

From carbon nanostructures to high-performance sorbents for chromatographic separation and preconcentration †

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Information on carbon nanostructures (fullerenes, nanotubes, graphene, nanodiamond and nanodispersed active carbon) used to develop high-performance sorbents of organics and heavy metal ions from aqueous solutions is collected and analyzed. The advantages in the synthesis of hybrid carbon nanostructures and the possibilities of surface modification of these systems in order to carry out fast sorption pre-concentration are considered. Prospects for application of these materials in sorption technologies and analytical chemistry are discussed.

The bibliography includes 364 references.

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I. Introduction

Carbon materials are widely used in various fields of science and technology. They are of great value for industry, power engineering, medicine and agriculture. The discovery of new allotropes of carbon was followed by rapid increase in the number of studies devoted to extension of the application fields of nanocarbon materials. In the last three to four years there has been a surge in the number of publications concerning nanocarbon materials. It clearly manifests itself even against the background of abrupt increase in the

number of publications on nanomaterials and nanotechnologies taken in their entirety.

The attention of many researchers is focused on carbon nanostructures, *e.g.*, fullerenes, carbon nanotubes (CNTs), graphene, graphene oxide and detonation nanodiamonds due to unique properties of these systems.^{1,2} Most of these

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materials are characterized by large specific surface area and manifestation of different types of intermolecular interactions. This offers new prospects for efficient application of the systems in question in sorption technologies and analytical chemistry.

Recent reviews^{3–8} are mainly devoted to the synthesis of particular types of carbon nanomaterials and to research on their structure and properties. Much less attention is paid to the analysis of their applicability as promising sorbents for analytical and technological purposes. However, the available reviews give no clear idea on the competitiveness of the novel carbon nanostructures and composites based on them compared with the available carbon sorbents, such as activated carbons and graphitized carbon blacks. The potential application fields of the novel materials are still to be clarified. Although expensive, these materials exhibit undoubted advantages. In addition, the reviews mentioned above give little information on the advances made by researchers from the Russian Federation in the field of design of carbon nanomaterials and sorbents based on them.

The aim of this review is to bridge the gap and to analyze modern trends in the engineering of carbon nanostructures from the standpoint of synthesis of sorbents based on them. The review covers publications reported since 2000 up to 2014.

II. Fullerenes

II.1. General. Main methods of synthesis

The discovery of fullerenes, a new allotrope of carbon, is a breakthrough in chemistry of the late 20th century.⁹ The molecule of a fullerene is a hollow, cage-type spherical molecule comprising an even number of covalently bonded carbon atoms occupying vertices of hexa- or pentagons.¹⁰

Fullerenes can be synthesized in different manner. In 1990, Kratschmer, Haffman and co-workers¹¹ proposed for the first time obtaining crystalline fullerene (fullerite) using arc discharge. More recently, laser vaporization of graphite to produce fullerenes was reported (c.w. lasers are used to this end).¹² Various versions of plasma synthesis of fullerenes, ohmic Joule heating, high-frequency heating, corona discharge and combustion of carbon-containing substances have been proposed.¹³ The most widely used version of plasma synthesis is arc discharge synthesis.^{14–16} Fullerenes of different structure and molecular mass can be separated using differences in their polythermal solubilities,¹⁷ as well as by the sublimation¹⁸ and liquid chromatography (LC) methods.¹⁹ Among the fullerene separation techniques, LC is the most efficient one. Pure individual fullerenes of a particular molecular mass are obtained by LC using carbon materials^{20–25} and organic-functionalized silicas^{26,27} as stationary phases. In addition to these materials, carbon-mineral sorbents combining the porous structure of the silica matrix and the sorption properties of the surface of carbon materials were proposed for fullerene separation.^{28–31} These sorbents proved their efficiency for the separation of mixtures of light-weight fullerenes. When immobilized on Silochrome, the sorbents retain the globular morphology characteristic of the silica matrix (see Fig. 1). They are characterized by large specific surface area ($120–130\text{ m}^2\text{ g}^{-1}$) and mesoporous structure.

The cavity of the fullerene molecule is suitable for encapsulation of atoms and molecules of various chemical

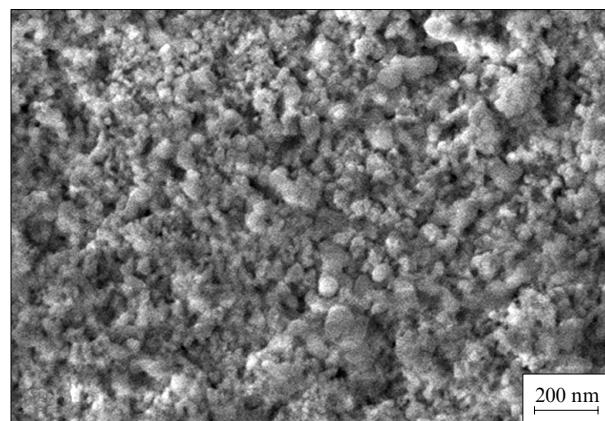


Figure 1. Photomicrograph of carbon-mineral sorbent.²⁹

compounds. Fullerenes are structurally similar to aromatics and have a common π -electron system. Combination of relatively high electron affinity and low ionization energy allows fullerenes to act as both electron donors and acceptors. In the condensed state, C_{60} is a molecular crystal bound by the van der Waals forces. Various parameters of C_{60} and C_{70} fullerenes were obtained from quantum chemical calculations.^{32,33}

II.2. The sorption properties of fullerenes

The adsorption capacity of fullerenes is associated with surface defects.³⁴ It is also assumed that adsorption on fullerenes is due to adsorbate penetration into the lattice. In particular, in the crystal of C_{60} fullerene the role of micropores is played by the space surrounding carbon nanoclusters; adsorbate molecules penetrate into this region through defects.^{35,36}

A comparison of the sorption activities of fullerenes and activated carbon towards various organic pollutants including aliphatic, cyclic and aromatic hydrocarbons revealed comparable sorption properties.³⁷ This was explained by the fact that adsorption on the fullerene surface is mainly due to dispersion interaction.

An NMR study of the adsorption of organic compounds on Aerosil A-300 modified with C_{60} fullerene showed that the material is characterized by lower affinity to water vapour than the untreated silica.³⁸ In the case of co-adsorption of water and nonpolar organic compounds the latter have little effect on the interaction of water with the surface. It was concluded that water and organic substances are adsorbed on different adsorption sites of the composite sorbent. The authors of that study believe that pronounced antimicrobial and antioxidant action of fullerenes makes the nanocomposites based on Aerosil A-300 modified with C_{60} fullerenes potential candidates for biomedical applications.

Yet another biomedical application of fullerenes and MWCNTs is considered in a study of the adsorption of *E. coli*.³⁹ These materials can be used for production of filters for biosensors. The authors of a review⁴⁰ on applications of nanomaterials in water treatment and environmental remediation also suggested the possibility of using fullerenes in fabrication of membranes of specified porosity.⁴¹

Various aspects of the interaction of biomolecules with carbon nanostructures including fullerenes have been considered.⁴² Original methods for the design of carbon adsorbents based on the introduction of fullerene microadditives as surface modifier of activated carbons were described⁴³ and different types of interactions between the surface of these sorbents and various metals ions were analyzed. It was found that fullerene microadditives influence the acid-base properties of the surface of the carbon sorbents.

A study⁴⁴ on the adsorption of peptides of ischemic origin on the surface of sorbents prepared by introducing fullerenes into porous silica gel showed that fullerenes change the adsorption properties of silica gel. The mechanisms of this influence were discussed based on NMR data. Heat treatment⁴⁵ of fullerene nano-whiskers produced micropores and ultramicropores in the samples. Porosities in the samples retained even upon heat treatment at > 2000 °C. The ultramicroporosity is indicative of the molecular sieve properties of the heat treated materials and suggests the possibility of their application as gas storage materials.

II.3. Fullerenes in sample preparation processes

A thorough analysis of potential applications of nanocarbon materials as adsorbents for preconcentration in analytical chemistry is available.⁴⁶ An appropriate system represents silica gel modified with C₆₀ fullerene.^{47–50} Information on the use of fullerenes as sorbents for preconcentration of heavy metals from aqueous solutions can be found in the literature.⁵¹

Fullerenes have smaller specific surface areas compared to other carbon nanostructures, thus being difficult to compete with the latter in the sorption preconcentration of low-molecular-mass organics. However, the fullerenes characterized by good kinetics and high extent of desorption of sufficiently heavy organic compounds, such as polychlorinated biphenyls (PCBs) and polynuclear aromatic hydrocarbons (PAHs), seem to be promising for sorption preconcentration of these compounds.⁴⁶

The efficiency of sorption of organic compounds from aqueous solutions decreases with increasing analyte polarity.^{52,53} According to Serrano and Gallego,⁵⁴ C₆₀ fullerene can be used for sorption extraction of benzene, toluene, ethylbenzene and xylene (these compounds have a common abbreviation 'BTEX'). Moreover, it is believed that fullerenes are more efficient in this respect than traditionally used adsorbents, such as alkyl-modified silica gel and Tenax TA, although the last-mentioned two systems are characterized by much larger specific surface areas than fullerenes. Yet another important advantage of fullerenes is the possibility of preconcentration of organics from acidic solutions.

Preconcentration of heavy metals in the form of chelates using various chelate-forming agents, *e.g.*, ammonium pyrrolidinedithiocarbamate or sodium pyrrolidinediethylcarbamate,⁵⁵ occupies a particular position among analytical applications of fullerenes. Chelates sorbed on fullerene columns are eluted with appropriate solvents and then determined by atomic spectroscopy. It was proposed to carry out fast screening for lead traces in water using a continuous flow system coupled to an atomic absorption spectrometer. A similar design was used for the determination of cadmium and organocadmium compounds in fish

liver,⁵⁶ inorganic lead and organolead compounds in rainwaters,⁵⁷ as well as various organometallic compounds in water and sediments.⁵⁸ Chromatographic analysis of preconcentrates combined with mass spectrometric detection ensured reliable speciation and quantitative determination of analytes at a level of a few fractions of microgramme per kilogramme.

Fullerenes exhibit high affinity for aromatic compounds and high thermal stability; this makes them attractive for solid-phase microextraction (SPME) applications which involve thermal desorption of extracted analytes.⁵⁹ In SPME, a fibre or a rod coated with a sorbent is placed in a sample solution to determine both volatile and nonvolatile analytes or in vapour above the sample to determine volatile analytes. As the sorption equilibrium is reached, the rod (fibre) is removed from the solution and analytes undergo thermal desorption in the case of gas chromatography (GC) or are eluted with an appropriate solvent in the case of LC. When the sorbent is chosen correctly, high extraction efficiency and sensitivity can be obtained. Thermal stability of fullerenes allows the operating temperatures to be varied over a wide range and the same sorbent unit to be used numerously. The main drawback of SPME consists in short operating life of conventional coatings. An SPME coating⁶⁰ made of polydimethylsiloxane (PDMS) modified with C₆₀ fullerene appeared to be highly efficient in the extraction of BTEX, naphthalene derivatives and phthalic acid esters from water samples. It provides better reproducibility of experimental results compared to that obtained using commercially available SPME sorbents.⁶¹

Fullerene-based coatings for SPME are usually synthesized using a sol–gel technology. For instance, hydroxyfullerene was used as the major component supported on the fused silica surface.⁶² Modification with hydroxyfullerene significantly improved the efficiency of sorption of PCBs and PAHs as well as the thermal stability and solvent resistance of the coating.

II.4. Fullerenes as stationary phases in chromatography

Nonporous structure and, correspondingly, small specific surface area as well as high thermal stability create prerequisites for application of fullerenes as GC stationary phases for the determination of high-boiling organics, such as PAHs and PCBs.^{5,63} Based on parameters of gas chromatography retention of organic compounds of different polarity, Kartsova and Makarov⁶⁴ found that the sorbent based on C₆₀ fullerene is of much higher polarity than graphitized carbon black, the free energy of adsorption of methylene unit (CH₂) on fullerene being about 2.5 times lower than on carbon black. They also discovered a synergistic effect in the C₆₀ fullerene + dibenzo-24-crown-8 mixed phase, which manifests itself in improved selectivity of separation of compounds of different polarity.⁶⁵

Pure fullerenes are difficult to use in chromatography because they are prone to aggregation like other carbon nanoparticles. Taking into account this fact, carbon nanomaterials are deposited on the surface of supports, most often silicas or polymers.⁵ Fullerenes act as reactive surface modifiers that govern the selectivity of the stationary phase, whereas the support has almost no effect on the retention parameters of the substances being separated. Fullerenes can be supported on, *e.g.*, silica surface^{66–68} and on poly(styrene-co-divinylbenzene)⁶⁹ by covalent^{67–69} and noncovalent⁶⁶ immobilization. Fullerene (usually,

C₆₀)-modified sorbents are used in GC, first of all, for the determination of PAHs and PCBs.

Most studies devoted to application of carbon nanomaterials for chromatographic separation concern GC; however, recently, there has been a trend towards utilization of these materials in high-performance liquid chromatography (HPLC).⁵ Applications of carbon nanostructures in HPLC were analyzed in a review.⁷⁰ Compared to the most widely used reversed-phase HPLC sorbent, octadecyl-modified silica gel, fullerene-based sorbents are more polar because their molecules contain a delocalized π -bond. Recently, fullerenes as stationary phase materials for chromatographic applications are gradually replaced by CNTs and nanodiamonds.^{3–8}

III. Carbon nanotubes

III.1. General. Main methods of synthesis

Since their discovery,⁷¹ CNTs have attracted the attention of researchers from the standpoint of design of novel carbon nanomaterials. Carbon nanotubes are cylindrical cage nanostructures which can be obtained by rolling a graphene sheet into a seamless cylinder.⁷² They exhibit unique properties, *e.g.*, high chemical, mechanical and thermal stability, have a large specific surface area and are thus attractive as a new type of sorbents. There are single- and multi-walled carbon nanotubes (SWCNTs and MWCNTs, respectively), the latter being much cheaper than the former. As a consequence, they are of considerable interest for practical applications.

The potential of CNTs as sorbents is determined by their structure, which depends on the methods of synthesis, purification and functionalization. Currently, CNTs are most often synthesized by the electric arc method, laser ablation and chemical vapour deposition (CVD). Metallic iron, nickel and cobalt are most widely used as bulk and supported catalysts. The sorption properties of CNTs depend on the synthesis conditions and on the nature of the catalyst.^{73,74} Using the cobalt-containing catalyst, one can obtain uniform thin MWCNTs, as was confirmed by transmission electron microscopy (TEM) (Fig. 2).

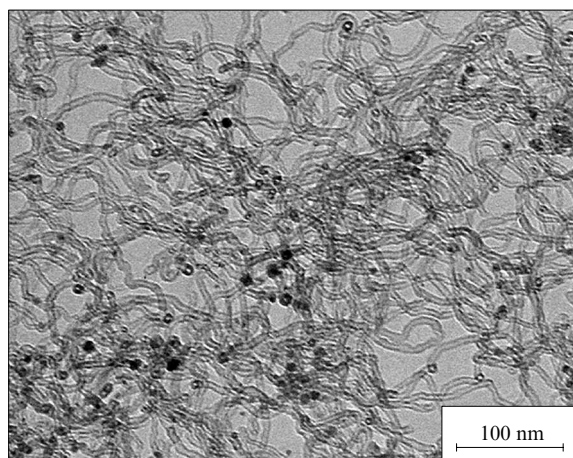


Figure 2. TEM image of MWCNTs synthesized in the presence of cobalt-containing catalyst.⁷⁵

Being a high-performance method, CVD is widely used in industry for the synthesis of CNTs.^{75,76} A version of the CVD method is based on catalyzed disproportionation of carbon monoxide at elevated pressure. Purified CNTs thus synthesized have a very large specific surface area ($> 1500 \text{ m}^2 \text{ g}^{-1}$),¹ which makes them candidate sorbents for various applications. Methods of synthesis and the structural features of CNTs have been documented (see, *e.g.*, Refs 1 and 77–80). In this review, the emphasis is placed on the studies of the sorption properties of CNTs and on their applications as sorbents.

III.2. The sorption properties of carbon nanotubes

The sorption properties of CNTs have been analyzed thoroughly.⁸¹ The specific surface area of CNTs spans a range from 150 to $1500 \text{ m}^2 \text{ g}^{-1}$, thus being much larger than that of fullerenes (see above). Carbon nanotubes can be covalently or non-covalently functionalized with various organic molecules to improve the selectivity of the interaction with sorbates. Some authors believe that CNTs have the potential to be next-generation sorbents for extraction of heavy metal ions and organic pollutants from wastewater.^{82,83}

Carbon nanotubes are high-performance sorbents of heavy metal ions including cadmium,^{84–86} lead,^{87,88} nickel,^{89,90} copper,^{91,92} as well as fluoride ions^{93,94} and radionuclides.^{95,96} They also exhibit high sorption affinity for many organic pollutants, such as dioxins,⁹⁷ organophosphorus esters,⁹⁸ organic acids,⁹⁹ pesticides, PAHs, herbicides, phthalate esters, *etc.*¹⁰⁰ With functionalized CNTs one can utilize various types of interaction between adsorbed molecules and the surface to improve the sorption selectivity.^{101–107}

Oxidized MWCNTs were used to prepare a composite with iron oxide. The composite represents an array of densely aligned CNTs containing iron oxide clusters, exhibits good adsorption properties for chromium ions¹⁰³ and its sorption capacity is higher than that of activated carbon. Such a composite was used for adsorption of Ni^{2+} and Sr^{2+} .¹⁰⁸ It was established that the adsorption of ions on this composite depends on pH value; therefore, ions can be desorbed with ease by varying pH. The composites MWCNTs– Fe_3O_4 ,¹⁰⁹ MWCNTs– Al_2O_3 ,^{110,111} and MWCNTs–manganese dioxide¹¹² for extraction of Pb^{2+} and Cu^{2+} ions from aqueous solutions were prepared by co-deposition. It was found¹⁰⁹ that adsorption is correctly described within the framework of the Langmuir model. Depending on pH value and temperature, the adsorption capacity of the composite varied from 10 to 31 mg g^{-1} . In the last-mentioned case, combining the oxidative properties of manganese dioxide with the adsorption properties of CNTs made it possible to design an efficient sorbent for extraction of As^{3+} and As^{5+} ions.

A nanocomposite based on oxidized MWCNTs, biopolymer (chitin) and magnetite was proposed for adsorption of organic dyes Rose Bengal^{113–119} and Congo red^{120,121} from aqueous solutions. These dyes are hazardous, highly toxic components of industrial wastewater which induce mutagenic and carcinogenic effects in the human body. The influence of the size and amount of MWCNTs, pH of the medium, the mixing time and the dye concentration on adsorption was studied. Operation under optimum conditions provides a high adsorption capacity (357 mg g^{-1}). The role of mesopores 10 to 50 nm in size was found to be

crucial to the adsorption process. It is believed¹²⁰ that MWCNTs whose sorption properties are superior to those of activated carbon are promising for cheap and safe wastewater treatment.

Nanocomposite materials based on CNTs and iron oxides combine the sorption and magnetic properties,^{121–124} thus being efficient for magnetic separation. In particular, a sorbent representing MWCNTs supported on magnetite (Fe_3O_4) was efficient in removal of methylene blue cationic dye from aqueous solution.¹²⁵ A chitosan/CNTs magnetic sorbent proved high efficiency in the adsorption of acid red anionic azo dye.¹²⁶

Carboxylation of MWCNTs can strongly influence their adsorption properties for proteins. In particular, carboxylation of side walls of MWCNTs affects the adsorption of bovine serum albumin and lysozyme (egg protein).¹²⁷ The adsorption of albumin on carboxyl-modified CNTs is suppressed, whereas that of lysozyme is enhanced. This behaviour was explained by competition between the hydrophobic and ionic interactions of MWCNTs with proteins.

It seems interesting to use CNTs and other carbon materials as biofilters, and *E. coli* adsorption study¹²⁸ revealed a great potential of SWCNTs. Various aspects of application of CNTs in biomedical studies have been documented;^{129,130} in particular, they are promising for target delivery of drugs, diagnostics and therapy.

III.3. Carbon nanotubes in sorption preconcentration

III.3.a. The advantages and disadvantages of carbon nanotubes as sorbents

At present, carbon materials based on CNTs are most often used in the sample preparation for chemical analysis.^{7,131–136} In addition to the properties mentioned above, unique features of CNTs from the standpoint of utilizing them for sorption preconcentration are as follows:¹³⁷

- high hydrophobicity; CNTs are almost insoluble in water, can be dispersed with ease in a few organic solvents and have a large specific surface area; these properties predetermine application of CNTs for sorption preconcentration of organic compounds from aqueous solutions;^{1,2,132}

- high thermal stability (to 1200 °C) in inert atmosphere; as a consequence, CNTs can be used as GC stationary phases and provide the possibility for thermal desorption to occur in the case of sorption preconcentration from gaseous media;^{3,5,132}

- the possibility of covalent functionalization to vary the sorption properties;^{138,139}

- the possibility of covalent immobilization on solid supports, such as silica or steel;¹³³ this creates prerequisites for fast sorption preconcentration from the flow of the media being analyzed.

However, it should be noted that large aspect ratios typical of CNTs favour their spontaneous aggregation. Being combined with high flexibility of particles, this increases the probability of clogging of the sorption and chromatographic columns packed with pristine CNTs, especially under HPLC conditions.

Covalent functionalization usually involves oxidation with strong oxidizing agents at high temperatures. As a result, COOH, OH and CO groups are incorporated into the CNT walls¹⁴⁰ and then various substitution reactions are conducted. The modified CNT surface has an isoelectric

point characterized by the pH value of the solution contacting the CNTs, at which the CNT surface is electrically neutral. At higher pH values, the CNT surface bears a negative charge and adsorption of positively charged species can occur. At lower pH values, the adsorption capacity of CNTs for positively charged species decreases. This can be used for, *e.g.*, elution of ions using acid solutions.

The surface area of covalently functionalized CNTs decreases by at most 10% because their structure remains unbroken.¹⁴¹ Functionalized CNTs can be deaggregated much more easily than corresponding untreated materials. Carbon nanotubes can form noncovalently bonded aggregates with surfactants as well as supramolecular complexes with polymers.¹³⁹ The solubility of these materials is governed by the van der Waals forces, π - π - and hydrogen bonds and electrostatic interactions. Noncovalent bonding makes bifunctionalization possible as a result of, *e.g.*, formation of CNT conjugates with carbohydrates, proteins, enzymes or DNA.¹³⁸ The CNT cavity enables encapsulation of guest molecules including fullerenes, metallofullerenes, metals, *etc.*¹⁴²

III.3.b. Carbon nanotubes in solid-phase extraction of metal ions and organics from aqueous solutions

Although not rigorously used, the notion ‘solid-phase extraction’ (SPE) can be found in most studies on analytical applications of CNT-based sorbents. The lack of rigor manifests itself in that the notions ‘adsorption’ and ‘SPE’ are not identical. The latter is as a rule used in the case of organic sorbates. Sorbents based on CNTs bear active sites on the surface of inner CNT walls, have cavities in the inter-tubular space and thus can adsorb metals.^{143–146} A series of recent studies^{144–146} is devoted to the complexation of metals for subsequent SPE. However, the correctness of terminology remains a moot question because in this case one deals with chelates (in fact, organometallic compounds) as sorbates. For instance, As^{3+} and Sb^{3+} were extracted from natural water samples using ammonium pyrrolidine-dithiocarbamate as chelate-forming agent and a cartridge filled with SWCNTs.¹⁴⁴ In the sorption of chelates an important role is played by the pH value, which not only controls the stability of the complex being formed, but also influences the efficiency of its sorption on SWCNTs. Efficient adsorption of metal complexes occurs at pH 2.0–5.0. Metal ions can also be extracted using CNTs without chelate-forming agents.^{147,148}

Most studies on the sorption of metals were carried out using modified CNTs.^{149–153} Oxidation with strong acids, ozone or plasma in severe conditions leads to incorporation of hydroxyl, carboxyl and carbonyl groups into the CNT walls. The adsorption capacity of oxidized SWCNTs for Cd^{2+} ions is almost six times higher than that of MWCNTs.¹⁵⁴ A comparison of the sorption properties of CNTs, activated carbon and carbon encapsulated magnetic nanoparticles (CEMNs) for Cu^{2+} and Co^{2+} cations revealed that CNTs and CEMNs are 2.5 to 6.5 times more efficient than activated carbon. This is explained by higher density of the surface charge, which depends on the ratio of the oxidized surface area to the total surface area of the sorbent. High density of the negative surface charge appears when, *e.g.*, two carboxyl groups are localized at the same site, and serves a prerequisite for strong binding between the CNT surface and doubly charged metal ions.

Table 1. Results obtained by SPE on CNTs.

Analyte	CNT type	Speciation method	Results		Ref.
			limit of detection	R (%)	
As ³⁺ , Sb ³⁺	SWCNTs	AFS	20–40 ng litre ⁻¹	91–105	144
	CNTs	Electrothermal AAS	20–50 ng litre ⁻¹	96–104	145
Cd ²⁺ , Co ²⁺ , Ni ²⁺ , Pb ²⁺ , Fe ²⁺ , Cu ²⁺ , Zn ²⁺	MWCNTs	Flame AAS	1–5 µg litre ⁻¹	88–104	146
Co ²⁺ , Cu ²⁺ , Ni ²⁺ , Pb ²⁺ , Fe ²⁺ , Mn ²⁺	Double-walled CNTs	Flame AAS	0.5–7 µg litre ⁻¹	75–100	147
Cu ²⁺ , Fe ²⁺ , Mn ²⁺ , Pb ²⁺	MWCNTs	Flame AAS	3.5–8 µg litre ⁻¹	23–106	148
Cd ²⁺	MWCNTs	Electrothermal AAS	0.01 µg litre ⁻¹	97–100	149
Ag	CNTs	Flame AAS	0.35 µg litre ⁻¹	96–108	150
Hg ²⁺	Oxidized MWCNTs	Cold vapour AAS	12 mg litre ⁻¹	88–95	151
Pd ²⁺	Oxidized MWCNTs	Flame AAS	0.3 µg litre ⁻¹	81–91	152
Pb ²⁺	MWCNTs–NH ₂	ICP AES	0.2–0.3 µg litre ⁻¹	95–110	156–158
V ⁵⁺ , Cr ⁶⁺ , Pb ²⁺ , Cd ²⁺ , Co ²⁺ , Cu ²⁺ , As ³⁺	CNTs	MS–ICP	0.4–3 ng litre ⁻¹	90–110	159
Ni, Pb	Oxidized CNTs	Electrothermal AAS	0.8, 0.07 ng litre ⁻¹	75–100	161
Triazines	MWCNTs–COOH	HPLC–UV	4–30 ng litre ⁻¹	86–102	165
Pesticides	MWCNTs	LC–UV	16–67 ng litre ⁻¹	36–101	166
Neurotransmitters	SWCNTs	HPLC	–	88–94	168
	MWCNTs	HPLC	–	82–94	168
Emodin	MWCNTs–MIP	HPLC	–	80–93	169
Sulfonamides	SWCNTs, MWCNTs–MIP	CE	30–70 ng litre ⁻¹	99–103	170
Quinolones	Oxidized MWCNTs	CE	30–100 ng litre ⁻¹	62–114	171

Note. Here and in Tables 2–6 *R* is the degree of extraction.

Functionalization of oxidized CNTs with various organic molecules resulting in the formation of amide bonds improves the selectivity of extraction of metal ions.^{155–161} The degree of functionalization is limited by the modification time because of possible destabilization of the CNTs structure, the appearance of surface defects and shortening of the CNTs.¹⁵⁵ Finally, speciation analysis of metals is usually carried out by atomic fluorescence spectrometry (AFS), atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP AES) and inductively coupled plasma mass spectrometry (ICP MS). Studies on the sorption of heavy metal ions from aqueous solutions have been analyzed in reviews.^{162–164}

Carbon nanotubes are widely used not only for extraction of metal ions, but also for pre-concentration of toxic organic micro-impurities.^{165–171} A possible method to improve the SPE selectivity of organic sorbates is to modify the CNT surface with molecularly imprinted polymers (MIP).^{169–170} Here, CNTs act as MIP supports and the mechanical strength and chemical stability of adsorbents are improved. Nonvolatile organic compounds are usually determined by HPLC with UV-spectrophotometric detector and by capillary electrophoresis (CE). Volatile organics are most often determined by GC with MS detection, flame ionization detector (FID) or electron capture detector (ECD). Anions are often determined by ion chromatography (IC) with electrochemical detector (ED). The potential of CNTs in solid-phase extraction of metal ions and organics from liquid media is illustrated by the data presented in Table 1.

III.3.c. Carbon nanotubes in new versions of solid-phase extraction

Traditionally, SPE on CNTs has a number of objective disadvantages, first of all, long time of the process due to low rates of the analyte diffusion and mass exchange in the sorbent pores. Aggregation of CNTs leads to a decrease in the permeability of sorption cartridges and thus has negative effect. Dispersive solid-phase extraction (DSPE) allows one to shorten the extraction time because the sorbent is dispersed over the entire volume of the analyte sample.^{172–178} This is a fast and simple sorption technique which involves hand shaking of samples followed by phase separation using high-speed centrifugation. The enrichment factors usually lie in the range from 10² to 10³.

A new version of DSPE, so-called magnetic solid-phase extraction (MSPE), is based on utilization of magnetic micro- or nanoparticles as adsorbents. In MSPE, the sorbent containing analytes can be removed from the solution under the action of a magnetic field. This considerably reduces the extraction time. The method can be used for extraction of both inorganic and organic analytes.^{179–183}

Usually, the MSPE experimental procedure involves the following:

1) dispersion of a magnetic sorbent in aqueous solution of the sample; adsorption of analytes on the magnetic sorbent occurs under agitation;

2) removal of the sorbent containing analytes from the suspension under the action of external magnetic field;

3) elution (desorption) of analytes from the sorbent;

4) removal of sorbent from the solution under the action of external magnetic field (in static version of desorption); and

Table 2. Results obtained by different versions of SPE on CNTs.

Analyte	SPE version	Speciation method	Results		Ref.
			limit of detection	R (%)	
Pesticides	DSPE	GC–MS	3–50 ng kg ⁻¹	71–110	173
Neonicotinoid insecticides	DSPE	HPLC	0.5–1.0 ng g ⁻¹	174	
Orthophosphate pesticides	DSPE	GC–MS	0.7–1.6 µg kg ⁻¹	86–114	175
Cyflumetofen	DSPE	HPLC–MS	0.7–9.8 µg kg ⁻¹	79–118	177
Phthalate esters	MSPE	GC–MS	25–50 ng litre ⁻¹	93–99	179
PAHs	MSPE	GC–MS	35–100 ng kg ⁻¹	81–97	180
Estrogens	MSPE	HPLC with fluorescence detector	1.2–2.4 µg litre ⁻¹	99.8–99.9	181
Triazine herbicides	µ-SPE	HPLC	0.2–0.5 µg litre ⁻¹	95–101	184
PAHs	µ-SPE	GC–MS	4.2–47 ng litre ⁻¹	70.9–96.8	185
	µ-SPE	GC–MS	1–150 ng litre ⁻¹	72–93	187
Cu ²⁺	µ-SPE	AAS	0.8 µg litre ⁻¹	94.0–95.9	188
Pb ²⁺	µ-SPE	AAS	1.80 µg litre ⁻¹	93.2–95	188
Cd ²⁺	µ-SPE	AES–ICP	1 µg litre ⁻¹	–	189

5) an analysis of the eluate using a particular analytical method.

Most often, Fe₃O₄ magnetic nanoparticles are used. To reduce the desorption time, a method was developed for the preparation of magnetic adsorbents with no chemical modification.¹⁸¹ Multi-walled CNTs can be readily adsorbed by magnetic nanoparticles under ultrasonic agitation.

The drawbacks of these versions of SPE on CNTs include complexity in process automation and high consumption of organic solvents. These problems can be solved using the so-called micro-solid-phase extraction (µ-SPE).^{184, 185} In the µ-SPE devices, the sorbent is enclosed in a shell (membrane) made of an analyte-permeable material. In particular, MWCNTs were enclosed within a polypropylene membrane and extracted triazines from samples of river water.¹⁸⁴ The test experiments included extraction of triazines from river water samples. The total extraction time was 25 min. This version of SPE is comparable in absolute and relative recoveries with commercially available triazine–MIP–SPE cartridges, namely, the absolute recoveries were 55%–71% for µ-SPE and 83%–90% for MIP, while the relative recoveries were 95%–101% and 85%–89%, respectively. The µ-SPE method made it possible to shorten the sample preparation time and to perform automated analysis in a flow injection design.^{186–189} The results obtained using the DSPE, MSPE and µ-SPE methods on CNTs are presented in Table 2.

III.3.d. Carbon nanotubes in solid-phase microextraction

Recently, CNTs have found use as adsorbents for solid-phase microextraction (SPME) due to their electronic properties, possibility of modification, relatively low cost as well as high mechanical and thermal stability. The most widely used methods for fabrication of CNT-based SPME fibres are as follows: physisorption,^{190, 191} sol–gel techniques,^{192–195} chemical bonding,^{196, 197} electrochemical polymerization,¹⁹⁸ electrophoretic deposition,¹⁹⁹ physical agglutination by an organic binder,^{200, 201} atom transfer radical polymerization²⁰² and magnetron sputtering.²⁰³

CNT-based fibres prepared by the sol–gel method are characterized by low reproducibility of their sorption properties (see a review¹³⁵). The problem can be solved using the

chemical bonding approach where the surface of gold fibres¹⁹⁶ or stainless steel fibres¹⁹⁷ serves as a substrate for MWCNTs. As in the sol–gel technology, preparation of SPME fibres requires surface modification of both CNTs and fibres. Amine-modified MWCNTs were attached to the surface of stainless steel fibres using the Michael reaction and polydopamine as organic binder.¹⁹⁶

Electrochemical deposition is based on the fabrication of SPME fibres using cyclic voltammetry. An example is provided by the fibres comprised of polypyrrole-modified MWCNTs as the stationary phase and a stainless steel rod as substrate.¹⁹⁸ Disadvantages of the fibres prepared by electrochemical polymerization consist in low thermal stability and swelling in organic solvents.

Electrophoretic deposition is based on the deposition of charged particles on a corresponding electrode. The thickness of the adsorption layer is controlled by the number of scan cycles and/or the deposition time. In a particular case, CNT fibres were prepared by the oxidation of CNTs followed by dispersion in dimethylformamide and subsequent deposition on a Pt plate.¹⁹⁹ The fibres were stable at 500 °C in hydrogen atmosphere and used in vapour-phase SPME because in this case the affinity for water molecules decreased.

Yet another route to CNT-coated fibres is to use various adhesives, *e.g.*, dibutyl phthalate²⁰⁰ or silicone rubber glue.²⁰¹ The fibres thus prepared were thermally stable up to 350 °C and their adsorption capacities remained unchanged during 150 operating cycles. Data illustrating the application of CNTs in SPME are collected in Table 3.

III.4. Carbon nanotubes as stationary phases for chromatography

The adsorption properties as well as high thermal and chemical stability of CNTs (see above) make them attractive for applications as stationary phases for GC and LC.³ Uniform porous structure of CNTs abruptly decreases the mass transfer resistance.²⁰¹ Compared to the available sorbents with a similar specific surface area, *e.g.*, Carbo-packs, CNTs as stationary phases provide better retention of compounds with relatively low boiling points, better resolution of the analyte peaks owing to more efficient

Table 3. Results obtained by SPME on CNTs.

Analyte	CNT type	Speciation method	Results		Ref.
			limit of detection	R (%)	
Monobutyltin, dibutyltin, tributyltin	SWCNTs	GC–MS	5 ng litre ⁻¹	76–85	190
Organophosphorus pesticides	SWCNTs	GC–MS	0.3 ng litre ⁻¹	75–85	191
Pyrethroid pesticides	MWCNTs–polypyrrole	GC–ECD	0.12–0.43 µg litre ⁻¹	83–112	198
Pesticides	SWCNTs	GC–MS	27–230 ng litre ⁻¹	75–118	201
Benzene, toluene, ethylbenzene, <i>o</i> -xylene	MWCNTs–poly(ethylene glycol)	GC–ECD	3–600 ng litre ⁻¹	90–102	192
Volatile organics	MWCNTs–COOH	GC–FID	0.5–0.7 ng litre ⁻¹	74–87	195
Methamphetamines, amphetamines	MWCNTs–polyacrylonitrile	GC–FID	2–3 µg litre ⁻¹		202
PCBs	MWCNTs–Nafion	GC–ECD	0.12–0.26 µg litre ⁻¹	47–66	193
Diazinon, fenthion	SWCNTs	GC–ECD	0.02–7.5 ng litre ⁻¹	81.9–106.1	194
Phenols	MWCNTs–COOH	GC–FID	0.2–0.3 µg litre ⁻¹	97–104	196
Phenol derivatives	MWCNTs–NH ₂	GC–FID	0.02–0.1 µg litre ⁻¹	97–104	197
Phenols	SWCNTs	GC–MS	0.10 mg kg ⁻¹	79–86	200
Phenols	MWCNTs–COOH	GC–FID	5–50 ng litre ⁻¹	73–142	201
F ⁻ , Cl ⁻ , Br ⁻ , NO ₃ ⁻ , SO ₄ ²⁻	MWCNTs–COOH	IC–ED	0.06–0.26 µg litre ⁻¹	65–121	199

mass exchange,^{204,205} comparable sorption capacity and isosteric heats of adsorption.²⁰⁶

Carbon nanotubes are used as GC stationary phases for both packed and capillary columns. A comparison of untreated MWCNTs with the Norit and Chemviron activated charcoals in relation to GC separation of lower alkanes and aromatic hydrocarbons revealed the advantage of MWCNTs from the standpoint of selectivity of the separation of isomeric alkanes C₄ and C₅.^{207,208} Most studies are devoted to application of CNTs as GC stationary phases in capillary columns. Such phases are prepared by CVD,^{206,209,210} covalent grafting and noncovalent immobilization.²¹¹ The selectivity can be improved using functionalized CNTs^{207,208,212,213} or CNTs and an ionic liquid.²¹¹

Single-walled CNTs were deposited on an open tubular capillary column by CVD with ethanol as the source of carbon and metallic cobalt as catalyst.²⁰⁶ Such columns were used for the separation of C₂–C₁₄ alkanes and PAHs. A comparison of the adsorption properties of SWCNTs and MWCNTs, on the one hand, and Carboxipack, on the other hand, in microtrapping volatile organics revealed the highest adsorption capacity for the SWCNTs with higher aspect ratio than that of the MWCNTs.²⁰⁴ Both SWCNTs and MWCNTs demonstrated their advantages over Carboxipack, first of all, higher efficiency of mass exchange and, therefore, narrower chromatographic peaks. Capillary columns packed with CNTs showed high selectivity in the separation of mixtures of Ar, H₂ and CO₂ (better results were obtained using SWCNTs rather than MWCNTs),²¹⁴ whereas carbon nanofibres demonstrated no noticeable separation of these gases.

A versatile method for improving the affinity of CNTs for polar organic compounds is to use covalent modification of CNTs, which precludes their agglomeration and enhances the selectivity.²¹⁵ For instance, carboxyl-modified MWCNTs demonstrated better chromatographic properties in the separation of linear and branched C₃–C₅ alkanes from liquefied petroleum gas.²⁰⁸ Covalent modification resulting in R–NH₂-modified MWCNTs (R is an organic

functional group) is particularly attractive for GC analysis of light aromatic hydrocarbons because of high resolution of chromatographic peaks. In addition, R–NH₂-MWCNTs appeared to be more efficient sorbents for the separation of some alcohols and esters compared with untreated MWCNTs.²¹² Using R–NH₂-MWCNTs as stationary phases, one can determine the side products of fermentation in strong alcohols. Alcohols are selectively sorbed in accordance with their molecular structure (linear or branched) and physicochemical properties. It was shown that R–NH₂-MWCNTs are superior to such popular stationary GC phases as Porapak QS.²¹² In particular, they demonstrated excellent separation of a mixture of analytes (alcohols + esters + ketones + alkanes + aromatics) with significantly different polarity and volatility. This made it possible to determine typical components of commercially available paint thinners.

The efficiency and selectivity of sorbents depend on the appropriately chosen functional groups that enter into specific reactions with analytes. The MWCNTs–R–NH₂ system is a convenient example of the modified CNT-based sorbent for HPLC separation.²¹⁶ In this sorbent, specific interactions with enthalpy of adsorption higher than the energy of the π–π-bond provide chemisorption and enhance the selectivity.

Treatment with oxidizing agents dramatically changes the adsorption properties of sorbents. Polar organic compounds, in particular, alcohols are better separated on oxidized CNTs compared to untreated ones. The selectivity increases by more than 100% while the number of theoretical plates increases by 60%. Contrary to this, untreated CNTs are more appropriate for separation of aromatics (*cf.* co-elution on carboxyl-modified CNTs) due to high density of carboxyl groups on the CNT surface; high polarity thus imparted to the surface was observed until 160 °C.

Modified CNTs improve the kinetics of mass exchange as compared to the untreated CNTs.^{207,209,212} Figure 3 presents the chromatograms obtained using different types of CNTs. Symmetrical chromatographic peaks obtained even from compounds characterized by strong retention

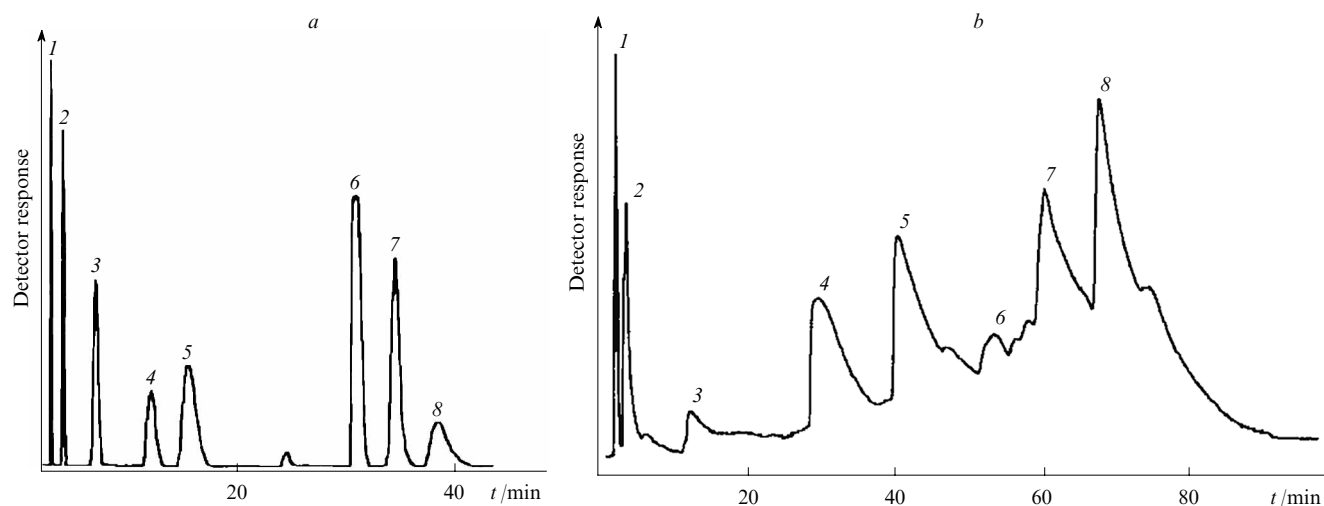


Figure 3. Chromatograms of a mixture of esters obtained using MWCNTs–R–NH₂ (a) and unmodified MWCNTs (b).²¹² Methyl acetate (1), ethyl acetate (2), methyl pivalate (3), *tert*-butyl propionate (4), *n*-butyl acetate (5), diethyl malonate (6), phenyl acetate (7) and ethyl lactate (8).

are indicative of rapid sorption–desorption process. However, one should keep in mind that functionalized CNTs can operate in a narrower temperature range compared to the untreated CNTs due to thermal instability of functional groups. Usually, the highest operating temperatures lie between 120 and 150 °C;²⁰⁷ this is an objective disadvantage of functionalized CNTs.

Hybrid materials are promising LC sorbents.²¹⁷ In these materials, CNTs are responsible for the retention of adsorbates and selectivity of separation, whereas the support (*e.g.*, SiO₂) is not involved in the separation process.^{218–220} The role of support for CNTs can be played by silica microspheres²¹⁸ or monolithic polymers.^{217–219} The potential of such composite sorbents was illustrated for the separation of PAHs on a stationary phase prepared by noncovalent adsorption of SWCNTs on silica gel in the course of treatment of amine-modified silica gel with pristine SWCNTs.²²¹ Using the same sorbent, linear polyphenyls were separated from analogous polycenes (*e.g.*, *p*-terphenyl and anthracene) owing to stronger adsorption due to tighter contact between analyte molecules and the bent CNT surface. Adsorption of linear polycene molecules was also stronger compared to nonlinear polycenes (*e.g.*, anthracene and phenanthrene) owing to ‘face-to-face’ bonding with CNTs.

An alternative method for immobilization of CNTs on silica support was proposed.²¹⁸ Hydroxylated MWCNTs were physisorbed on silica and then immobilized by dehydration at elevated temperature. Generally, stationary phases based on CNTs exhibit the adsorption properties of typical reversed-phase sorbents, but specific interactions additionally enhance their selectivity to certain ions, as was demonstrated²²² by the determination of traces of inorganic anions in organic matrices.

An example of application of CNTs as stationary phases for chromatography is provided by a monolithic capillary column for HPLC, prepared by adding MWCNTs to solid poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) and by physisorption of carboxyl-modified MWCNTs on the

same material.²¹⁹ To attach CNTs to the porous surface of the polymer, it was treated with ammonia to give a monolith bearing primary amino groups that could electrostatically interact with the oxidized CNTs. The adsorption of CNTs was found to depend on the pH of the medium. It was also reported that in the case of acidic mobile phases CNTs can be removed from the column.

Another method for incorporation of CNTs into sorbents for HPLC consists in grafting on aminopropyl-functionalized silica activated with glutaraldehyde.²²⁰ Functionalization involved imine formation between the aldehyde group of silica and an amine group from SWCNTs–NH₂. The composite sorbent provided good results in the separation of peptides.

To retain the sp²-hybridized structure of CNTs, noncovalent functionalization of monolithic silica with SWCNTs was carried out.²²³ Ultrashort SWCNTs with an average length of 7.5 nm were dynamically adsorbed on meso(macro)porous columns packed with silica. In particular, CNTs suspended in 1-methylpyrrolidin-2-one filled the silica pores (average pore size was 13 nm for mesopores and 2 μm for macropores). This is a reliable method for production of sorbents with reproducible retention factors of analytes in a wide temperature range at different compositions and flow rates of the mobile phase. Such sorbents are more efficient than the typical C₁₈ phase in the separation of various aromatic compounds and demonstrate no significant decrease in the degree of separation even at high flow rates (8.5 ml min^{−1}).

Preparative biochemical synthesis is an important application of CNT-based sorbents. Chromatography using CNTs as stationary phases seems to be promising for separation of biomolecules, *e.g.*, proteins. In particular, possible applications of sorbents modified with MWCNTs to improve the performance of an enzyme reactor were considered.²²⁴ A monolithic stationary phase containing CNTs was obtained by polymerization and then an enzyme, arginase, was covalently immobilized on it. A significant increase in the arginase activity due to the presence of CNTs

was confirmed by an increase in the yield of the major product, *m*-nitroaniline.

Columns packed with MWCNTs were used in the refinement of the mechanism of the interaction between MWCNTs and serum proteins.²²⁵ It was established that, unlike lysozyme, albumin is not adsorbed on CNTs; namely, in the basic phosphate buffer the acidic protein albumin exists in the ionic form, while the basic protein lysozyme exists in the molecular form and thus only the latter is adsorbed on conventional MWCNTs that are suitable for molecular adsorption only.

Among relatively new analytical applications of CNTs, there are CNT-based stationary phases for capillary electrochromatography (CEC).^{226–229} Recently, CNTs have been immobilized on the walls of quartz capillaries using mainly chemical bonding^{226–230} because it provides the best reproducibility of the adsorption properties for this type of stationary phases. Examples of application of the stationary phases prepared by covalent modification of a silica capillary column with oxidized MWCNTs are provided by the determination of melatonin in wine and plant extracts²³⁰ and illicit drugs in horse urine.²²⁶

IV. Graphene

IV.1. General. Main methods for production of graphene

Graphene (G) is a monatomic sheet of sp²-hybridized carbon atoms that form a hexagonal 2D crystal lattice through σ - and π -bonds. Pioneering studies on the properties of graphene were carried out by Geim and Novoselov²³¹ in 2004. Graphene belongs to the most intensively studied materials because of its unique electrical, electrochemical, optical, mechanical and sorption properties. It is used in electronics, catalysis, in production of sensors, capacitors and in biomedicine.^{232–236}

Increasing interest in graphene as sorbent is due to the following:

- graphene is characterized by high mechanical strength and has a readily accessible and very large specific surface area (theoretical value is 2630 m² g⁻¹, see Ref. 237) which is responsible for high adsorption capacity and rapid establishment of sorption equilibrium;

- a significant advantage of graphene over CNTs and fullerenes consists in simple synthesis from abundant and cheap raw material (graphite) which does not require complex equipment;²³⁸ graphene can be obtained with ease in most chemical laboratories; this favours wide use of the material and enables large-scale production at low cost;[‡]

- graphene can be synthesized from graphite using no metallic catalysts; this is an advantage over CNTs, which are synthesized in the presence of large amounts of catalyst impurities that can negatively influence the properties of CNTs;²⁴¹

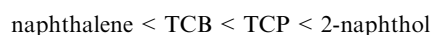
- it is the delocalized π -electron system of graphene that is responsible for high affinity of the material for aromatic compounds including the most hazardous environmental pollutants and many pharmaceuticals; to impart the sorption properties for other types of analytes, graphene can be functionalized or modified by, *e.g.*, transformation to graphene oxide (GO).²⁴²

[‡] Information on methods for production of graphene and its derivatives can be found in reviews.^{239, 240}

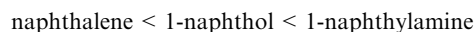
IV.2. The sorption properties of graphene and graphene derivatives

The unique properties of graphene (see above) predetermine the past, current and future interest of researchers in the synthesis of G-based sorbents. Organic molecules can be involved in noncovalent interactions with carbon nanoparticles.²⁴³ In the case of graphene, its very large delocalized π -electron system makes the major contribution to the formation of strong π - π -bonds with phenyl groups of organic compounds. The sorption properties can also be affected by the interaction between cations and the π -bond²⁴⁴ which occurs by the mechanism of cation-induced polarization and through electrostatic interaction between the cation and permanent quadrupole of the π -electron-rich aromatic structure.²⁴⁵

Graphene oxide bears numerous functional groups suitable for hydrogen bonding and(or) electrostatic interaction with polar organic molecules bearing oxygen- and nitrogen-containing functional groups. Pei and co-workers²⁴⁵ studied the adsorption of aromatic compounds of different structure [2,4,6-trichlorophenol (TCP), 2-naphthol, 1,2,4-trichlorobenzene (TCB), naphthalene] on graphene and graphene oxide. TCP and 2-naphthol are structurally similar to naphthalene and TCB, respectively, and differ from them only by a polar hydroxyl group. Although have different chemical properties, these compounds demonstrated similar adsorption capacities on graphene. This suggests a contribution from not only hydrophobic interaction, but also π - π -interaction to the adsorption on graphene. Compared to graphene, graphene oxide is characterized by lower π -electron density and a larger number of oxygen-containing functional groups. Adsorption of TCP and 2-naphthol on graphene oxide is stronger than on graphene, which can be due to the formation of hydrogen bonds between hydroxyl groups in analyte molecules and oxygen-containing functional groups in graphene oxide. The adsorption affinities of the aromatic compounds for graphene oxide increases as follows:



A study on the adsorption of 1-naphthylamine, 1-naphthol and naphthalene on a magnetic composite RGO/Fe₃O₄ (where RGO is functionalized graphene oxide) showed that the major contribution to the sorption properties comes from the donor-acceptor interaction. The adsorption capacity increases with the polarity of adsorbates in the following order:²⁴⁶



Information on the mechanism of adsorption of tetracycline antibiotics on graphene oxide can be found in the literature.²⁴³ In this case, high adsorption capacity of graphene oxide can be explained by the π - π -interaction and by the interaction between the cation and π -bonds that are formed between readily protonatable amino group in the tetracycline molecule and π -electrons in graphene. The tetracycline molecule comprises four aromatic rings, each ring bearing different functional groups (phenoxy, hydroxyl, oxo and amino groups); therefore, adsorption can also be favoured by electrostatic interactions and hydrogen bonds. Graphene oxide, functionalized graphene oxide and magnetic nanocomposites based on it are used as

adsorbents for removal of organic contaminants from aqueous solutions.^{243, 247–252}

A comparison of the sorption properties of graphene, SWCNTs and graphene oxide showed that GO exhibits the highest sorption capacity ($\sim 500 \text{ mg g}^{-1}$) for lysozyme.²⁵³ The mechanism of lysozyme adsorption on graphene oxide is mainly electrostatic and controlled by ionic interaction, while adsorption on graphene and SWCNTs is due to van der Waals forces. An important applied result obtained in that study consists in the proof that these nanomaterials are superior to the traditional sorbents based on activated charcoal in efficiency of wastewater purification from protein contaminants.

In connection with very high degree of delocalization of the π -electron system one can suggest that graphene is an ideal sorbent for organic compounds. However, hydrated metal ions or metal ions as constituents of complexes bonded to simple anions are not adsorbed on graphene. For adsorption of metal ions to occur, they should be preliminarily transformed to some hydrophobic form. Another situation is in the case of graphene oxide. Oxygen-containing functional groups have a lone electron pair and can act as nonpolar ligands in the metal complexes due to the ability to participate in donor–acceptor interaction. It was established that adsorption of Co^{2+} , Cd^{2+} , Cu^{2+} , Cr^{3+} , Zn^{2+} , Au^{3+} , Pd^{2+} , Pb^{2+} , U^{4+} and Eu^{3+} ions on graphene oxide can occur by the complexation sorption mechanism.^{254–267} Often, the adsorption capacity of graphene oxide is much higher than that of all known sorbents including nanomaterials, *e.g.*, modified CNTs.²⁶⁴ This can be explained by not only large specific surface area of graphene oxide, but first of all by high content of oxygen ($\sim 30 \text{ mass } \% \text{ vs. } < 5 \text{ mass } \% \text{ for oxidized CNTs}$).

To increase the adsorption capacity of graphene oxide for metal ions, Madarang *et al.*²⁶² linked chelate-forming groups to graphene oxide surfaces through silanization reaction between *N*-(trimethoxysilylpropyl)ethylenediamine tetraacetic acid (EDTA–silane) and hydroxyl groups on GO surface. Grafting of EDTA to the surface of graphene oxide significantly enhanced its adsorption capacity for, in particular, Pb^{2+} ions.

Graphene-based composites combine the properties of the modified and untreated graphene oxide with those of metal oxides or polymers. In particular, magnetic composites with metal oxides were reported.^{263–269} In these sorbents, graphene sheets can act not only as support for the growth of oxide nanoparticles, but also as spacer to inhibit the aggregation of nanoparticles.²⁶³ In addition, metal oxides can efficiently bind ions of other metal sorbates; therefore, graphene-based composites have higher adsorption capacity for these metal ions compared to the modified graphene oxide. Nevertheless, metal oxide/graphene oxide composites are characterized by lower adsorption capacities than graphene oxide because the metal oxide occupies some area on the surface of GO nanosheets, thus reducing the number of accessible adsorption sites. High-adsorption-capacity composites can be prepared by modification with organic molecules that contain atoms with lone electron pairs and readily form complexes with metals, *e.g.*, chitosan²⁶⁸ or β -cyclodextrin.²⁶⁴

The results presented above demonstrate high sorption activity of graphene and its derivatives (graphene oxide, modified graphene oxide) for a large group of organic and inorganic compounds. This allows sorbents based on these

carbon nanostructures to be used in sample preparation and solid-phase extraction.

IV.3. Applications of graphene in sample preparation

IV.3.a. Graphene and traditional solid-phase extraction

Researchers from P.R.China reported the first evaluation of graphene as an adsorbent for SPE in its traditional (cartridge) format²⁶⁵ and demonstrated the extraction of eight chlorophenols from environmental water samples. Quantitative extraction using graphene cartridges can be attained at relatively small mass of the adsorbent (20 mg) and minimum volume of organic solvent (0.3–0.5 ml). This favours miniaturization of sample preparation devices and realization of the ‘green chemistry’ concept. An important advantage of the graphene-based sorbents over the SPE sorbents consists in high affinity for various organic compounds. Nevertheless, mention was made of incomplete elution on the graphene-packed cartridge due to the formation of strong π – π -bonds with analyte molecules; in this connection, the choice of appropriate eluent may be difficult. Since graphene is almost insoluble in acetonitrile, tetrahydrofuran and solutions bases, these solvents can be used as eluents for desorption. The results obtained²⁶⁵ revealed that the adsorption properties of graphene are superior to those of octadecyl-modified silica gel, graphitized carbon black and CNTs.

Graphene cartridges were used for sorption preconcentration of analytes of different nature, *e.g.*, for solid-phase extraction of glutathione from human plasma samples and neuromediators (glycine, γ -aminobutyrate, taurine)²⁷⁰ from rat brain samples and chloramphenicol from aquatic products.²⁷¹ Tabani *et al.*²⁷² reported the use of graphene as adsorbent and material for electromembrane extraction in ultra-preconcentration of chlorophenoxy acid herbicides from environmental samples and subsequent determination of analytes by capillary electrophoresis. The results obtained by SPE of analytes from liquid media on graphene are collected in Table 4.

In the case of SPE on graphene-packed cartridges the enrichment factors of various analytes lie in the range from 10^2 to 10^4 . Like CNTs, graphene is often used in DSPE.^{276–278}

Although graphene as adsorbent offers undoubted advantages, its utilization may face some difficulties. First of all, passage of analyte solution through a graphene-packed cartridge may be accompanied by the formation of bonds between graphene sheets. Also, dust entrainment of highly dispersed graphene particles may occur. This can influence the extraction efficiency and the possibility of re-use of the cartridge.

To eliminate these drawbacks, novel GO–silica and G–silica adsorbents were developed.²⁷⁹ Carboxyl groups of graphene oxide are linked to amine groups of silica to form a GO–silica composite sorbent. To prepare a non-polar graphene–silica sorbent, silica-supported graphene oxide is reduced with hydrazine. Nonpolar (graphene–silica) and polar (GO–silica) sorbents can be used for reversed-phase and normal-phase SPE, respectively. This extends the field of application of graphene to organic media.

Another method for the preparation of graphene-modified silica is to immobilize graphene sheets on SiO_2 through electrostatic forces.²⁸⁰ The sorbent thus obtained was used for selective isolation of hemoglobin from human blood.²⁸¹

Table 4. Results obtained by SPE on graphene.

Analyte	Graphene type	Speciation method	Results		Ref.
			limit of detection	R (%)	
Pb ²⁺	Fe ₃ O ₄ –chitosan–GO	Flame AAS	–	90	268
	G	Flame AAS	610 ng litre ⁻¹	95–100	273
Chlorophenols	G	HPLC–UV	100–400 ng litre ⁻¹	77–116	269
Glutathione	G	AFS	0.01 nmol litre ⁻¹	98–108	270
Chloramphenicol	G	HPLC–MS	0.4 ng ml ⁻¹	92–103	271
Herbicides	G	CE	300–500 ng litre ⁻¹	98–103	272
Imines	G	HPLC–MS	< 1.5 µg kg ⁻¹	78–90	274
Malachite green and its metabolites	G	HPLC–MS	0.63 µg kg ⁻¹	82–103	275
PAHs	G–SO ₄	GC–MS	0.8–4 ng litre ⁻¹	82–114	276
Pesticides	G–NH ₂	LC–MS	0.1–8.3 µg kg ⁻¹	75–100	277
DNA	G	SALDI–MS ^a	100 fmol litre ⁻¹	–	278

^a Surface activated laser desorption/ionization mass spectrometry.

It was found that adsorption of proteins on graphene oxide enhanced at pH values close to corresponding pI values due to formation of additional hydrogen bonds. At pH 7, the efficiency of hemoglobin adsorption on the GO–SiO₂ composite was as high as 85%, adsorption of other proteins having little effect. The graphene–SiO₂ adsorbent is suitable for efficient isolation of high-molecular-mass lipophilic proteins and phosphorylated peptides and can therefore be used for the preparation of biological samples which is often coupled with surface-activated laser desorption/ionization (SALDI) or matrix-activated laser desorption/ionization (MALDI) mass spectrometry.

IV.3.b. Graphene in magnetic solid-phase extraction

Graphene is an ultralight material; therefore, it is difficult to isolate from suspension even by high-speed centrifugation. The problem is solved using magnetic solid-phase extraction.^{282–284} Fabrication of graphene-based composites with magnetic materials may significantly facilitate the separation and preconcentration steps. In MSPE, the magnetic sorbent is dispersed over the entire volume of the liquid sample rather than placed in column like in the traditional version of SPE; this allows one to exclude centrifugation or filtration.

Magnetic graphene composites can be recycled after washing.²⁸⁵ However, nanoparticles from the magnetic sorbents for MSPE are usually characterized by low magnetic susceptibility, which makes isolation of the particles from suspensions difficult. The problem can be solved by integrating nanoparticles and graphene into nanocomposites. Recently, the design of such systems has attracted the attention of many researchers.²⁸⁶ Luo *et al.*²⁸⁷ prepared magnetic adsorbents based on graphene, Fe₃O₄ and SiO₂ by physisorption and utilized them for extraction of six antibiotics from water samples. In the case of physisorption the initial graphene structure remains unchanged; however, it is believed that the graphene-based composite can be unstable when used repeatedly.

An adsorbent based on graphene and Fe₃O₄ was obtained²⁸⁸ by chemical co-deposition of Fe²⁺ and Fe³⁺ in an alkali solution in the presence of graphene. The MSPE enrichment factors of carbamate pesticides (500–900) were

higher than those obtained using dispersive liquid–liquid microextraction (DLLME) and ultrasound-assisted surfactant-enhanced emulsification microextraction. The same material was used for extraction of fungicides,^{289,290} insecticides,²⁹¹ triazine,²⁹² chloroacetanilide²⁹³ and polyaromatic esters²⁹⁴ from environmental water samples. Recently, researchers from the same group coupled MSPE and DLLME for extraction of five acetanilide herbicides from water and green tea samples and subsequent GC analysis of the extracts. The use of the G–Fe₃O₄ adsorbent led to higher enrichment factors.²⁹⁵ The new joint MSPE–DLLME preconcentration technique allows one not only to improve the extraction efficiency, but also to change the composition of the organic extractant during the DLLME step in such a manner that it is appropriate for GC analysis.

Karamani *et al.*²⁹⁶ synthesized a magnetic composite material comprising free iron, iron oxyhydroxide and graphene [G–Fe⁰–FeO(OH)] by reduction of trivalent iron with sodium borohydride in aqueous solution in the presence of graphene oxide. The material was used as sorbent for preconcentration of PAHs, PCBs and phthalate esters and demonstrated a higher target extraction efficiency compared to that of graphene.

Magnetic composites can also be prepared by hydrothermal synthesis. Namely, a magnetic graphene composite was obtained by one-pot synthesis from iron salts and graphene oxide placed in a Teflon-coated stainless steel autoclave by deposition of nanometre-thick Fe₃O₄ layer on reduced graphene oxide.²⁹⁴ The sorbent was used for adsorption isolation of phthalate esters from environmental water samples and beverages; the enrichment factors were of the order of 10³. Also, a magnetic graphene composite synthesized by the hydrothermal method was utilized for preconcentration of the active compounds from traditional Chinese medicine.²⁹⁷

Recently, a graphene-based magnetic hybrid material with high porosity and 3D structure was synthesized by the so-called one-step solvothermal method.²⁹⁸ The material has a large specific surface area (400–900 m² g⁻¹), high adsorption potential and high magnetization. Unlike chem-

ical deposition, the solvothermal method provides relatively uniform magnetic composite particles.

The simplest method for fabrication of magnetic composites based on graphene is to deposit magnetic nanoparticles onto graphene sheets. However, utilization of such composites as sorbents revealed the following disadvantages:^{299, 300}

- a proportion of adsorption sites on graphene sheets are occupied by magnetic particles and thus become inaccessible to the analyte molecules;

- the sorption and magnetic properties of magnetic particles are changed upon extraction and recycling;

- graphene sheets are prone to aggregation, which leads to partial loss of the sorption capacity of the adsorbent; and

- composites prepared by simple physisorption or electrostatic interaction are characterized by low reproducibility of their properties upon recycling.

To eliminate these drawbacks, magnetic microsphere-confined graphene with a core–shell structure ($\text{Fe}_3\text{O}_4\text{--SiO}_2\text{--G}$) was synthesized.³⁰¹ During the synthesis the nanomaterial based on ferrite-modified SiO_2 was functionalized with 3-aminopropyltriethoxysilane (APTES) and then graphene oxide was grafted to the surface of the amine-functionalized silica by condensation between amino group and the carboxyl group of graphene oxide. Eventually, $\text{Fe}_3\text{O}_4\text{--SiO}_2\text{--G}$ nanoparticles were synthesized by reduction of graphene oxide ($\text{Fe}_3\text{O}_4\text{--SiO}_2\text{--GO}$) with hydrazine hydrate. The $\text{Fe}_3\text{O}_4\text{--SiO}_2\text{--G}$ composite was used for preconcentration of some PAHs³⁰⁰ from environmental water and soybean milk samples. Since the SiO_2 layer provides a good protection for Fe_3O_4 particles, chemical bonds of graphene on the surface of magnetic microspheres ensure stability of the magnetic nanoparticles and improve the efficiency of extraction of PAHs. The material was also tested in the preconcentration of carbamate³⁰² and neonicotinoid insecticides³⁰³ from environmental samples.

A $\text{Fe}_3\text{O}_4/\text{GO}$ sorbent with the core–shell structure was synthesized through simple electrostatic interaction.³⁰⁴ It was characterized by high sorption capacity (181.8 mg g^{-1}) and good adsorption kinetics. The material was used as adsorbent for the preconcentration of bovine serum albumin and demonstrated the advantages of the GO shell over conventional shell materials such as polymers and SiO_2 . Core–shell $\text{Fe}_3\text{O}_4\text{--GO}$ composites seem to be promising

even for magnetic bioimaging.³⁰⁵ The results obtained by SPE of analytes from liquid media on graphene are collected in Table 5.

Methods for fabrication of magnetic composites based on graphene are relatively complicated and labour-consuming. Also, in some cases the selectivity of adsorption on these composites and the reproducibility of results are low. Therefore, the design of magnetic nanomaterials characterized by high physical and chemical stability, long operating life, high adsorption capacity and high efficiency of extraction remains topical.

IV.3.c. Graphene in solid-phase microextraction

Typically, the SPME method is used in the analysis of samples of complex composition, the key role being played by the chemical, thermal and mechanical stabilities of the SPME fibres.³⁰⁶ There is a limited choice of SPME fibres and the fibres are relatively expensive. Therefore, recently researchers have paid attention to fibres based on nanomaterials including CNTs, fullerenes and graphene.⁶

Graphene SPME fibres were for the first time prepared by Chen *et al.*³⁰⁷ A graphene coating was formed on a steel wire immersed into a graphene suspension. The fibre thus obtained was dried in air. The procedure was repeated until the desired thickness of the coating ($6\text{--}8 \mu\text{m}$) was attained. The fibres were used for SPE of pyrethroid pesticides from natural water samples. The extraction efficiency of the graphene-coated fibre was on the average 1.5 to 2 times higher than that of the fibres based on PDMS and divinylbenzene. High performance of the graphene fibre can be explained by its porous structure and rough surface. The benefits of the graphene fibres developed include low cost, reproducibility of the sorption properties, long operating life (> 250 sorption/desorption cycles), high thermal stability ($> 330 \text{ }^\circ\text{C}$), as well as the chemical and mechanical stability. In addition to the example mentioned above, the SPME fibre coated with graphene immobilized through physisorption was also used for the determination of carbamate pesticides³⁰⁸ and triazine herbicides.³⁰⁹ The efficiency of extraction with this fibre increased as the graphene coating thickened to a threshold value, namely, as the thickness of the coating exceeded a value of $100 \mu\text{m}$, the fibre became unstable and shed during the extraction process.³⁰⁸

Table 5. Results obtained by MSPE on graphene.

Analyte	Graphene type	Speciation method	Results		Ref.
			limit of detection	R (%)	
Sulfonamide antibiotics	$\text{Fe}_3\text{O}_4\text{--GO}$	HPLC–UV	$90\text{--}160 \text{ ng litre}^{-1}$	74–104	287
Carbamates, pesticides	$\text{Fe}_3\text{O}_4\text{--G}$	HPLC	$20\text{--}40 \text{ ng litre}^{-1}$	87–97	288
Imide fungicides	$\text{Fe}_3\text{O}_4\text{--G}$	GC–ECD	$1.0\text{--}7.0 \text{ ng litre}^{-1}$	79–102	289
Triazine herbicides	$\text{Fe}_3\text{O}_4\text{--G}$	HPLC	$25\text{--}40 \text{ ng litre}^{-1}$	89–96	292
Phthalate esters	$\text{Fe}_3\text{O}_4\text{--G}$	HPLC–UV	$10\text{--}40 \text{ ng litre}^{-1}$	80–106	294
	$\text{Fe}_3\text{O}_4\text{--SiO}_2\text{--G}$	HPLC–UV	$70\text{--}300 \text{ ng litre}^{-1}$	87–109	301
Polychlorinated biphenyls	$\text{Fe}^0\text{--G}$	GC–MS	$0.5\text{--}2 \text{ ng litre}^{-1}$	90–93	296
Pharmaceuticals, nicotine metabolites	$\text{Fe}_3\text{O}_4\text{--G}$	MALDI–MS	$1\text{--}10 \mu\text{g mlitre}^{-1}$	–	297
Proteins, peptides	$\text{Fe}_3\text{O}_4\text{--SiO}_2\text{--G}$	MALDI–MS	$3.8\text{--}68 \text{ fmol litre}^{-1}$	58–101	299

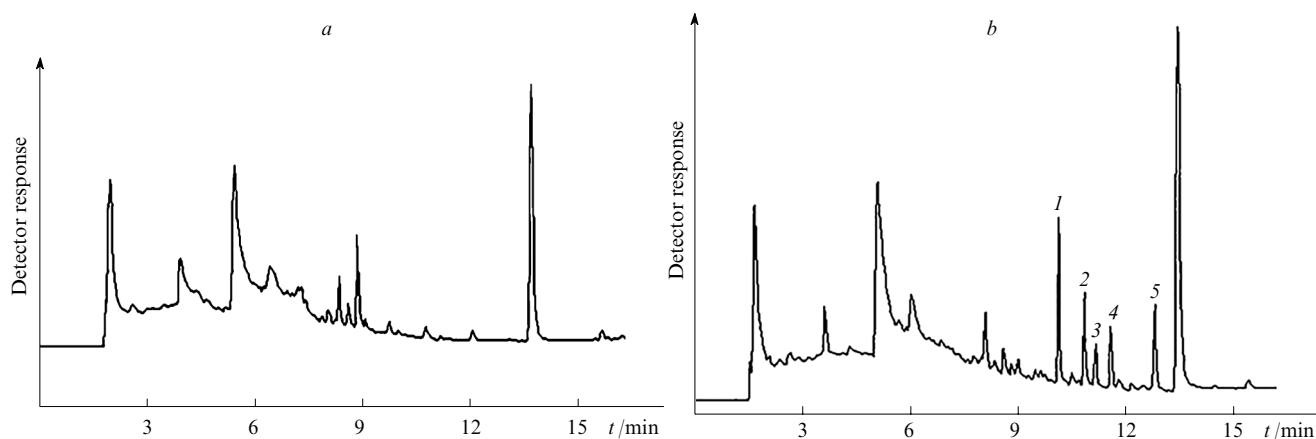


Figure 4. Chromatograms of river water obtained by GC analysis using SPME on polypyrrole–graphene composite.³¹⁴ Blank sample (a); wastewater containing organochlorine pesticides (b); 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene (10 ng litre⁻¹) (1); dieldrin (30 ng litre⁻¹) (2); endrin (20 ng litre⁻¹) (3); 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane (20 ng litre⁻¹) (4); and 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (30 ng litre⁻¹) (5).

To improve the stability of graphene coatings, a sol–gel technology was developed for coating a stainless steel plunger wire located within the microsyringe tip with graphene.³¹⁰ The plunger was etched with HF to create a rough and porous surface and then immersed into graphene oxide hydrogel. The thickness of the coating was controlled by varying the duration of the etching. Then, graphene oxide was reduced to graphene. This coating technology produces a porous 3D structure with a large specific surface area. Fibres thus prepared were used for the determination of trace amounts of various organics.^{310–312}

A polypyrrole–graphene composite supported on a stainless steel wire was prepared by electrochemical polymerization and used for the determination of phenols in water samples.³¹³ A graphene-coated stainless steel SPME fibre for one-step microwave-assisted headspace SPME of organochlorine pesticides from water samples was developed.³¹⁴ Graphene powder was immobilized using a solution of silicone glue; the average thickness of the coating was 50 µm. Figure 4 presents the chromatograms obtained by GC of river water samples contaminated with pesticides. The extraction efficiency was higher than in that achieved with traditional SPME fibres.

Yet another graphene fibre was prepared by the hydrothermal method and used as sorbent in the determination of organochlorine pesticides in environmental water samples by headspace SPME with subsequent GC analysis.³¹⁵ The fibre has a uniform porous structure and rough surface. Compared to commercially available PDMS fibres, the novel fibre is characterized by higher thermal stability and sorption efficiency and by longer operating life.

The studies devoted to the development of novel methods for noncovalent immobilization of graphene coatings on fibres were carried out within a two-year period (see above). They do not include the results of comparative tests of these coatings. At best, they provide information on the advantages of the new sorbents for SPME over the commercially available systems. Nevertheless, a recent trend towards chemical grafting of graphene coatings to fibres suggests that physical methods of coating are not always appropriate.

Covalent bonding significantly improves the reproducibility of the sorption properties of fibres. Graphene oxide was chemically grafted to the surface of a fused silica fibre.³¹⁶ A novel SPME fibre C₁₈/GO/Si/stainless steel wire was reported.³¹⁷ Initially, a stainless steel wire was coated with an intermediate Si layer using magnetron sputtering. Next, graphene oxide was grafted to the Si layer following a known procedure.³¹⁷ Finally, octadecyltrichlorosilane molecules were grafted to graphene oxide through the formation of the C–O–Si bonds. Then, a comparative test of the novel composite (fibre I) and the GO/Si/stainless steel composite (fibre II) was carried out. The test involved the extraction of three classes of compounds, *viz.*, n-alkanes, phenols and PAHs from water samples. Fibre I was more efficient than fibre II in the extraction of n-alkanes and PAHs. This can be explained by the influence of hydrophobic interactions that govern the adsorption of n-alkanes and PAHs on C₁₈. The trend was violated in the case of phenols because their molecules contain hydrophilic groups. However, we believe that the method of grafting C₁₈ to graphene oxide through the C–O–Si bond is unsuitable owing to instability of the bond to hydrolysis.³¹⁸ The ability of graphene oxide to form covalent bonds and its stable structure underlie many benefits of GO-based sorbents including high rigidity, the possibility of repeated use and stability in organic solvents, acid and alkali solutions, as well as thermal stability.^{319, 320} The results obtained by SPME on graphene are listed in Table 6.

IV.3.d. Graphene in sample preparation for MALDI–MS studies

In the sample preparation for MALDI–MS analysis graphene can not only act as adsorbent, but also serve as matrix for ionization of analytes. The MALDI–MS analysis using graphene does not require the elution step. Analytes adsorbed on graphene sheets are immediately exposed to MALDI ionization. Dong *et al.*³²¹ reported a MALDI–MS analysis of low-molecular-mass compounds with a graphene matrix. In this case, a suspension of graphene was added to the analyte solution for DSPE and then graphene was isolated by centrifugation and intro-

Table 6. Results obtained by SPME on graphene.

Analyte	Graphene type	Speciation method	Results		Ref.
			limit of detection	<i>R</i> (%)	
Pyrethroid pesticides	G	GC–ECD	3.7–70 ng litre ⁻¹	83–110	297
Carbamate pesticides	G	HPLC	0.1–0.8 ng mlitre ⁻¹	83–95	298
Organochlorine pesticides	Polypyrrole–G	GC–FID	340–3400 ng litre ⁻¹	80–101	304
	G	GC–ECD	0.83–11.5 ng litre ⁻¹	81–121	310
Polybrominated biphenyl ethers	G	GC–ECD	0.2–5.3 ng litre ⁻¹	74–81	300
UV filters	G	GC–MS	0.5–6.8 ng litre ⁻¹	99–114	301
Sulfur-containing organic compounds	ZnO/G	GC–MS	100–700 ng litre ⁻¹	80–91	302
Phenols	G	GC–ECD	0.16–0.93 ng litre ⁻¹	74–103	303
PAHs	Poly(ethylene glycol)–methacrylate–G	GC–MS	0.5–5 ng litre ⁻¹	55–141	305
	GO	GC–FID	< 80 ng litre ⁻¹	84–118	306
	C ₁₈ –GO	GC–FID	5–5 ng litre ⁻¹	85–116	307

duced into the MALDI interface for MS analysis using a pipette. Dong and co-workers³²² also used this method for the determination of nonpolar PAHs in environmental samples.

The advantages of graphene over conventional matrices are as follows:

- improved efficiency of the desorption/ionization of analytes owing to simple, monatomic structure and unique electronic properties of graphene;

- minimum matrix noise;

- good reproducibility of results due to uniform distribution of analyte molecules over the surface of graphene; this eliminated ‘hot spots’ produced during co-crystallization with conventional matrices; and

- little effect of salt content on the results of analysis.

Zhang and co-workers³²³ reported the advantages of graphene oxide over graphene used for preconcentration and ionization of long-chain fatty acids for MALDI–MS analysis. The choice of graphene or graphene oxide for the MALDI–MS determination depends on the nature of analytes. The morphology of graphene significantly influences the MS signals. A study of the MALDI–MS determination of dioxin using graphene films and graphene powder as matrix showed that the former provide better reproducibility of the results of analysis than the latter.³²⁴

An original method for improvement of extraction selectivity in biochemical analysis was proposed by Gulbakan *et al.*,³²⁵ who prepared aptamer-conjugated graphene[§] oxide for selective preconcentration and detection of cocaine and adenosine in human blood serum. Thiol-modified cocaine and adenosine aptamers were conjugated with graphene oxide by activating carboxyl groups and by introducing bifunctional poly(ethylene glycol) molecules as spacer units. The adsorbent thus obtained was highly specific for cocaine and adenosine. In addition, graphene oxide served as low-noise matrix for the MALDI–MS studies, while the aptamer conjugated to graphene oxide

was an efficient functional group for selective preconcentration of analytes for subsequent MS analysis.

Summing up, it should be noted that, unlike other carbon nanostructures, graphene is still rarely used as chromatographic stationary phase.^{5,319} However, our analysis of the sorption properties of graphene suggests that surface-modified sorbents based on graphene are promising for chromatographic applications. Probably, research activity in this field faces difficulties related to complexity of procedures for deposition of graphenes on the surface of inert porous supports.³¹⁹

V. Nanodiamond

V.1. General and methods of synthesis

Detonation nanodiamond, or, more often, ultradispersed diamond (UDD), is a carbon nanostructure 1–10 nm in size with the diamond crystal lattice. It is synthesized by explosive decomposition of high-explosive mixtures in blast chambers. Surface-modified UDD nanoparticles bearing various functional groups form aggregates, *i.e.*, microdispersed sintered detonation nanodiamonds (MSDN) 50–100 nm in size with a specific surface area from 250 to 350 m² g⁻¹ and a pore volume from 0.3 to 1 cm³ g⁻¹.³²⁶ According to IR spectroscopy data, carbonyl, hydroxyl, methyl, carboxyl, nitrile and some other functional groups can be attached to the surface of UDD. The synthesis, purification and treatment conditions influence the composition of functional groups on the surface of UDD. Treatment of UDD with oxidizing agents (a mixture of sulfuric and nitric acids, ozone, oxygen) on heating causes oxidation of the surface while treatment with nitrogen or hydrogen leads to decomposition of oxygen-containing groups.^{327,328} Certain functional groups, *e.g.*, fluorine and chlorine atoms and amino groups, can be immobilized by chemical modification of the surface of UDD.^{329,330} The composition of the surface functional groups may have a crucial impact on the sorption and chromatographic properties of the material.

V.2. The sorption properties of nanodiamond

A GC study on the sorption properties of two UDD samples treated with boiling potassium dichromate–sulfu-

[§] Aptamers are small nucleic acid molecules that can act as highly specific receptors of low-molecular-mass organic compounds. Aptamers are single-stranded oligonucleotides that bind to target molecules with very high affinity and specificity.

ric acid mixture and with gaseous ozone showed that the heats of adsorption of n-hydrocarbons on both samples are close to that of graphitized carbon black.³³¹ Evaluation of the contributions of specific interactions to the total energy of adsorption of benzene and polar compounds showed that these contributions are larger for the samples treated with ozone because of higher surface concentration of active acid groups. Chlorination and amination of the UDD surface leads to reduction of the specific retention volumes and retention times of hydrocarbon molecules under GC conditions (except polar molecules that can be involved in specific interaction).³³⁰

Adsorption of organic compounds of different structure on the UDD surface was studied by the dynamic sorption method under GC conditions.³³² In this case, adsorption proceeds by the physisorption mechanism. Studies on adsorption of hydrophobic organic compounds (dyes, indicators and some pharmaceuticals) on the UDD surface revealed higher sorption capacity and improved sorption properties for the samples treated in argon or hydrogen stream. The best results were obtained for the samples treated in hydrogen stream at 800 °C.³³³ An important role of electrostatic interactions was demonstrated taking adsorption of fluorescent dyes and pharmaceuticals on the UDD surface as an example.^{334,335} For instance, the nanodiamond surface covered with positively charged acid groups is a good sorbent of anionic forms of these analytes.

The potential of UDD as sorbents for chromatographic separation of organic compounds is due to their properties, e.g., the mechanical strength, rigidity, resistance to swelling in organic solvents, highly developed surface and mesoporous structure.^{328,336,337} A study³³⁸ on the regularities of chromatographic retention of phenols on MSDN from aqueous-organic solvents showed that at high content of organic solvent the process occurs by the mechanism of normal-phase LC, while the retention parameters of phenols are inversely proportional to the acidity of phenyl groups and MSDN can thus be used as sorbent for selective separation of substituted phenols including structural isomers (Fig. 5). This result is due to the presence of polar functional groups on the nanodiamond surface. It was confirmed experimentally.³³⁹ The concentration of carboxyl groups on the oxidized UDD surface can be as high as 9.6 $\mu\text{mol m}^{-2}$, which is higher than the concentration of silanol groups on a fully hydroxylated silica surface (8 $\mu\text{mol m}^{-2}$).

A comparison of the sorption properties of MSDN and some other sorbents (silica gel, alumina, porous graphitized carbon) showed better sorption properties of nanodiamond for aromatic hydrocarbons and higher selectivity in the separation of structural isomers (an efficiency of >45 000 theoretical plates per metre was attained).³³⁹ This confirmed the promise of MSDN as stationary phase for HPLC and gave an impetus to research into UDD-based sorbents for reversed-phase HPLC.^{340,341} The method proposed is based on chlorination or fluorination of the surface followed by treatment with octadecyllithium. The sorbents thus prepared are stable in alkaline media, thus being superior to the sorbents based on silica.

Mention should be made of some difficulties related to application of UDD as sorbents for HPLC. Problems associated with high flow resistance appear during both filling and operation of chromatographic columns. To overcome this resistance, one should significantly increase the

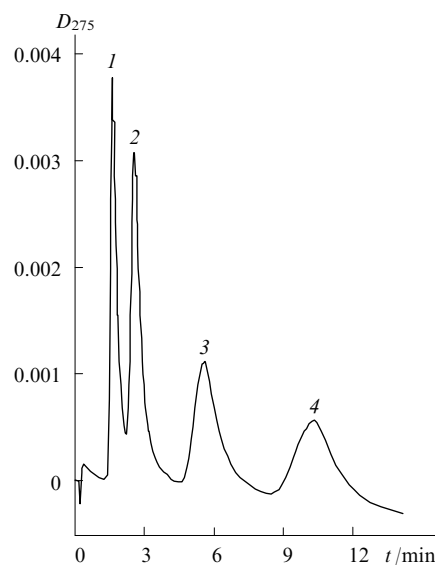


Figure 5. Chromatogram of the separation of phenol derivatives on a 100×4.6 mm column with MSDN.³³⁸ The mobile phase was acetonitrile:water (90:10), flow rate was 0.5 ml min^{-1} , UV detector (275 nm), column temperature was 60 °C, the sample volume was 3 μl . Sorbates: 2-*tert*-butyl-4-methylphenol (1), 4-methylphenol (2), 2,5-dichlorophenol (3) and 2,6-dichlorophenol (4). D_{275} is the optical density at 275 nm.

pressure in the system. However, loose and soft nanodiamond aggregates (Fig. 6) break down at elevated pressure. In this connection, composite sorbents based on UDD are of considerable interest. For instance, a composite material based on carbonized polymer microspheres coated layer-by-layer with poly(allylamine) and UDD layers is available. The sorbent exhibits good mechanical properties, is stable at pH 11.3 and a temperature of 120 °C and is characterized by an efficiency of 112 000 theoretical plates per metre. The sorbent was used for the separation of four essential oils by gradient elution.³⁴²

Chemical inertness, biocompatibility and the lack of cytotoxicity make materials based on UDD promising for isolation and purification of biologically active substances.

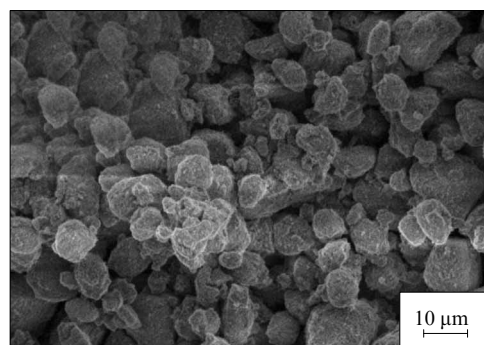


Figure 6. Electron photograph of micro-dispersed sintered detonation nanodiamonds.³³⁷

A sorbent based on Sepharose 2B coated with nanodiamonds was prepared and used for highly selective isolation of luciferase enzyme by low-pressure liquid chromatography.³⁴³ Adsorption of bovine serum albumin on UDD by hydrophobic interaction with the formation of a complex between UDD and albumin was studied.³⁴⁴ It was found that key structural features of the protein are preserved, whereas MSDN partially breaks up. These results are of interest for UDD-based biosensor applications.

VI. Nanodispersed active carbon

Nanodispersed active carbon (NAC) is a novel carbon material. Methods of synthesis and the properties of NAC have been documented.^{345–353} The chloromethane method for the synthesis of NAC (combustion of methane in chlorine) was developed by researchers from the Russian Federation.^{345, 346} The synthesis was conducted in a flame localized within a tailor-made reactor. An original design of the reactor enables efficient manipulation of the flame shape and thus influence the properties of NAC.

The synthesis of NAC can be treated as a kind of controlled flame synthesis. The raw product resulting from incomplete combustion of methane in chlorine contains not only carbon, but also large amounts of hexachlorobenzene and other chlorine-containing impurities, which play the role of templates promoting the formation of a porous structure.^{347, 348} They are removed by treatment of the raw product with nitrogen, argon and hydrogen at 1000 °C. An ESCA and Auger spectroscopy study of refined NAC showed that it contains almost 100% of carbon and that the specific surface area determined by the Brunauer–Emmett–Teller method from the low-temperature adsorption of nitrogen is larger than 1000 m² g⁻¹.³⁴⁹ As can be seen in the electron photomicrograph (see Fig. 7), refined NAC is a material comprised of globular nanoparticles with a narrow size distribution.

The sorption properties of NAC in the form of surface-layer sorbent (SLS) were studied in comparison with those of birch activated charcoal (BAC) as the sorption-active

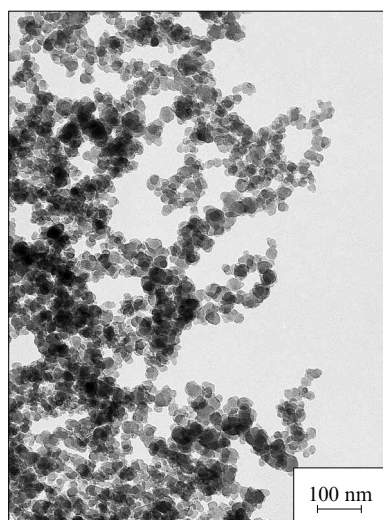


Figure 7. Electron photomicrograph of nanodispersed active carbon.³⁵²

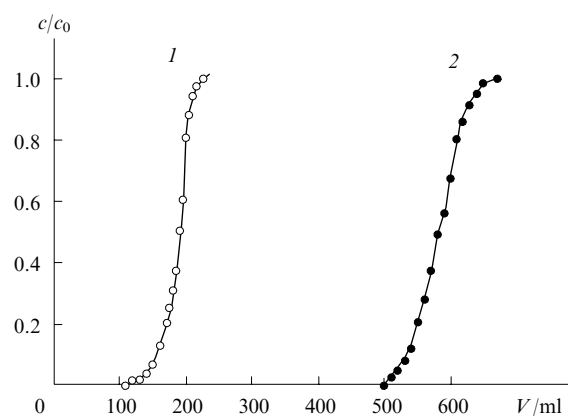


Figure 8. Retention curves of chloroform from aqueous solution.³⁵⁰

For 1, 2, see text. $c_0 = 10 \text{ mg litre}^{-1}$ is the concentration of chloroform in the solution, c is the concentration at the column outlet; a $7.5 \times 0.6 \text{ cm}$ column, solution flow rate was 5 ml min^{-1} , V is the volume of the solution passed.

material (SAM) using porous polytetrafluoroethylene (PTFE) as support.³⁵¹ The sorbents were prepared by shaking PTFE with SAM which penetrates into the support pores and is held there by adhesive forces. The sorbents were tested using the sorption of chloroform and butyl acetate from dilute aqueous solutions as examples. Figure 8 presents the output retention curves of chloroform from aqueous solution. The results obtained for the two SLS demonstrate that NAC (curve 2) is five times more efficient than BAC (curve 1).

The direct use of NAC and other nanocarbon materials as adsorbents is difficult due to their aggregation which leads to abrupt increase in the hydraulic resistance of the packed columns and cartridges. Typically, the problem is solved by depositing the sorption-active nanomaterials on the surface of relatively coarse-grained supports, *i.e.*, by fabrication of SLS. This method is treated as a compulsory measure which is uncondusive to improvement of the efficiency of sorption preconcentration.

However, in the mid-20th century these sorbents were proposed to improve the efficiency of chromatographic separation³⁵⁴ and found application in rapid preconcentration of analytes by passing a water sample being analyzed through a column packed with sorbent at high velocity that is abnormal to bulk-porous sorbents (BPS).³⁵⁵ In the case of SLS, the processes responsible for efficient mass exchange proceed within a thin surface layer rather than the bulk of the grain. Therefore, all other things being equal, SLS provide a much higher efficiency of mass exchange than traditional BPS. The sorption layer in SLS can be deposited on either the surface of a nonporous support or on the inner walls of a capillary and in pores of a porous support.

Surface-layer sorbents on nonporous supports are known in analytical practice as surface porous sorbents.³⁵⁶ They are used in both GC and LC, whereas SLS on porous supports are used in GC only.^{356–358} It is accepted that a stationary state, in the support pores, of the liquid phase where the diffusion coefficient is a few orders of magnitude smaller than in the gas phase should lead to slow mass

transfer. However, this choice of support is due to incorrect idea of the mechanism of retention of analytes on the reversed-phase sorbents. From this point of view, retention occurs through adsorption of analytes at the liquid/solid interface while the absence of convective mixing of liquid in the support pores makes SLS on nonporous supports more preferable in LC.³⁵⁹ In addition, this clarifies a negative effect of nonwettability of hydrophobic sorbents in the sorption preconcentration from aqueous solutions.^{360,361}

However, it was reported^{362,363} that retention of volatile organic compounds (VOC) from aqueous solutions on hydrophobic sorbents occurs from the stationary gas phase rather than mobile liquid phase. The stationary gas phase is unavoidably present in micro- and mesopores of the materials owing to negative capillary pressure produced because the sorbent is unwetted with water and aqueous solutions. In this mechanism of mass exchange, VOC initially go from the aqueous phase to the gas phase and are then adsorbed at the gas/solid interface. Since the diffusion coefficients of substances in the gas phase are 10^4 – 10^5 times higher than in the liquid phase, the efficiency of mass exchange in the retention of VOC from aqueous solutions on nonwetted sorbents appears to be higher than on the wetted ones. This effect is also observed on SLS where the sorption-active material (activated carbon, NAC) is in pores of the water-unwettable PTFE. It should be noted that the advantages of SLS in the rate of mass exchange manifest themselves in preconcentration of VOC from not only the liquid phase, but also the gas phase.³⁶⁴

The design of carbon nanomaterials gives a new impetus to wide use of SLS in analytical practice, first, for rapid preconcentration of organic analytes and, second, in order to implement theoretically substantiated attempts to conduct HPLC on SLS at high pressures and, consequently, high elution rates.

The potential of carbon nanomaterials in sorption technologies and analytical chemistry depends strongly on the specific surface area. In this respect, graphene, CNTs and NAC are much superior to nanodiamonds and fullerenes (see Table 7).

Table 7. Specific surface area (*s*) values of carbon nanomaterials.

Carbon nanomaterials	<i>s</i> /m ² g ⁻¹	Ref.
Nanodiamond	250–350	326
CNTs	150–1627	75, 77
Graphene	433–2630	27, 237
Fullerene	5–424	82
Nanodispersed active carbon	650–2800	346

It should also be noted that graphene, CNTs and NAC can be readily immobilized on the PTFE surface through hydrophobic interaction and can be used to prepare SLS.

VII. Conclusion

An analysis of general trends in the application of carbon nanomaterials as sorbents suggests that in large-scale sorption technologies, such as purification of water and air from organic pollutants, replacement of traditionally used carbon

sorbents by more efficient nanocarbon materials is still an open issue due to higher cost of the latter. Carbon nanostructures undoubtedly have a great potential as sorbents for preconcentration and chromatographic separation in analytical chemistry and even on the preparative scale. Prospects for practical applications of these systems seem to be clear. This particularly concerns CNTs and graphene. Indeed, their functionalization significantly extends the field of application and in some cases allows one to improve the efficiency of isolation and separation of organic and inorganic compounds from liquid media compared to traditional sorbents.

Compared to CNTs and graphene, the future of fullerenes as sorbents looks much more modest, although progress in methods of synthesis of fullerenes and their derivatives may dramatically change the situation. Considering the potential of nanodiamonds from the standpoint of chromatographic separation taking into account their mechanical and thermal stability, stability towards hydrolysis in a wide range of pH values and the possibility of being used immediately in HPLC columns, one can assume that they will find a niche where they will compete with the best stationary phases.

As to the recently synthesized nanodispersed active carbon, one can only say that, like most other carbon nanomaterials, it seems to be a promising sorption-active material for the design of SLS for high-performance transport of analytes to sorption sites and for rapid sorption preconcentration.

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