (Quick, Easy, Cheap, Effective, Rugged, and Safe — fast, simple, cheap, efficient, reliable, and safe), in which gas or liquid chromatography-mass spectrometry is used for detection after liquid extraction and dispersion solid-phase extraction [114, 123, 124]. Due to the high detection sensitivity, solvent evaporation is not required for additional concentration of the sample. A change in the signal-to-noise ratio is often considered as a parameter for comparing sorbents in this sample preparation option [123, 125]. In [123], the features of the modification of SBA-15 and its use in dSPE in the determination of polychlorinated biphenyls and polyaromatic hydrocarbons in strawberries were considered. Silicones with grafted N-[3-(trimethoxysilyl)groupspropyl] aniline (SBA-15-AN) improves the signal-to-noise ratio by 20% compared to the commercially available PSA sorbent (primary/secondary amine), which is most commonly used in the QuEChERS method.

Iskara et al. [124] used mesoporous silica and their analogues modified with amino groups in the sample preparation of QuEChERS for the extraction of biologically active substances from herbs. In the case of nanostructured sorbents with grafted amino groups, there is an improvement in the metrological characteristics of the determination of substances (detection limits were 0.7–2.8 μg/kg) compared with unmodified ordered silica and traditional sorbent (PSA).

Another variant of dSPE is magnetic DSPE, in which sorbents are nanocomposites based on magnetite. The sorbent with retained analytes is extracted from the suspension using a magnet, which further reduces the duration of sample preparation. Composites based on ordered mesoporous silica have been successfully applied in magnetic SPE [80, 126–130]. The authors of [127] note that, despite the low sensitivity of the determination of substances by gas chromatography with flame ionization detection, due to the high sorption capacity of the Fe_3O_4/MCM-41-NH_2 nanocomposite, relatively low detection limits (0.2–0.9 μg/L) can be achieved when determining parabens in cosmetic products.

* * *

The papers published over the past 10–20 years considering the use of nanostructured silicones in solid-phase extraction options (classical SPE, SPME, matrix solid-phase dispersion, dispersive SPE, magnetic SPE, etc.) at the stages of extraction and concentration of substances for their subsequent determination in complex multicomponent matrices are analyzed. The sorption properties of ordered silicones (MSM-41, MSM-48, SBA-15, KIT-6, UVM-7, HSM, etc.) improved in comparison with traditional sorbents (silica gels, zeolites, polymer materials), especially under dynamic conditions of sorption of target components. These nanostructured silicas are considered in SPE variants to increase the completeness of analyte extraction, reduce detection limits, and expand the range of detectable concentrations of substances. The advantages of ordered silicones with hexagonal and cubic mesophase structures are achieved due to the higher sorption capacity of materials with a developed surface (up to 1000 m^2/g), with a large volume of mesopores (up to 1 cm^3/g) and a narrow mesopore size distribution.

Depending on the nature of the substances to be determined, the sample matrix, and the sample preparation option, it is important to use silica as sorbents for SPE, which make it possible to vary the density of surface silanol groups, the size of the specific surface area, or the pore size. In the case of solid-phase microextraction, the size of the mesopores is decisive. Matrix solid-phase dispersion requires a highly developed external surface of the sorbent.

Varying the SPE variants and the dispersion conditions of the analyzed sample with the sorbent makes it possible to control the completeness of sorbate extraction from the matrix. In dispersion SPE, when using nanostructured materials, it is possible to reduce the duration of sample preparation and significantly reduce the detection limits of substances, despite the absence of the need to completely extract the analyte from the sample. A significant improvement in the metrological characteristics of methods for the determination of substances was noted when combining SPE variants (with ordered silica) with HPLC and GC methods.

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CONFLICT OF INTERESTS

The authors of this paper declare that they have no conflict of interest.

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