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REVIEWS

Modern Approaches to the Extraction and Preconcentration of Biologically Active Compounds from Plant Samples by Microextraction Methods for Their Determination by Chromatography–Mass Spectrometry

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Abstract—The review considers the main trends in actively developing methods of solid-phase and liquid–liquid microextraction for the extraction, purification, and preconcentration of analytes from medicinal plants and plant materials, the use of new extractants and approaches to the preparation of samples of plant origin, and their compatibility with mass-spectrometric detection. Particular attention is paid to the analytical capabilities, advantages, and limitations of each of the approaches to extracting analytes from plant materials for the subsequent analysis of the obtained extracts by chromatography–mass spectrometry.

Keywords: microextraction methods, plant samples, HPLC–MS, GC–MS, preconcentration, biologically active substances

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The quality control of food products and new medicines based on plant raw materials is extremely relevant, which is also confirmed by environmental monitoring data on the pollution of plants growing in a particular area. In recent years, worldwide interest has grown in the use of herbal medicine for the prevention and treatment of various diseases.

Plant samples are complex matrices containing a large number of substances (proteins, fats, carbohydrates, vitamins, polyphenols, carotenoids, pigments, etc.) that differ in molecular weights, polarity, and chemical properties. Sample preparation is a key step in the analysis of plant samples; it ensures the selective extraction of biologically active compounds (BAC), which is not an easy task, because the components present in the matrix can not only hinder the extraction of analytes, but also affect the analytical parameters (sensitivity, accuracy) of the further determination of these compounds. All this must be taken into account in the subsequent analysis of extracts by chromatography–mass spectrometry (GC–MS and HPLC–MS).

Among the advantages of the chromatography–mass spectrometry method for the analysis of natural samples are, first of all, the high selectivity and sensitivity of the analysis (units of pg/g), a possibility of identifying unknown components in plant extracts by MS and MS^2 spectra, and obtaining information on the composition of the analyzed sample even at the incomplete chromatographic separation of the components. To date, gas chromatography–mass spectrometry is in demand not only in the research work, but also in routine production practice.

Nevertheless, in performing analyses by chromatography–mass spectrometry, especially in HPLC–MS/MS, a number of problems arise, such as strong matrix effects that cause the suppression or, conversely, an increase in the signals of the analytes. This requires special attention to the development of methods for the sample preparation of plant samples.

The main tasks to be solved at the stage of sample preparation for analysis by chromatography–mass spectrometry are as follows:

— selective extraction of analytes from the sample matrix;

— sample purification of interfering components, reduction of matrix effect;

— preconcentration of analytes;

— sample conversion into a form compatible with the subsequent analysis method (HPLC and GC with mass spectrometric detection);

– preservation of the most complete information about the composition of the studied plant sample.

The extraction efficiency of biologically active substances depends on such parameters as their solubility,

rate of mass transfer between the sample and the solvent, and nature of the specimen matrix and the sample. In the case of liquid samples (vegetable juices, oils), the target analytes can be directly extracted with a suitable solvent; solid samples (fruits, leaves, plant roots, etc.) require some preliminary procedures before extraction, i.e., grinding to increase the efficiency of mass transfer or drying to reduce moisture content. Solid samples are often dried before grinding using freezing or lyophilization, with removing significant amounts of water and retaining the BAC content of the sample to the maximum extent, thereby ensuring its representativeness. Next, the solid powder is extracted with a suitable solvent, which is then processed as a liquid sample.

Classical methods for extracting biologically active substances from plant samples are various types of solvent extraction: maceration, Soxhlet extraction, hydrodistillation, percolation, perforation, and also methods such as supercritical fluid extraction, subcritical water extraction, pressurized liquid extraction, and enzymatic extraction, which can be supplemented by vortex, microwave (microwave extraction), and ultrasonic treatment (ultrasonic extraction) to increase recovery. At that, non-selective extraction of analytes and insufficient purification of samples from interfering components (lipids, sterols, chlorophylls, etc.) may require the inclusion of additional stages of extract purification before their analysis by GC–MS or HPLC–MS, complicating and increasing the duration of the extraction process itself with the use of significant amounts of toxic organic solvents. Modern extraction methods have the following requirements: high selectivity, rapidity and simplicity of technology, and compliance with the basic principles of "green chemistry" [1]. Extraction methods, taking into account these requirements, are being developed in the following areas [2–26]:

— development of methods for selective solid-phase and liquid–liquid microextraction (SPME and LLME) of biologically active substances;

— search for new effective and environmentally friendly extractants (ionic liquids (IL), deep eutectic solvents (DES), solvents with switchable hydrophilicity, subcritical water, supercritical fluids), and the so-called "designer extractants";

— combination of methods of liquid–liquid and solid-phase extraction (sorbent dispersion);

— automation of the process and creation of special kits and devices for sample preparation.

In recent decades, efficient microextraction methods based on solid-phase extraction (SPE) and liquid–liquid extraction (LLE) have been developed. Thus, on the basis of LLE, liquid–liquid microextraction (LLME), dispersive liquid–liquid microextraction (DLLME), single-drop microextraction, and hollow fiber-based liquid-phase microextraction have been proposed. Miniaturization also affected sorption versions: solid-phase microextraction, microSPE in a pipette tip, dispersive SPE (DSPE), matrix solid-phase dispersion (MSPD), magnetic SPE (MSPE) [23–26] with the implementation of the QuEChERS methodology—Quick, Easy, Cheap, Effective, Rugged and Safe [21]. In MSPD, the sorbent is preliminarily dispersed and mixed with a sample, and then the mixture is transferred to the cartridge. Any type of sorbent can be used in DSPE, while only magnetic nanoparticles can be used in MSPE. These microextraction methods are increasingly used in the study of plant samples as alternatives to traditional extraction versions, because, being more environmentally friendly, they meet the needs of "green chemistry".

SOLID-PHASE MICROEXTRACTION FOR THE EXTRACTION OF ORGANIC COMPOUNDS FROM PLANTS

Solid-phase microextraction, first proposed by Arthur and Pawliszyn in the early 1990s. [27], is widely used in the extraction of trace amounts of volatile and medium volatile organic compounds from plant samples with their subsequent determination by gas chromatography, including MS detection [28–31]. This is a rapid, simple, sensitive, and highly efficient method that combines sampling, extraction, preconcentration, and injection of a sample into a chromatograph in one analytical cycle, which is convenient in the field, when the prepared samples can be analyzed in a laboratory much later without significant losses [32–35].

There are three main versions for SPME: (i) direct immersion of a fiber in the sample matrix; (ii) headspace sampling, in which analytes are adsorbed from the gas phase being in an equilibrium with the samples; and (iii) extraction on a membrane-coated sorbent to recover less volatile compounds. The SPME methods are widely used for the extraction of volatile organic compounds (VOC) from plant samples (flowers, fruits, and leaves of plants) in the study of plant species, to assess the effect of climatic conditions on the metabolism and storage conditions, in breeding work, etc. [28–31, 33]. The nature of the sorption fiber coating largely determines the selectivity and efficiency of the extraction. Various sorption materials are used as coatings: polydimethylsiloxane (PDMS), polydivinylbenzene (PDVB), polyethylene glycol, carbovax (CV), polyacrylonitrile, carboxene (CX), silica with attached octadecyl groups (C18), and also block copolymers consisting of monomers of different polarity for the joint extraction of substances with different properties: PDMS-CX, PDMS-DVB, PDMS-DVB-CX, CV-DVB, and Carbopack Z-PDMS.

Thus, using SPME in combination with headspace analysis (HSA) and the subsequent GC–MS determination, volatile components of the floral aroma of *Aquilegia japonica* L. and *A. amurensis* L. plants, common in Northeast China, in North and South Korea,

Japan, Siberia, and Mongolia, were revealed [28]. The authors compared the efficiency of three types of SPME fiber coatings (PDMS-DVB, PDMS-CX, and PDMS-DVB-CX). Using the SPME–GC–MS method with PDMS-DVB-CX fiber, it was shown in [30] that the treatment of roses with growth stimulants (benzyladenine and naphthaleneacetic acid) led to a significant increase in VOC emissions, increasing the aromatic value of flowers. In [29], the composition of VOC in the flowers of five species of the plant *Abeliophyllum distichum* Nakai, a promising sample for the production of aromatic oils in the perfume industry, was established. Chromatographic VOC profiles were obtained by GC–MS using SPME with fibers of the composition PDMS-PDVB-CX. A relationship between the found structural fragments of analyte molecules and their morphological features was revealed. The application of this approach made it possible to identify and determine the content of 66 volatile components of this plant. In [36], the dependence of the change in the flavor of common flax seeds (*Linum usitatissimum* L.) on the duration of heating was established by preconcentrating volatile components in real time on rods coated with CX and PDMS. In [37], using the SPME–GC–MS method and the subsequent chemometric processing of the obtained characteristic profiles, it was possible to divide samples of raw and processed rice into clusters depending on the growing region. A combination of SPME and an "electronic nose" made it possible to reliably determine the quality of fruits of the delicacy actinidia (*Actinidia deliciosa* A. Chev., kiwi fruit) [38], to draw a conclusion about the origin of Sichuan pepper (*Zanthoxylum* L. spp.) [39], and to simulate the smell of false starburst heterophyllous (*Pseudostellaria heterophylla* Rupr. & Maxim.) [40] and tuber onion (*Allium tuberosum* L.) [41]. Currently, an active search for and application of new sorption coatings is continued [42–45].

An interesting approach to phytochemical analysis, in which a direct contact of SPME probes with the interstitial fluid of plants was implemented, was proposed. It was shown that in vivo SPME causes minimal damage to plants, takes less time than the traditional solvent extraction, and makes it possible to obtain unique "fingerprints" for all studied plants that were not detected by traditional extraction. It was reported [46] about specially made steel rod cartridges—microextraction probes containing a mixture of C16-amide and pentafluorophenyl sorbents for the SPE of alkaloids *in vivo* from several species of the genus Psychotria (*Psychotria* Ruiz & Pav.), *Tabernaemontana* L., Uncaria (*Uncaria* Schreb.), and Nightshade (*Solanum* L.) followed by profiling. Such a cartridge (microextraction probe) was introduced into a leaf, fruit, or a drilled hole in the bark, and, after 30 min, it was removed, sealed in an evacuated vessel, and cooled until an analysis.

A significant improvement in analytical characteristics and a simplification of sample preparation was provided by sorbents with molecular imprints, which were obtained as fibers for the analysis of pyrrolizidine alkaloids of coltsfoot (*Tussilago farfara* L.) flowers. Thus, in [47], a version of ultra-HPLC (**UHPLC**)–MS was proposed in combination with solid-phase microextraction with a sorbent with a molecular imprint for the rapid determination of trace amounts of toxic pyrrolizidine alkaloids from Farfarae Flos, dried flower buds of *Tussilago farfara* L. Pyrrolizidine alkaloids represent a class of widespread phytotoxins, exhibiting strong hepatotoxicity, and plants containing pyrrolizidine alkaloids are the most common poisonous plants affecting humans. The fibers obtained in the work showed an ability of selectively adsorbing four pyrrolizidine alkaloids, including europine, echimidine, lasiocarpine, and heliothrin, with limits of detection in the range 0.32–0.60 ng/g. In [48], cinnamic acid derivatives were determined by hollow fiber-based extraction, in which hydrophobic DES of the composition tetrabutylammonium chloride–hexanoic acid (1 : 1, mol.) was present as an extractant. The limits of detection (LOD) in this case turned out to be at a level of 10–30 ng/g.

Possibilities of the extraction of phenolic compounds with chitosan were studied in [49]. An extract from olive fruits (*Olea europaea* L.) contained both phenolic acids (gallic, ellagic) and flavonoids (rutin, luteolin glycoside), LOD was 69.6–358.4 ng/g. Magnetic nanoparticles based on chitosan have been successfully used [50], and DES of the composition β-cyclodextrin–lactic acid (1 : 10, mol.) has been used for the back extraction of analytes. The selectivity of the receiving phase provided a LOD of 20–160 ng/mL.

It is known that plant hormones have a regulatory function and control growth and development processes. The study of changes in their metabolism due to stressful conditions is extremely important. Phytohormones are also actively used in agriculture, which requires the search for approaches to the effective control of their contents. At that, plant hormones are characterized by extremely low effective concentrations. Analysis by chromatography–mass spectrometry provides possibilities of both qualitative and quantitative determination. In [51], the use of magnetic nanoparticles for SPME was discussed. A scheme was proposed for the synthesis of a sorbent based on boron nitride nanolayers with Fe_3O_4 particles included in its cavities (Fig. 1); it was used to analyze a mixture of growth regulators in tomato fruits. This approach provided the determination of 0.007 ng/g of 2-naphthoxyacetic and abscisic acids, as well as a of number of other phytohormones. The authors emphasized that the resulting particles could be used for the selective extraction of polar analytes (heterocyclic phytohormones, phytohormones with polar groups, sulfonamides). In this case, low-polarity molecules were not

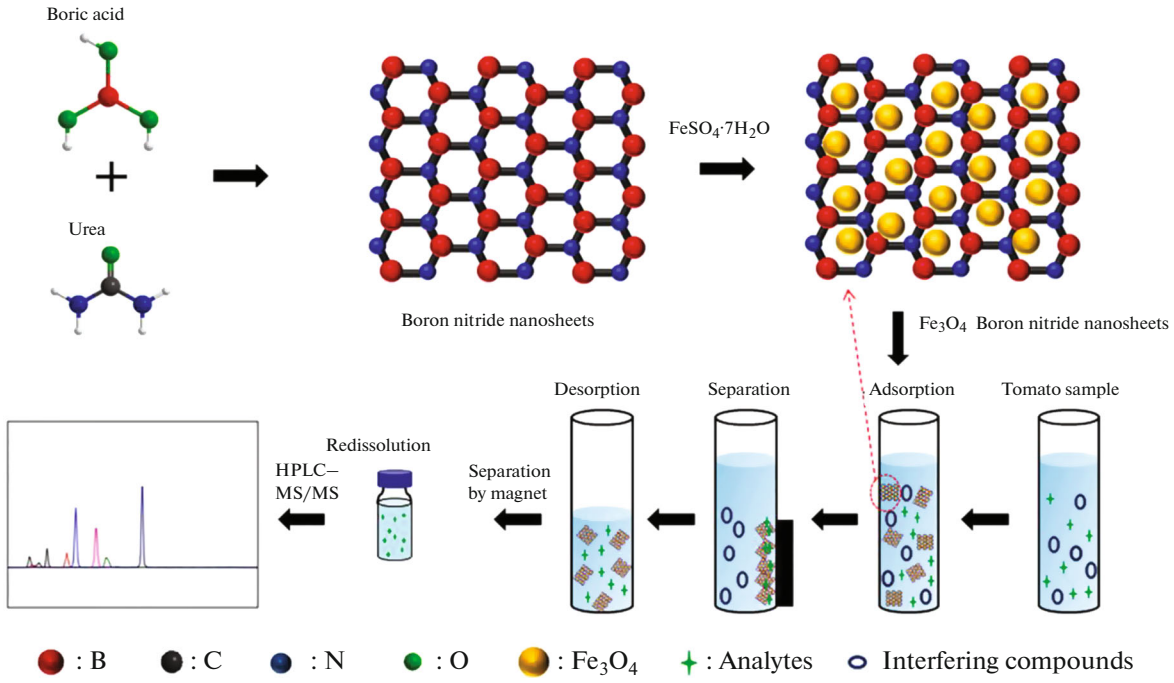

Fig. 1. Scheme for the synthesis and application of boron nitride nanosheets with inclusions of iron oxide (II, III) [50].

sorbed even in the presence of conjugated systems in their composition. An advantage of such sorbents is a possibility of their repeated use.

An interesting version of microSPE was considered in [52]. It was proposed to use glass beads with particles of an organometallic matrix (OMM) attached through polydimethylsiloxane. An OMM based on zirconium was chosen for the determination of phytohormones in citrus fruits. It was possible to achieve limits of detection of 0.09–0.17 ng/g. Among the undoubted advantages of the proposed approach are a possibility of an independent effortless production of the sorbent, a simplified sample preparation operation (the extractant phase is extracted with tweezers), a possibility of reuse, and also small volumes of analyzed samples.

Another example [53] concerns the synthesis in capillaries of a monolithic layer of polyacrylamide with surface sulfo groups, the derivatization of the prepared monolith with 2-methyl-4-phenylaminomethylphenylboronic acid, and the online preconcentration of brassinosteroids (Fig. 2). The achieved limits of determination were tenths of ng/g. The main advantages of this approach are a possibility of automation, rapidity, and a significant reduction of the matrix effect.

METHODS FOR LIQUID–LIQUID MICROEXTRACTION OF ANALYTES FROM PLANTS

In LLME, analytes are extracted from an aqueous sample (donor phase) into a small volume (several μL) of a water-immiscible organic solvent (acceptor phase) [23, 54, 55]. The main versions of LLME are single-drop microextraction, hollow fiber-based liquid-phase microextraction, and dispersive liquid–liquid microextraction. As in LLE, the choice of a solvent is the main parameter determining the efficiency and selectivity of the extraction of analytes. The solvent must possess good affinity to the target analytes, low solubility in water, stability throughout the extraction procedure, and compatibility with the conditions of the determination of analytes by chromatography–mass spectrometry. Water-immiscible organic solvents, such as 1-butanol, *n*-octanol, and isooctane, are commonly used in single-drop microextraction; 1-octanol, toluene, *n*-hexane, and *o*-xylene are used in hollow fiber-based liquid-phase ME; and chlorobenzene, carbon tetrachloride, and dichloromethane are used in DLLME [23, 54, 55]. In accordance with the principles of "green chemistry", many studies were devoted to the search for environmentally friendly solvents as extractants. In this regard, ionic liquids and deep eutectic solvents are of great interest because of their unique properties. Ionic liquids have low vapor pressures, high viscosity and thermal stability, do not ignite, have specific electrochemical characteristics,

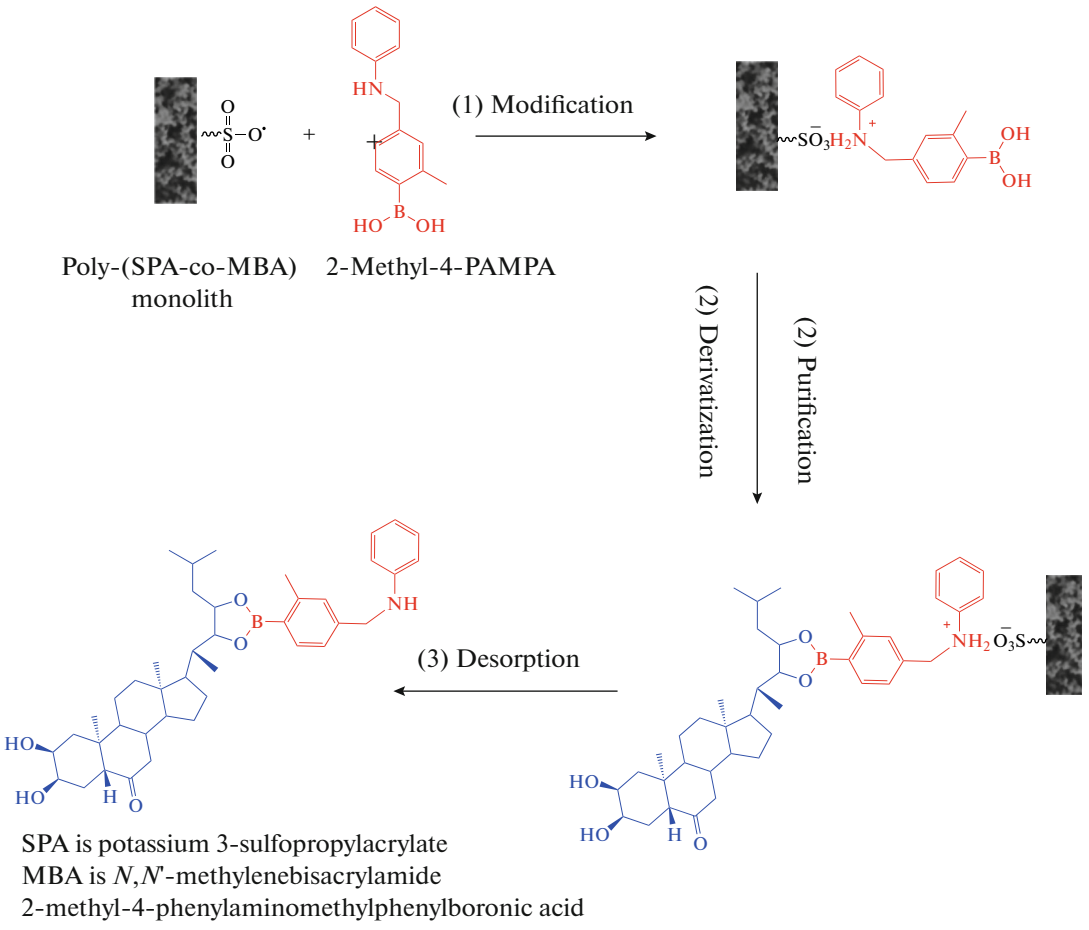

Fig. 2. General scheme of the interaction of a brassinosteroid with a sorbent [53].

and are capable of dissolving various organic and inorganic compounds, providing an alternative to traditional organic solvents [56–58].

LLME methods are effectively used to extract biologically active substances from plant samples and products based on plant extracts. For solid plant samples, pre-extraction with a suitable solvent is used. In [59], a simple and a rapid procedure of homogeneous LLME, based on changing the volume ratio of solvents, in combination with GC–MS, was developed for the preconcentration and determination of caffeine in tea and coffee samples. In the proposed procedure, the primary extraction of analytes from solid samples was carried out with an ethanol–water mixture (2 : 1, by volume). The system was then homogenized with a small volume of dichloromethane. After vigorous shaking, an additional volume of water was added, which led to phase separation due to a change in the volume ratio of the solvents. In [60], to implement liquid–liquid–liquid microextraction, a vortex mixer was used to extract fourteen phenolic acids from honey, tea, and coffee drinks. A small volume of a ternary mixture of organic solvents (1-pentanol, propyl acetate, and 1-hexanol), dispersed in an aqueous sample, was used; an alkali solution was added to strip the analytes from the organic solvent. This method can be combined with subsequent determination. By chromatography–mass spectrometry. Dispersive liquid–liquid microextraction is based on the extraction of analytes with an extractant microemulsion containing the target analytes, which significantly increases extraction efficiency [23]. The use of DLLME for the extraction of a number of bioactive compounds from plant samples with the subsequent determination by chromatographic methods was reported: phenols from leaves of the plum *Prunus domestica* L. [61], vitamin E, and phenols from roots of the plant *Harpagophytum procumbens* Burch. (Devil's Claw) [62], flavonols and sulfur-containing organic compounds from garlic [63, 64] were determined. An efficient method was developed in [65] for the determination of phytosterols in medicinal herbs and functional foods (vegetable oil, orange juice, milk) using DLLME with ultrasonic treatment in combination with microwave derivatization followed by an analysis by UHPLC with MS/MS detection. In [66], DLLME with hydrophilic DES based on betaine and lactic, pyromucous, and phenylacetic acids dissolved in isopropanol were used to

determine phenylpropanoids in vegetable oils. A number of hydrophobic DES were tested [67] for the implementation of DLLME of cannabioids and flavonoids in *Cannabis sativa* L. Dispersion was carried out in an ultrasonic bath, and then a chromatographic analysis of the DES phase diluted with methanol was performed. The selectivity of extraction with respect to acid derivatives of cannabiol due to non-polar interactions was noted. A similar approach using DES choline chloride–sesamol (1 : 3) was proposed for the determination of the antioxidant *tert*-butylhydroquinone [68] in soybean oils.

Single-drop microextraction is another example of liquid–liquid microextraction, which makes it possible to achieve high concentration factors of analytes, because the volume of the extracting solvent is limited to one drop. A drop of an extracting solvent is introduced into a sample solution using a microsyringe (or pipette) and then removed from it. The authors of [69] proposed using magnetic IL (**M-IL**) in single-drop microextraction by dispersing one drop of a solvent containing M-IL in a sample solution and extracting it back with a magnet. Using M-IL containing tetrachloromanganate anion, low LOD values (0.43 nM) were achieved in the determination of ascorbic acid in orange juice. This approach can be successfully combined with the subsequent determination by chromatography–mass spectrometry.

Hollow fiber-based liquid-phase microextraction greatly simplified the process of the extraction and preconcentration of an analyte in the extractant by facilitating the procedures for dosing and fixing the extractant and has become widespread for the extraction of biologically active substances from liquid plant samples. In [70], cinnamic acid derivatives were determined by reversed-phase HPLC–UV with preliminary extraction into a hollow fiber containing a hydrophobic DES of the composition tetrabutylammonium chloride–hexanoic acid (1 : 1, mol.). The limits of detection in this case turned out to be at a level of 10–30 ng/g. A similar approach [71] using DES of the composition serine–lactic acid (1 : 5) made it possible to determine the concentration of caffeic acid in samples of coffee, green tea, and tomato.

COMBINATION OF LIQUID–LIQUID AND SOLID-PHASE EXTRACTION METHODS: EXTRACTION WITH SORBENT DISPERSION

In extracting biologically active substances from solid plant samples, substances are usually treated with an organic solvent at the first stage to obtain an extract, which is purified at the next stage using selective sorption materials [72, 73]. A significant variety of sorbents (reversed-phase, ion-exchange, mixed, molecularly imprinted polymers, magnetic nanoparticles (**MNP**), multi-walled carbon nanotubes, organometallic frameworks, etc.) provide wide opportunities for the selective extraction of analytes with different chemical properties. Currently, a search for and the development of new sorption materials with specific characteristics depending on the type of analytes is being performed, which makes it possible to achieve high extraction efficiency and the degree of sample purification from impurities.

One of directions is the miniaturization of methods based on sorbents, microparticles of which are dispersed in a solution (in a liquid sample), which makes it possible to increase the surface area and the extraction efficiency. Thus, in the method of dispersive solid-phase extraction [74–84], the main approaches are matrix solid phase dispersion, magnetic solid phase extraction, microsolid phase extraction, and the μQuEChERS method. Matrix SPD is an effective universal method for extracting a wide range of drugs, natural components, pesticides and other compounds from complex plant samples. The sample is dispersed over the surface of a substrate material of a bound phase, forming a phase of mixed composition due to hydrophobic and hydrophilic interactions of various components for the separation of the target analyte [73]. Magnetic SPE is based on the use of sorption materials deposited on magnetic nanoparticles, such as carbon nanotubes [85], natural materials (chitosan) [86], and molecularly imprinted polymers [86, 87]. The main advantage of MSPE is that the sorbent contains magnetic nanoparticles that can be easily modified and quickly removed from the solution using a magnet.

The DSPE method has been applied to the identification and determination of rosmarinic acid in medicinal plants [86], to the extraction of *p*-coumaric acid and *p*-hydroxybenzoic acid from fruit juices [81] and flavanones from citrus fruits [82]. Matrix SPD has been successfully used to extract various polyphenols from olives [83]. In [84], the use of matrix SPD based on a diol sorbent ensured the extraction of 13 bioactive compounds (seven coumarins and six phenolic acids) from *Angelicae Pubescentis Radix* (dried roots of *Angelica pubescens Maxim*.) with subsequent analysis by UHPLC [84]. For the determination of isothiocyanates in plants, an approach was proposed [88] with derivatization with *N*-acetyl-L-cysteine and the use of a C18 cartridge followed by an analysis by HPLC–UV–MS. The authors noted that a similar scheme is also applicable to the determination of indoles, which perform a hormonal function in plants.

One of directions in the development of SPE methods with sorbent dispersion in a sample solution is associated with the development of new sorbents for the selective extraction of analytes from complex matrices. An increase in the selectivity of BAC extraction from plant samples can be achieved using MNP coated with sorbents with different specific properties. Thus, magnetic SPE based on a synthesized nanocomposite material, consisting of graphene

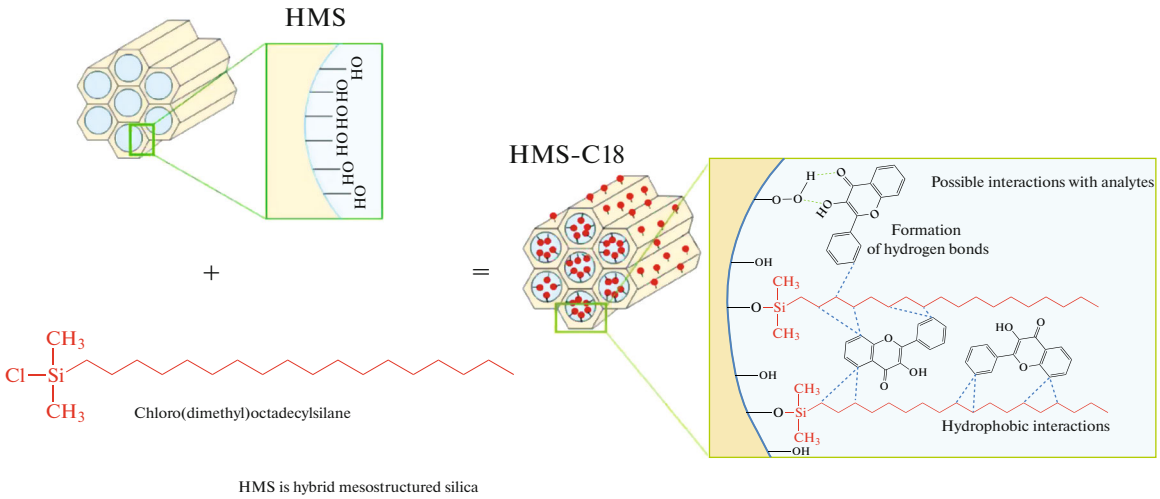

Fig. 3. Mechanism of possible interactions of polyphenols with surface groups of mesostructured modified silica [86].

and magnetic nanoparticles of iron oxide Fe_3O_4, was used to extract flavonoids (kaempferol, quercetin, luteolin) from tea samples, as well as wine and urine for subsequent HPLC determination [76]. Hydrophilic groups on the surface of graphene oxide and its large surface area ensured high extraction efficiency. In [85, 87], the use of MNP coated with a molecularly imprinted polymeric sorbent provided high selectivity in the extraction of phenolic acids (gallic and chlorogenic acids) from fruits and juices.

Another example of a selective sorbent is the synthesized mesoporous silica modified with octadecylsilanol (C18) groups [89]. The resulting hybrid material ensured the simultaneous extraction and purification of 20 polyphenols from mixed fruit and vegetable juices by DSPE (Fig. 3). Higher degrees of recovery were obtained compared to commercial amorphous C18-modified silica. The extraction step was combined with determination by ultra-HPLC and detection by ion trap tandem mass spectrometry.

An interesting version of DSPE was considered in [90]. The authors drew attention to the incomplete phase separation during DSPE, which, in turn, affected the repeatability and led to a reduction in the service life of chromatographic systems. As an alternative, it was proposed to use glass beads with OMM particles attached through PDMS. An OMM based on zirconium, UiO-66, was chosen for the determination of phytohormones in citrus fruits. It was possible to achieve limits of detection of 0.09–0.17 ng/g and limits of determination of 0.29–0.56 ng/g. Among the undoubted advantages of the proposed approach are a possibility of the independent effortless production of the sorbent, a simplified sample preparation operation (the extractant phase is extracted with tweezers), a possibility of reuse, and also small volumes of the analyzed samples.

To reduce the negative impact of traditionally used organic solvents on the environment, IL and DES were studied as possible eluents at the stage of analyte desorption in dispersive SPE; this ensured an increase in the efficiency of extraction and reduced the effect of the sample matrix [91–95]. Magnetic DSPE based on magnetic agarose nanoparticles using deep eutectic solvents as eluents in the process of the desorption of analytes was developed for the isolation and preconcentration of three flavonoids (morin, quercetin, and kaempferol) from plant products (tea, vegetable and fruit juices), followed by determination by HPLC–MS [91]. Matrix DSPE with natural DES based on choline chloride and lactic acid made it possible to effectively extract phenolic compounds from *Helichrysum arenarium* L. plants, such as chlorogenic acid, naringenin-4'-*O*-glucoside, tomoroside A, naringenin-5-*O*-glucoside, isosalipurposide, and naringenin [92]. To determine morin, quercetin, apigenin, and naringenin in juice and green tea samples, the conditions of sorption on particles of the composition graphene oxide–chitosan–Fe_3O_4 and the subsequent elution of DES choline chloride–urea (1 : 2) with the addition of an aloe vera gel (*Aloe vera* L.) were optimized [93]. Ionic liquids are also successfully used: in [94], neohesperedin and naringin were adsorbed on florisil from lime fruit (*Citrus aurantium* L.) by joint grinding, and then eluted in a cartridge with 1-butyl-3-methylimidazolium tetrafluoroborate. In a similar way, but using silica and 1-dodecyl-3-methylimidazolium bromide, the contents of several catechins, flavonoids, and terpenoids was determined in Knotweed (*Polygoni multiflora* L.) [95].

μQuEChERS MICROEXTRACTION METHOD

In 2003, a new approach to sample preparation was proposed; it was characterized as quick, easy, cheap,

effective, rugged, and safe (QuEChERS) [96]. This is a two-stage process for the separation of solid and liquid phases with the effect of salting out and DSPE. At the first stage, analytes are extracted from a homogenized sample with an organic solvent, often acetonitrile, in the presence of salting out agents and buffer solutions until an equilibrium is reached (to ensure a more efficient extraction of pH-dependent analytes, as well as to reduce the degree of decomposition of unstable analytes). The extract is then purified of interfering components of the sample matrix by DSPE using various porous sorbents, such as C18, a polar sorbent based on primary-secondary amine (PSA), and graphitized carbon black (GCB) [97].

Initially, the QuEChERS strategy was used to determine pollutants in environmental samples [98–101]. However, in recent years, the QuEChERS methodology has been successfully miniaturized and its scope has been significantly expanded, also to the determination of biologically active substances [102–106] and pollutants in plant samples [107]. Thus, the used of this approach made it possible to efficiently extract 12 polyphenols from fruit-based baby food (fruit juices and purees) [102]. The profiles of polyphenolic compounds in flowers of blue mallow (*Malva sylvestris* L.), hibiscus (*Hibiscus rosa-sinensis* L.), and nasturtium (*Tropaeolum majus* L.) were studied using μQuEChERS followed by chromatographic analysis by UHPLC–DMD [103]. In [104], the μQuEChERS strategy was successfully applied to the extraction of bitter acids and xanthohumol from hops (*Humulus lupulus* L.). The effectiveness of the μQuEChERS strategy followed by an UHPLC–MS/MS analysis for the determination of phenolic acids and flavonoids in little-studied varieties of red pepper (*Capsicum* spp.) has been shown; this is important for the cosmetic and pharmaceutical industries [105].

In [106], the μQuEChERS method in combination with UHPLC–MS/MS was used for the simultaneous detection of the tolfenpyrad insecticide and its four main metabolites in five tea samples (leaves of *Camellia sinensis* L.) (fresh tea shoots, green tea, black tea, infusion green tea and black tea infusion). For analyte extraction, acetonitrile with 1% formic acid was chosen in combination with C18, graphitized carbon black, hydroxylated carbon nanotubes, and $MgSO_4$ to purify the extract.

Currently, a search for and a study of new sorbents for purification in the QuEChERS format are being conducted. Sorbents based on mesoporous silica, a sol–gel material with improved textural properties, have been proposed as alternative materials. Thus, the μQuEChERS strategy was proposed in [107] for the simultaneous extraction of 21 pyrrolizidine alkaloids from various aromatic herbs (thyme (*Thymus vulgaris* L.), basil (*Ocimum basilicum* L.), rosemary (*Rosmarinus officinalis* L.)) in combination with HPLC–MS/MS determination. Analytical capabilities of various mesoporous silicas, both unmodified and modified with amino groups, were studied.

CONCLUSIONS

The analysis of plant samples is not an easy task because the complex composition of the sample matrix in combination with the low concentration of analytes. The preparation of such samples, including extraction processes, is one of the most important steps in any analysis, ensuring the selectivity and accuracy of the analyte determination and influencing the methodology of the subsequent analysis. The review considered modern approaches to sample preparation used to extract bioactive compounds from plant samples, their possibilities and influence on analytical parameters during the subsequent determination of analytes by chromatography–mass spectrometry. In recent years, in the sample preparation of plant samples, there has been a trend to move from traditional extraction versions (liquid–liquid and solid-phase) to miniature formats, simpler, faster, more economical, and more convenient to use, taking into account the basic principles of "green" analytical chemistry, such as SPME, LLME, DSPE methods, etc. One of the newest directions in the extraction of plant samples is the use of ILs and DES as extractants in various microextraction formats. They have proved useful both as extraction solvents and for modifying and improving the extraction efficiency and selectivity of other sorbents, such as nanoparticles and silica. A serious limitation of many innovative approaches to microextraction is their commercial inaccessibility, which limits their further application. From this point of view, microextraction versions, such as microSPE will benefit from the use of traditional formats, but their potential will certainly be increased by the introduction of more efficient sorbents. Thus, the prospects for "green" microextraction methods depend on the development of new sorption materials, further miniaturization and automation, and a possibility of combining them with analytical instruments.

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CONFLICT OF INTEREST

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

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