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*Dedicated to Academician Yu.A. Zolotov in the year of his 90th birthday*

# Coordination Compounds (Chelates) in Analytical Chemistry: Solutions, Sorbents, and Nanoplatforms

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**Abstract**—Brief characterization is given for periods of the hundred-year history of application of coordination compounds (chelates) based on chromophoric organic reagents (ORs) for the spectrophotometric and luminescent determination of metal ions. Four periods can be distinguished: detection of the efficacy, synthesis of the first ORs for metal determination, and development of the theoretical fundamentals for their action; period of targeted synthesis of ORs, systematic research of the coordination of metal compounds to ORs, and extensive use in chemical analysis; period of modification of the ORs in solution and on the sorbent surface; and period of application of liquid and solid nanoplatforms and supramolecular processes for enhancing the properties of coordination compounds of metals with organic analytical reagents. The achievements and application areas for each period are given.

**Key words:** metal chelates, history, applications, analytic chemistry

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## INTRODUCTION

Coordination compounds, in particular metal chelates, are widely used in industry, household activities, and agriculture [1], for water treatment [2], land reclamation [1, 3, 4], in medicine [5–7], biochemistry [8], pharmacy [9], as food supplements [10–12], as parts of new materials, in microelectronics [13], and in many other fields of science and technology. Chelates play an important role for living organisms and plants: hemoglobin, chlorophyll, and vitamin B12 are chelates. For more than 100 years, chelates have been widely used in analytical chemistry for titrimetric, photometric, luminescent, atomic absorption, and electrochemical analysis [14–17], chemical test methods [18], and for masking, separation, and preconcentration techniques such as extraction [19], gas liquid and high performance liquid chromatography (HPLC) [20–22], and sorption preconcentration [23–25]. It is noteworthy that in molecular spectrometry methods (spectrophotometry and luminescence), metal chelates formed by chromophore ligands are used most often, whereas in other determination methods and for separation and preconcentration this is not required.

This communication proposes periodization of research in the synthesis, study of properties, and application of coordination compounds of metals in spectrophotometry and extraction and photometric and luminescence analysis and shows the advantages of transition from homogeneous solutions to nanoheterogeneous organized solutions (nanoreactors) and from solutions to immobilization on a solid surface, including nanoparticles.

## METAL CHELATES IN ANALYSIS: INITIATION OF THE RESEARCH AREA

Historical analysis of the research into coordination compounds and their application in analytical chemistry shows the existence of several periods without strict time boundaries between them; the classification is based on the following characteristics:

— detection of the efficacy, study and application of coordination compounds (chelates) with single organic reagents (ORs) in aqueous solutions, development of the main statements of the theory of action of ORs;

— modification of OR properties by using organic solvents;

— modification of ORs via the formation of ion associates of ORs and chelates with hydrophobic counterions in analytically active groups or via outersphere association, including surfactant counterions;

— modification via the formation of mixed-ligand complex compounds, often involving ligand–ligand interactions;

— modification via immobilization on the sorbent surface;

— modification via solubilization in micellar nanosystems (supramolecular effect and local change in the microenvironment polarity);

— modification on the surface of solid nanoparticles and combination with quantum size effects.

**The first period** included understanding of the considerable advantages of organic ligands for metal ion determination over inorganic ligands such as bright colors, high molar absorption coefficients, and high sensitivity and selectivity of complex formation. This period is characterized by the synthesis of simple ORs of various classes, studying their reactions with metal ions in aqueous solutions, development of the theory of action of ORs, and initiation of a new line of research: application of ORs for determination of metal ions (from the beginning up to the 1950s) [16, 26]. This line of research has actually formed at the boundary between organic, inorganic, coordination, and analytical chemistry. Well-known reagents were introduced into chemical analysis, such as dimethylglyoxime, diphenylcarbazide, cupferron, dithizone, 8-hydroxyquinoline, *o*-phenanthroline, $\alpha,\alpha'$-bipyridine, simple azo compounds (eriochrome black T, arsenazo I, thoron, beryllon II), thiourea and alizarin derivatives, $\beta$-diketones, and, at the end of the period, also aminopolycarboxylic acids (complexons). Organic reagents have been used in complex formation and precipitation reactions in solutions and in drop reactions on paper [26–31].

During this period, basic concepts appeared, e.g., the concepts of functional analytical group (FAG), i.e., the group that participates in complex formation, and active analytical group (AAG), which changes the solubility and color of the OR and chelate; the key factors influencing the selectivity and sensitivity of metal determination were analyzed; and the first monographs devoted to the theory, properties, and applications of ORs (including their particular representatives) were published [27–31]. Considerable contributions during this period were made by F. Feigl, R. Belcher, L.M. Kul'berg, V.I. Kuznetsov, I.M. Korenman, N.A. Tananaev, I.P. Alimarin, A.K. Babko, and A.T. Pilipenko. L.M. Kul'berg described and classified the main FAGs and AAGs [27]. V.I. Kuznetsov proposed the idea of the chromophore action of elements and the intramolecular ionic state of metal complexes with ORs; he also put forwards the "hypothesis of analogies," which qualitatively correlated the hydrolysis, formation of sulfides and ammoniates, and the formation of coordination compounds with FAGs containing oxygen, sulfur, or nitrogen [32].

**The second period** (1960s to the mid-1980s) had several characteristic features related to the goal of improving the analytical properties of ORs, most often, by synthesizing new reagents or modification of the properties of known reagents upon transition from aqueous solutions to aqueous organic or purely organic solutions. A large group of highly efficient bis-azo compounds (arsenazo III, chlorophosphonazo III, carboxyarsenazo, sulfochlorophenol S, nitchromazo, and other (a total of approximately 100 compounds of this series)), implementing the principle of doubling of the chromophore site, were synthesized during this period and started to be actively used [33]. There appeared new efficient monoazo compounds such as lumogallion, picramine epsilon, picramine R, and several dozen other, as well as a large group of heterocyclic monoazo compounds [34]. New reagents were implemented into practical photometric analysis: triphenylmethane derivatives (pyrocatechol violet, xylenol orange, phthalexones, phenolcarboxylic acids) [15, 35, 36], trihydroxyfluorones (disulfophenylfluorone, salicylfluorone), and xanthene derivatives (pyrogallol and bromopyrogallol red) [37]. The main advantages of trihydroxyfluorones and halogenated heterocyclic monoazo compounds with a diethylamino group are very high molar absorption coefficients, which often reach $(1–4) \times 10^5$, high contrast, and better selectivity compared to classical reagents of this type [34, 37]. This was a period of extensive investigation of ORs throughout the world, practical implementation of ORs in analytical laboratories, and solution of relevant practical tasks of national economy and defense, in particular, development of methods for determination of uranium, thorium, transplutonium elements, and refractory metals [14, 15, 35–43].

The use of NMR made it possible to correct the formulas and structures of organic reagents and coordination compounds they form with metal ions [44–46]. Quantum chemical methods started to be widely used to calculate characteristics of ORs and chelates; the idea of quantum chemical design of photometric reagents with maximum possible photometric characteristics was put forward [47].

The enhanced attention to organic reagents all over the world during this period is indicated by the fact that OR nomenclature, classification, and application issues were considered by a special IUPAC commission [48, 49]; a laboratory of organic reagents was founded at the Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences; these reagents were synthesized at the Research Institute of Organic Intermediates and Dyes (NIOPIK) and at the Research Institute of Chemical Reagents and High-Purity Chemicals (IREA); there appeared reference books containing data on hundreds of organic reagents for metal ions [50, 51] and numerous monographs [14, 19, 20, 33–42, 44–47, 52–56]. During this period, great contributions to the synthesis and study of new reagents and their complexing properties were made by S.B. Savvin, V.I. Kuznetsov, Yu.M. Dedkov, A.M. Lukin, and N.N. Basargin. Apart from color reactions, organic reagents and their coordination compounds also became an inherent part of luminescence analysis [57–59]. The reagents that were extensively used for luminescence analysis include hydroxyflavones, Schiff bases, hydrazones, monoazo compounds, and derivatives of 8-hydroxyquinoline, phenylfluorone, anthraquinone, and (when extraction is used) rhodamines.

The replacement of aqueous media by aqueous organic and purely organic solvents during this period was mainly driven by the goal of eliminating the competing coordination of water molecules by the metal ion. It was found that this is accompanied by a number of other benefits: improved solubility of reagents (especially hydrophobic ones) and changes in the protolytic and tautomeric equilibria and conditions of hydrolysis, solvation of metal ions, and kinetics and thermodynamics of complex formation [33, 60, 61]. In some cases, the use of organic solvents gave rise to many interesting analytical reactions accompanied by vivid changes in the absorption spectra of metal chelates formed by azo compounds [33, 34, 62]. Three types of color reactions of metals with bis-azo compounds were described, which made it possible to improve both the sensitivity and selectivity of determination of a number of metal ions [63]. New opportunities regarding the selectivity and contrast of reactions between metal ions and ORs were provided by the technique involving the use of highly acidic solutions [64].

Systematic research demonstrated that in different solvents, the same ORs can crucially change their properties (protolytic, tautomeric, redox, donor-acceptor, complexing, solubility, etc.), and, consequently, the sensitivity, selectivity, contrast, and the rate of analytical reactions, which may give entirely different complexation products [16]. It was found out that a modifying solvent is not only the medium in which the reactions take place, but is also an active participant of the reactions. The solvent effect on a chemical reaction is mainly dictated by two important characteristics: donor-acceptor properties and dielectric constant of the medium. According to [65], these factors enable the control over the chemical process, first of all, by changing the type of solvation of both OR and the metal ion.

One more trend in changing the properties of ORs and complexes they form that appeared during this period was related to the use of coordination compounds with different metals and different ligands in analysis [66, 67]. A goal of the use of different-ligand complexes was also to displace water molecules from the metal coordination sphere. In [66], outer-sphere complexes were also assigned to different (mixed)-ligand complexes [68]. The complexation in such systems was accompanied by batho- and hyperchromic effects and led to better extractability of the metal chelates. During this period, the OR properties were also modified by the formation of hydrophobic ion associates with large organic counterions, e.g., tetrabutylammonium, trioctylammonium, diphenyl- or triphenylguanidinium, and tetraphenylphosphonium cations and tetraphenylborate and naphthalenesulfonate anions or the anions of acidic dyes such as bromophenol blue [16, 19, 56]. The most numerous examples of using ion associates in the 1960s–1980s were concerned with extraction systems, the theory and application of which was greatly boosted by Yu.A. Zolotov [19, 56].

## MODIFICATION OF ORGANIC REAGENTS: NEW OPPORTUNITIES

**The third period of research** (mid-1980s–1990s) focused on modification of the properties of ORs and coordination compounds they form. This was due to a weighty reason. A comparison of the results of extensive studies of organic reagents and conditions of complex formation with metal ions showed that, despite the theoretically infinite options for the design of new organic molecules that can, in principle, be used as ORs, there are only several dozens of classes of compounds representatives of which have been generally recognized to be effective as ORs [16]. This is due to the fact that ORs must necessarily contain functional analytical groups, which determine the ability of ORs to react with metal ions and enable the subsequent measurement of an analytical signal. Dozens, but not hundreds, of such FAGs have been described. This stimulated further development of the idea to improve the formation conditions and properties of coordination compounds by OR modification in solution or by OR immobilization on the surface of inorganic or polymer sorbents [16, 69]. The purpose of OR immobilization on the surface is to concentrate a single metal or a group of metals before their determination by physical methods such as ICP AES and ICP MS, to use immobilized ORs in the solid-state photometry and in chemical sensors or strip tests.

First of all, it is necessary to define what is meant by the term "modification." In [16], this term is described as "complication of the reagent that does not change its chemical structure, but changes its analytical properties, i.e., this is a targeted change in the properties not related to the formation of new chemical compounds." Then the main feature of the modified reagent is reversibility of the modification, i.e., decomposition into the original components upon variation of conditions: change in the pH, dilution of the solution, replacement of the solvent, etc. [69]. Examples of such modification in solution are a change in the OR (and metal ion) solvation caused by partial or complete replacement of the solvent, formation of ion associates at active analytical groups or adducts with, for example, another ligand, and formation of different-ligand coordination compounds. It is worth mentioning that OR modification involving the formation of ion associates was occasionally utilized in the first and second periods to precipitate or extract chelates; however, only in the third period, the range of modification types was expanded and modification started to be used to change the OR properties.

New types of modification initiated in this period include the use of ion associates of ORs and metal chelates with long-chain ($C_{12}$–$C_{16}$) surfactants, most often cationic surfactants (CSurf) [16, 70], and water-soluble polymeric polyelectrolytes [16, 71]. The formation of $R^{-}$ $^{+}$CSurf ion associates not only promoted hydrophobization of the reagent and the whole chelate, but also induced a change in the type of hydration from hydrophilic to hydrophobic and, as a consequence, induced dehydration of the metal ion in the chelate and increase in the number of metal-coordinated OR ligands [72–75]. As a result, the absorption spectra of ORs and chelates showed considerable batho- and hyperchromic effects, i.e., the contrast of the color reactions of chelate formation and the sensitivity of metal determination increased [70, 75]. It was found that the analytical reactions of elements with surfactant-modified reagents are significantly superior to the best of known reactions in terms of their sensitivity, selectivity, and contrast. Whereas classical counterions such as the diphenylguanidinium cation should be present in a 10–100-fold excess, in the case of CSurf, a 3–5-fold excess was sufficient to observe the effect. The most studied reagents that exhibited the most pronounced effects include sulfophthaleins (pyrocatechol violet, xylenol orange, phthalexones), triphenylmethane-based phenolcarboxylic acids (chrome azurol S, eriochrome cyanine R, eriochrome azurol B, sulfochrome), trihydroxyfluorones (disulfophenylfluorone, salicylfluorone), other xanthene reagents (pyrogallol and bromopyrogallol red), and some other OR classes [70].

The modifying action of these surfactant ions is manifested when they react with ORs at an active analytical group, usually a sulfo group; this reaction does not compete with the metal ion complexation with the FAG of the reagent. Using this approach, it is possible to generate numerous practically new, more efficient modified reagents possessing a unique set of chemical and analytical properties starting from known ORs. Thus, this pathway is employed for ionogenic surfactants and oppositely charged polydentate chromophore chelating agents.

*Four features of complex formation* inherent in surfactant-modified ligands were identified. This is the increase in the number of coordinated ligands in the analytical forms, multisite interaction of polydentate reagents, activation of complex formation in highly acidic solutions, and increase in the stability of chelates. A fifth feature, that is, extension of the plateau of the complex formation pH toward the acidic or alkaline regions, was also mentioned [70, 76, 77].

The distinction of *polyelectrolytes* from surfactant solutions is the absence of foaming or precipitation in the solution, which is fairly important for photometric analysis. Hydrophobic and water-insoluble ORs are solubilized by the polymer via hydrophobic interactions with its nonpolar hydrocarbon skeleton and electrostatic interactions between charged groups. Since charged cationic centers of the polyelectrolyte are not blocked during solubilization of neutral OR molecules, both the proper polyelectrolyte and the product of its reaction with the reagent do not lose their initial properties and remain readily soluble in water. In the case where the functional analytical groups of ORs responsible for the complex formation with metal ions are also not blocked, the modified OR does not lose its analytical chemicalc properties, and the color reaction that determines the analytical value of OR is retained. Both surfactant and polyelectrolyte modifications are accompanied by an increase in the stability constant of the modified chelate [16].

The modification via *OR immobilization on a solid surface* is highly multivariable regarding the nature of sorbent, the sorption mechanism, as well as the use of this phenomenon in analysis [16, 23, 24, 69, 78–81]. Sorbents are modified by complexing reagents under either dynamic or static conditions, or reagents are preliminarily grafted to the sorbent surface. The sorbents may represent inorganic oxides (most often, silica), various types of carbon materials, including nano-sized forms, and various types of natural and synthetic sorbents, which are described in detail in monograph [80].

Materials widely used in this period are silicas with noncovalently immobilized analytical reagents and xerogels, most often based on transparent silica, titania, or alumina, bearing organic reagents not only on the surface, but also throughout the bulk, as ORs are introduced during the sol–gel synthesis. Silica-based xerogel films have been modified by dozens of ORs, e.g., azo compounds, phthalein and sulfophthalein reagents, flavonoids, porphyrins, dimethylglyoxime, and other reagents, including enzymes and antibodies [18, 23, 80, 82]. Such xerogels are most widely used in sensors and biosensors, in particular, in the molecular imprinting technique [83, 84].

Organic polymer sorbents are highly diverse. Well-known among them are chelating sorbents, the synthesis, properties, and applications of which are considered in monographs [80, 81, 85]. Their high selectivity towards metals was ensured by the nature of functional groups and sorption conditions. An advantage of cellulose-based sorbents is easy impregnation with solutions of group or selective organic reagents such as trihydroxyfluorones, azo compounds, dithizone, nitrosonaphthols, dimethylglyoxime, and other [18, 86–92]. Numerous paper strip tests for determination of metals were developed using these materials [18, 86]. In addition to cellulose, organic reagents are immobilized on styrene–divinylbenzene copolymer, hyper-crosslinked polystyrene, polymethyl methacrylate, polytetrafluoroethylene, and polyurethane [80]. Recently, polyurethane foams have become especially popular [93]; studies of these materials have been summarized in a monograph [94]. Thus, organic reagents immobilized on the solid phase and their coordination compounds have gained new applications and received a second life in this way.

## CHELATES ON NANOPLATFORMS

**During the fourth period** (from late 20th century up to now), the key trend of modification of ORs and chelates they form has been their solubilization and immobilization in/on various nanoobjects used as nanoplatforms. This is due to the fact that in the late 20th and early 21st century, the global attention of researchers (including analytical chemists) was attracted by liquid and solid nanoobjects, which, together with nanotechnologies, have formed the subject of a new branch called nanoanalytics [95, 96]. The advent of nanoobects and nanotechnologies gave rise to the use of new physical effects, principles, approaches, and new varieties of known methods in analytical chemistry and to elucidation of new relationships needed for the development of theory and practice of chemical analysis [97].

Liquid nanosystems (micelles, microemulsions, liposomes, vesicles, cyclodextrins, calixarenes, etc.) form the so-called *organized media* with the major solvent, or solutions that are homogeneous single-phase systems on a macroscopic scale, but microheterogeneous two-phase systems on the nanolevel [95–99]. Micelles and microemulsions can be considered to be the most typical nanostructures in terms of both their size (from three to several tens of nm) and unique characteristics and properties. The term “nanostructure” has a true meaning for micelles, as they have no macroscopic analogues and can exist in solutions only in the nanosized state [95–97]. An important benefit of micellar systems is the possibility of controlling their composition, properties of the interface with the solvent and the hydrophobic (hydrophilic) core by changing the ionic strength of the solution, surfactant concentration, and the nature of hydrophilic and hydrophobic groups and by adding so-called co-surfactants (short-chain alcohols or amines). This provides additional control over the characteristics of complex formation reactions in various methods of analysis. The effect of the ionic strength of the solution was clearly demonstrated in relation to chrome azurol S and sulfochrome chelates with some metal ions [100].

A fundamental distinction of microheterogeneous liquid organized media from conventional homogeneous solutions is that the crucial role belongs to the local effect based on solubilization (dissolution) hydrophilic and hydrophobic ORs and chelates in the nano-volume of a micellar system [98, 99]. In this case, the change in the properties and reactivity of organic reagents is due to the change in the state of only their microenvironment rather than the whole bulk of the solvent, which actually does not change. This differs fundamentally from the replacement of water by an organic solvent where the whole medium changes, as was done at the end of the second period and in the third period to modify the properties of chelates. If the analytical reaction occurs in the nanosized pseudophase rather than in the main bulk of the solvent, this pseudophase is called a microreactor or a nanoreactor [99].

The second distinction of micellar systems is microheterogeneity of the medium across the nanoreactor between the interface with water (or another solvent) and the center; this is manifested as a sharp change in the physicochemical properties of the medium in the microenvironment of the solubilized reactant and chelate molecules and the physicochemical properties of the reactants and reaction products. It was shown using various molecular probes that the effective dielectric constant of the medium inside the micelle varies from 60 to 10 units at the center of the core, while that on the surface is close to 80 [101].

The third distinction of the microheterogeneous organized media from macrohomogeneous systems is that the former can bring together and concentrate the components of an analytical reaction in the nanophase of an organized system (nanoreactor), even if the components differ significantly in hydrophobicity. There are methods for controlling the distance between the reaction components in the micelle, which is clearly seen for energy transfer effects in chelates of europium, terbium, and other rare earth elements and sensitized fluorescence in their binary and different-ligand chelates [102]. It is noteworthy that both the formation of micellar nanoreactors and solubilization of components of analytical reactions in them and also formation of chelates occur via self-assembly, i.e., these are supramolecular self-assembly processes inherent in living nature.

It was shown that OR solubilization in micelles, microemulsions, and cyclodextrins changes their protolytic, tautomeric, redox, and complexing properties [70, 103–106]. These changes, in turn, result from the change in the properties of the reaction medium (micropolarity, microacidity, microviscosity, and dielectric constant) in the microenvironment of the solubilized reactants and in their hydration [101]. Numerous uses of organized systems to modify the complexing properties of ORs in the photometric and luminescence analysis over 20 years are integrated in a monograph [70] and in reviews [75, 77, 95–99, 107–109]. It is worth noting that local changes in the properties of the microenvironment of chelate components were also inherent in the formation of chelate associates with the sulfo group of an organic reagent with long-chain CSurf in aqueous solutions [98, 99, 101]. There are recent studies devoted to the formation of chelates in multilayer Langmuir films at the interface between liquid and gas phases and in Langmuir–Blodgett films on the solid phase [110].

Modification of conventional ORs and their complexation on the *solid nanoparticle surface* has not been addressed consistently. One of the reasons is that sorption on the surface of oxide or metal nanoparticle was mainly studied for compounds suitable for the recognition of biomolecules, which is now the key trend of research in this area. The tasks of detecting metal ions have retreated to the background. Nevertheless, some studies in the coordination and analytical chemistry using nanoparticles are still carried out and bring interesting results. A specific feature of nanoparticle modification is that ligands perform a dual function, including protection of nanoparticle surface and preventing nanoparticle aggregation and complexing properties. For this purpose, ligands of different nature are, in some cases, used for modification [111].

It was noted that the choice of the ligand significantly affects the stability of the nanoparticle over time and the selectivity and sensitivity of determination using this nanosensor. In addition, a certain role is played by the hydrophobicity of the nanoparticle surface. In relation to gold nanoparticles, it was shown that predicting the effects of monolayer components on the hydrophobicity of nanoparticles is a challenging task due to the non-additive, cooperative perturbations of the interfacial structure of water, which determine the hydrophobicity at the nanolevel [112]. In [112], a method was proposed for quantitative determination of nanoparticle hydrophobicity using molecular dynamics simulation to calculate the local free energies of hydration at the interface between the nanoparticle and water. The simulation showed that the hydrophobicity of large gold nanoparticles was mainly determined, as expected, by the chemical composition of the ligand terminal groups. However, in the case of small gold nanoparticles, long alkanethiol ligands interact to form anisotropic links, which leads to significant spatial variations of the hydrophobicity even for homogeneous monolayer compositions. Thus, it is stated that the nanoparticle hydrophobicity is determined by a change in the ligand structure and chemical composition and the size of the gold core, i.e., the ligand properties alone are insufficient to characterize the hydrophobicity of gold nanoparticles (GNPs).

Yet another issue related to chelate formation on the nanoparticle surface is the origin of the analytical signal. Most often, this is the change in the absorption maximum of the surface plasmon resonance (SPR) of the nanoparticle, already customary for researchers. Another possible source is a change in the absorption spectrum of the reaction product and the appearance or quenching of fluorescence caused by chelate formation or displacement from the surface into the solution. A few examples related to the formation of chelates or other coordination compounds are discussed below.

Most studies are devoted to the synthesis, modification, and analytical application (for metal determination) of gold nanoparticles, which are analyzed in reviews [113, 114], and silver nanoparticles [115]. The number of such reviews is much greater, but here we mention only those describing the use of nanoparticles to form coordination compounds. Consider several examples. Functionalization of GNPs with 1,10-phenanthroline was used for selective determination of lithium in water in the presence of sodium and potassium based on GNP aggregation accompanied by a shift in the SPR spectrum [116]. The ligands grafted to the GNP surface react with lithium ions to give a 2 : 1 complex, which is accompanied by nanoparticle aggregation. It was found that 4 nm GNPs are more sensitive to lithium than 32 nm particles.

Modification of the surface of GNPs with a zinc porphyrin complex was described; the resulting nanosystem was suitable for determination of chloride ions and monosubstituted phosphoric acid ions [117]. A method for selective determination of Cr(III) ions using GNPs modified with 5,5'-dithio-bis(2-nitrobenzoic acid), not interfered with by many sorts of cations, was proposed [118]. Especially numerous are studies devoted to the application of GNPs for determination of mercury and lead, which are analyzed in reviews [113, 114]. Mention should be made of a highly selective method for mercury determination using 2,6-pyridinedicarboxylic acid [119], which is not interfered with by alkali, alkaline earth, and many transition heavy metals, and a method using 2-[3-(2-amonoethylsulfanyl)propylsulfanyl]ethylamine as the ligand [120]. Finally, it should be stated that studies of the formation and analytical application of coordination compounds using nanoparticles are yet not numerous.

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## CONFLICT OF INTEREST

The author declares that he has no conflicts of interest.

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