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Organic reagents in spectrophotometric methods of analysis

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Abstract. The role of organic, in particular, complex-forming, reagents in the formation and development of spectrophotometric analysis is discussed. The prospects for the use of organic reagents in modern analytical methods are considered; the attention is focused on modified and immobilised reagents, receptor molecules and on the use of nonaqueous and organised media. The bibliography includes 170 references.

I. Introduction

For many years, organic reagents play an important role in the chemical and physicochemical methods of analysis. They are employed for qualitative or quantitative determination of chemical elements and compounds (both organic and inorganic), as well as for separation, concentration, masking and other auxiliary operations that precede or accompany the analysis.

Theoretically, the possibilities of design of new organic compounds for analytic purposes are boundless; however, in practice only several dozens of classes of chemical compounds are effective as organic reagents.[1] The requirements for the organic reagent are dictated by the analytical method used.

The reagent for the determination of metals should, first of all, contain a proper functional analytical group that enables its interaction with the determined element and subsequent observation of the respective analytical signal. Currently, several tens of such functional analytical groups are known and documented.[2, 3]

The determination of organic compounds requires that the reagent molecule contained specific groups able to react with functional groups of determined compounds (hydroxyl-, carbonyl-, halogen-, sulfur-, nitrogen-containing) with the formation of intensely coloured or luminescent products. Reactions used for the determination of functional groups differ considerably from those used for inorganic ions. In particular, the nature of the molecular core (aliphatic or aromatic) is important. Besides that, the course of many reactions depends substantially on the media and the reactions are not often sufficiently selective.

New problems that the chemical methods of analysis encounter with have stimulated wider studies of organic reagents. Novel directions have appeared, that are associated with the modification and immobilisation of the conventional organic reagents, as well as with the use of non-aqueous, water – organic and organised media. The variation of conditions of the analytical reactions, *viz*., the control over the reaction rates and solvation processes, changes in the solubilities or hydrophobicity of the reactants, utilisation of solid matrices, is becoming more and more popular.

There are also completely new directions dealing with the use of receptor molecules and reagents based on the principles of supramolecular chemistry, host – guest interaction mechanisms, as well as immune reactions with organic and bioorganic compounds. Some organic compounds act as reagents in excited states; reagents that form π-complexes with analytes, bacteria and micelles (vesicules), *etc*. are also known.

At present, organic reagents are widely used not only in spectrophotometry[2–10] and luminescence analysis,[11, 12] but also in atomic absorption[13–16] and atomic emission spectrometry,[17] inverse voltammetry,[18–21] in the methods based on the use of ion-selective electrodes[22] and different chemical sensors,[23] in the kinetic,[24, 25] flow-injection[26] and tracer analysis,[27] in capillary electrophoresis,[28] and in liquid[29] and gas chromatography.[30] As usual, organic reagents play a crucial role in titrimetry,[31, 32] extraction[33, 34] and many other methods of determination, separation and preconcentration.[35–37] Comprehensive textbooks[38, 39] on the use of organic reagents in the inorganic analysis have been published.

In the present review, we discuss the role of organic reagents (mostly, complex-forming) in the spectrophotometric analysis and consider the perspectives of their use in modern analytical methods.

II. Individual organic reagents

In the first third of the 20th century, a new scientific direction based on the application of chelating reagents, mostly organic, in chemical analysis emerged at the joint of organic, inorganic, coordination and analytical chemistry. The concept of functional analytical groups was formulated, the effects of substituents (called later the analytical active groups) in the reagent molecules were studied, and the general conditions of formation of stable complex compounds were revealed.

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In the next years, organic reagents have acquired wider applications in different analytical methods. New more efficient reagents were synthesised and exploited, *viz*. oxine (8-hydroxyquinoline), dithizone (1,5-diphenylthiocarbazone), cupferron (*N*-nitroso-*N*-phenylhydroxylamine ammonium salt), dialkyldithiocarbamates, arsenazo I [sodium 2-(2-arsonophenylazo)-1,8-dihydroxynaphtaline-3,6-disulfonate], 1,3-diketones. Theoretical concepts on the mechanisms of their action were developed. It can be said for sure that Russian science has made a major contribution to the development of theory and practice of the use of organic reagents in the analytical chemistry.[40]

In the 1950–1980's, complexones,[31] the reagents of the triphenylmethane [4–7,41] and fluorone [42] series, antipyrin derivatives,[43] mono- and bis-azo compounds, for example, arsenazo III,[44] acquired a broad use in the photometric analysis. Hydroxyflavones, hydrazones and Schiff bases were often used in the fluorimetric analysis, whereas rhodamines, in the version with extraction.

In the last two decades, heterocyclic mono-azo compounds,[45,46] including both the well-known 1-(2-pyridylazo)-2-naphthol (PAN), 4-(2-pyridylazo)resorcinol (PAR) and 4-(thiazol-2-ylazo)resorcinol (TAR), and especially halogenated heterocyclic compounds began to play an important role in the photometric analysis. Extremely high molar extinction coefficients of the latter [often reaching $(1.0-1.5)\times10^5$], contrast ranges and higher selectivity as compared to PAN and PAR are their main advantages. Complexes of water-soluble analogues of natural porphyrins also possess high molar extinction coefficients.[47] Besides, new principles of the reagent design were developed, using the concept of functional analytical group duplication. In particular, the series of bis-azo compounds of the arsenazo III group has been considerably broadened.

The unusually high apparent molar extinction coefficients [$\varepsilon_{mol} = (1-10)\times10^5$] were obtained in the flotation of ionic pairs of organic reagents (Rhodamine 6G, Crystal Violet, Methylene Blue, *etc*.) with analytes.[48] The highly sensitive kinetic and catalytic methods for the determination of metal ions, anions and organic compounds in photometric and fluorimetric versions, are very promising.[49–51] A number of works on the determination of different anions with the use of organic reagents that have been analysed in detail in a fundamental review,[52] should be specially noted. Many of the above-mentioned applications of organic reagents for the analytical purposes have been discussed.[53]

Quantum-chemical methods for the calculation of the characteristics of the coloured compounds gained further development. An attempt was made of quantum-chemical design of photometric reagents with optimal characteristics.[54]

However, it is obvious that the synthesis of many novel organic reagents for the determination of metal ions will not give considerable benefits. At present, diverse modifications of the known organic reagents by complication of their chemical structures or changes in the media properties where the analytical reaction is carried out, are becoming popular. In particular, non-aqueous and water–organic media, as well as organised media, are used more and more widely.

III. Modified organic reagents

1. Types of modifications of organic reagents

There is still no clear definition of a modified reagent. One can consider the modification as the purposeful change in the properties not related to the formation of new in principle chemical compounds. According to this definition, a chemical compound with an additional substituent is a new organic reagent. It can be similar to the prototype reagent in its chemical and analytical properties (*e.g*., in the selectivity, provided that the functional groups were not affected), but cannot be considered as the modified reagent.

On the other hand, different salts, ionic and other associates of organic reagent with other organic and inorganic conpounds formed due to electrostatic or hydrogen bonds or hydrophobic interactions, can be regarded as modified organic reagents. Solvates (adducts) involving the organic solvent molecules also fall in this category. In our view, the solubilisation of organic reagents in various types of nanosized organised systems, which serve as the nanoreactors in analytical reactions, is also a kind of modification.

One of the main features of the modified reagent, according to our definition, is the reversibility of the modification, so that upon changes in the conditions, *e.g*. upon acidification or dilution of the solution or change in the solvent, *etc*., the reagent dissociates into the starting components.[1] It is noteworthy that the modification of organic reagents has long been employed, especially for their hydrophobisation upon formation of neutral ion associates. However at present, diversification of the modification pathways and the use of this approach in the routine analysis is in progress. Several examples of analytical systems where, in our view, the authors deal with the modified organic reagent, are discussed below.

2. Modification upon association of organic reagents

This type of modified organic reagents comprises different associates, *viz*. associates of the initial organic reagent with its counterion (ion associates or pairs), associates of an acidic organic reagent with a base (amine or amide) or of a basic organic reagent with a proton donor (see, for example, Ref. 55). In 1954, it was proposed [56] to use organic co-precipitants to concentrate elements from very dilute ($1:10^{10}$ and more) solutions. The use of large molecules as organic co-precipitants and for the determination of trace amounts of elements proved beneficial. Different types of co-precipitants were found. The mechanism of their effect is described in the original works, reviews and monograph (see, for example, Refs 56–58).

Let us limit ourselves to the consideration of the mechanism of co-precipitation of ionic associates, poorly water-soluble and containing an extended hydrophobic organic fragment. It is known that the majority of organic reagents that form complexes with precipitated metal ions contain sulfo, carboxy, and other negatively charged groups. Their effect on the solubility can be levelled by formation of a salt or an ion associate with a 'heavy' hydrophobic organic cation. In this case, it is pertinent to consider this as a modification of the respective organic reagent by organic cations, since it is the salt or ion associate that serves as the ligand for the metal ion. Other versions are also possible, for example, precipitation of actinides by the arsenazo-type reagents and the precipitate of diphenylguanidinium anthracene-α-sulfonate,[57,58] precipitation of thorium by SPANDS [sodium 2-(*p*-sulfophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonate] and Methylene Blue, and precipitation of rare-earth elements by stilbazo[4,4′-bis(3,4-dihydroxyphenylazo)stilbene-2,2′-disulfonic acid] and so on.[55]

In the 1960–1980's, ion associates were most often employed in extraction systems. The role of reagent modification for the extraction of charged complexes is similar in many aspects to that of counterions in the precipitation reactions, since in both cases charge neutralisation is required for the passage of a complex to another phase (solid or liquid). In the extraction of anionic chelates it is necessary to block sulfo, hydroxy, and other hydrophilic groups by 'heavy' hydrophobic organic (or sometimes inorganic) cations, which thus serve as the modifiers of the original organic reagent. Large hydrophobic organic cations include, *inter alia*, tetrabutylammonium, tetraphenylarsonium, trioctylammonium, and potassium is used as the inorganic cation.[33] The use of diphenyl- and triphenylguanidinium salts as a source of cations and extraction with higher alcohols allowed one to expand this approach onto a large group of complex organic reagents belonging to the family of azo-dyes.[44]

Chelates with multiply charged metal cations can have a positive charge. To compensate it, a sufficiently hydrophobic anion (*e.g*., tetraphenylborate, naphthalenesulfonate, or acid dye

anions) should be added to the solution.[34, 55] In any case, it can be said that the anionic or cationic chelates are modified by hydrophobic cations or anions, respectively.

3. Modification upon formation of multicomponent complexes and outer-sphere chelates

The passage from binary to ternary and multicomponent systems is a well known (since the 1950's) approach aimed at improving the analytical characteristics of photometric organic reagents. Hundreds of papers on the so-called mixed-ligand complexes were published in the 1970 – 1980's; a monograph devoted to this topic appeared, in which the authors propose the term 'heteroligand' for such complexes. The interactions between ligands can differ in nature, namely, hydrophobic interactions, stacking interactions, π-bonding, hydrogen bond. On the whole, they lead to the change in the character of complex formation by the original organic reagent.[55, 59 – 61] It is believed that the interacton between two ligands gives a new 'compound' reagent, which is more efficient than the original reagents.

Yet another route to the modification characteristic of multicomponent systems is the outer-sphere complexation, which also changes the analytical parameters of the reaction products.[55, 62] A specific effect of the outer-sphere reagents enhances the differentiating action of organic reagents in respect of metals. Outer-sphere complexes occupy an intermediate position between the inner-sphere complexes and ion associates.[55]

4. Modification of organic reagents caused by changes in the media properties

a. Non-aqueous media

Extensive investigations into non-aqueous solutions, especially in the mid-20th century, has led to their use not only in research studies, but also in the routine chemical analysis. It was found that the properties of organic reagents (protolytic, redox, donor-acceptor, complex forming, tautomeric, solubility, *etc.*) vary dramatically in different solvents, therefore changing the sensitivity, selectivity, contrast and rate of a reaction, and even the end products. Thus, a solvent is not only a medium, but is rather a kind of an active reactant. Its effect on the chemical process is determined primarily by the two principal characteristics, *viz.,* donor-acceptor properties and dielectric permeability. As a result, one can control the process by changing the character of solvation of both the reagent and the element under study.[63]

However, the change in solvent results in simultaneous changes in both the dielectric permeability and donor – acceptor properties. Therefore analytical chemists have begun to use mixed (non-aqueous and water – organic) solvents. New ways of increasing the selectivity and contrast of metal ion reactions with organic reagents were revealed also in the use of strongly acidic media.[64]

Despite a sufficient progress in the control over chemical processes with the use of such solvents, many problems still remain unsolved. In addition, these media are sometimes unsuitable due to toxicity, strong odour or volatility. Non-aqueous media have certain advantage only in the extraction version of photometric, fluorimetric and atomic absorption methods, because they allow one to unite separation, preconcentration and determination, thus increasing both selectivity and sensitivity of the analysis.

b. Surfactants

A broad class of ionic surfactants can serve as versatile modifiers of physico-chemical properties of chromophore polydentate multifunctional organic reagents of different chemical nature.[65] It is for this reason that the analytical determination of elements with the use of surfactant-modified reagents considerably exceeds the best known conventional methods in sensitivity, selectivity and contrast. A vast literature on the theoretical aspects and analytical applications of surfactants includes two books [65, 66] and a number of reviews.[67 – 72]

Formation of ion associates is one of the main routes of modifying electronegative or electropositive organic reagents by surfactant ions of the opposite charge. The surfactant ions interact with the analytical active group of the organic reagent, so that no competition with the complexation of the metal ion occurs. This allows creation of many new and more efficient modified organic reagents from the known ones. It is applicable to ionogenic surfactants and chromophore polydentate chelating or, more generally, complex forming reagents.

The best known and the most analytically efficient reagents belong to the following classes: sulfophthalein indicators (Pyrocatechol Violet, Xylenol Orange, Phthalexones), phenolcarboxylic acids of the triphenylmethane series (chromazurol C, eriochromcyanin R, eriochromazurol B, sulfochrom), trihydroxyfluorones (disulfophenylfluorone, salicyl fluorone) and other reagents of the xanthene series (Pyrogallol Red, Bromopyrogallol Red), as well as from some other classes of organic reagents.[65, 70, 72 – 78] For the modification of organic reagents with the negatively charged analytically active groups, one should use a long-chain cationic surfactant with no less than twelve carbon atoms in the alkyl chain, *i.e.*, salts of quaternary ammonium bases (for example, cetyltrimethylammonium bromide), alkylpyridinium salts (*N*-cetylpyridinium chloride) and salts of other heterocyclic amines, primary, secondary and tertiary amines that can be protonated in water with the formation of cations.[65, 70 – 78]

The basic idea of modification of this type of organic reagents is the concept of formation of ion pairs or ion associates.[65, 75] The scheme of a reaction of a reagent $R(OH)_2$ containing one functional analytical group and one analytical active group (CO_2H, OH, SO_3H) with a cationic surfactant (Sur) can be written as follows:

$$n\,R(OH)_2 + n\,Sur^+ + M^{n+} \longrightarrow M^{n+}[RO_2^{2-}\,Sur^+]_n + 2n\,H^+.$$

Due to the addition of the biphilic surfactant cation with a large non-polar chain to the organic reagent molecule, the associate becomes significantly more hydrophobic than the original more hydrophilic reagent, *i.e.*, the character of the species hydration changes.[65, 78, 79] As a result, a local decrease in the polarity of the medium occurs in the microenvironment of the organic reagent molecule.[72] This leads to a decrease in the hydration of the functional analytical group and the bound metal ion, which, in turn, causes the change in protolytic properties of the groups involved in the functional analytical group,[65, 72] and the increase in the number of adjoining chelating ligands.[65, 78]

There are at least four features of the complexation with surfactant-modified ligands:[65, 78] the increase in the number of coordinated ligands in the analytical forms; the multisite interaction of polydentate reagents; activation of complex formation in strongly acidic media; and the increase in the stability of the chelates. A widening of the pH plateau of complex formation to acidic or basic region is sometimes considered as the fifth effect.[65] These factors ensure the increased sensitivity and selectivity of the reactions in the presence of surfactants. Cationic surfactants in such systems bring into interaction both analytical functional and analytical active groups, *i.e.*, induce multicentre interaction involving the chromophore π-electron system. Thus, the potential of the given reagents can be used to their full extent in order to enhance the contrast of the photometric reaction. In the case of multiply charged metal cations, the number of coordinated ligands increases, which also leads to an increase in the sensitivity of the determination. For instance, in the case of titanium complexation with Pyrocatechol Violet, the molar extinction coefficient of the complex reaches 1.5×10^5 and the contrast of the reaction $\Delta\lambda$ is 250 nm upon modification of the reagent by cationic surfactants.

It should be noted that in the case of a stoichiometric component ratio in the reagent – surfactant system, as a rule, neutral ion associates precipitate. Their solubilisation can be effected by addtiion of a 2 – 5-fold excess of the surfactant, which

causes surfactant adsorption on the precipitate particles, their charging and dispersion to the virtually molecular level. Such charged particles of ion or chelate associates containing small excess of the surfactant ions, are sometimes called mixed micelles.[66]

c. Water-soluble polymers

Water-soluble polymers are commonly used in chemical technology, for example, in water purification. However, their use in the analytical chemistry has long been limited to the concentration by membrane filtration.[80,81] Later it was found [82] that the modification by water-soluble polymers is an almost versatile way to transform water-insoluble (hydrophobic) organic analytical reagents or dyes into the water-soluble form. The molecular mass of these organic polymeric compounds is usually in the range of $10^4 - 10^5$; they contain both the hydrophobic chain and the hydrophilic groups incorporating tertiary or quaternary nitrogen atoms.

The mechanism of the interaction of water-soluble polymers with the organic reagents is as follows. Hydrophobic (water-insoluble) organic reagents are solubilised as a result of their hydrophobic interaction with the non-polar carbon skeleton of the polymer molecules.[65,83] Since the solubilisation of the neutral organic reagent molecules does not block the cationic centres of the water-soluble polymer, its interaction product with the reagent retains the properties inherent in the original polymer and is also water-soluble. Moreover, if the analytical functional groups of the reagent responsible for the complexation of metal ions are neither blocked by the water-soluble polymer, the modified organic reagent does not lose its chemical analytical properties with retention of the coloration reaction, which determines the analytical value of the organic reagent. In addition, due to the solubilisation and related structurisation of water in the close vicinity of the chelate, the stability constant of the complex of the polymer-modified reagent with the metal ion increases, which favours virtually complete binding of the element.

The use of the organic reagent – water-soluble polymer systems, as well as the organic reagent – surfactant systems, broadens the potential of the spectrophotometric analytical methods. For example, the use of organic reagents in the flow-injection analytical methods is limited due to the reagent sorption on the capillary walls and on the other parts of the flow system. Due to higher affinity of the hydrophobic organic reagent to the water-soluble polymer than to the material of the instrument parts, the introduction of water-soluble polymer solves this problem and prevents the organic reagents and their metal complexes from sorption on the working parts of the instrument. The use of water-soluble polymers also broadens the potential of the classical titrimetric analysis due to the use of metal indicators of different nature. For example, a scheme of a reaction of poly[N-(4-vinylbenzyl)trimethylammonium] chloride, $(VBMA)^+Cl^-$, with the two-basic reagent $H_2RSO_3^-$ containing one dissociated sulfo group and doubly-charged metal cation M^{2+} can be written as follows (for one unit of the polymer chain):

$$H_2RSO_3^- + M^{2+} + (VBMA)^+Cl^- \longrightarrow MRSO_3(VBMA) + 2H^+ + Cl^-$$

The water-soluble polymer – organic reagent – M systems are successfully used for retention and preconcentration (for example, by the membrane filtration method) with the subsequent determination of elements.[84,85] Ionenes represent yet another example of charged water-soluble polyelectrolytes used in analysis.[86]

d. Organised micellar media

Organysed media differ in principle from the classical homogeneous media described above since they are microheterogeneous. They consist of a solvent and a huge number of ensembles of tens or hundreds of distributed biphilic surfactant molecules or ions. The species in such an ensemble form a nano-sized micellar pseudo-phase (dispersed phase), the properties of which differ sharply from those of the bulk solvent (a dispersion medium), which produces a reaction medium of a new type, combining the properties of both polar and non-polar media.[70,71,87,88]

More complex micellar systems can contain two or three components in addition to the surfactant molecules. The examples of surfactant-based micellar systems are represented by direct and inverse micelles, microemulsions ('oil-in-water' and 'water-in-oil'), vesicles, liposomes, lipid membranes, Langmuir – Blodgett films (LBF), liquid crystals and other systems.[71] Micellar systems can also appear on the solid surface being in a contact with the solution in a form of hemimicelles (half-micelles) or adsorption bilayers.[66]

A peculiarity of the nano-sized phase created by an ensemble of surfactant species is that it has virtually no macroscopic analogue.[89] It is worth noting also that the formation of micellar systems as a result of self-organisation (self-assembly) of surfactant molecules or ions does not include a formation of intermolecular chemical bonds, and is therefore related to supramolecular chemistry, a new section of chemistry that emerged in the last decade of the 20th century.[90]

The microheterogeneous organised media differ in principle from the common homogeneous solutions in that the main feature of the former is the local effect based on the solubilisation of hydrophilic and hydrophobic reagent molecules in the nanoscale volume of the micellar system.[70,71,87,88] In this case, the change in properties and the reactivities of organic reagents is determined by the change in the state of the medium in their microenvironment (rather than in the entire volume). If the analytical reaction occurs in the nano-sized microphase rather than in the bulk, the former is called a micro- or nano-reactor.[71,87,88]

It was shown that the solubilisation of organic reagents in micelles, microemulsions, LBF or cyclodextrins changes their protolytic,[91–94] redox [95] and complexation [65,66,96] properties, as well as the tautomeric transformations.[94,97–99] These changes in turn result from changes in the properties of the reaction media (polarity, acidity, dielectric permeability) in the microenvironment of the solubilised reagents and changes in their hydration type.[72,100–102] Numerous applications of the organised media for the modification of the organic reagent's properties are summarised in books [65,66] and reviews.[67–71]

IV. Immobilised organic reagents

The term 'immobilisation' of organic reagents on the surface layers or in the bulk of a solid phase (matrix) has come to analytical chemistry from biochemistry. If, as a result, some properties of the compound change (which is the goal of immobilisation in the analytical chemistry), this compound can be considered modified. Thus, it is possible to consider that the immobilisation is a particular case of the modification.

1. Complex-forming sorbents

Complex-forming sorbents are organic or inorganic polymeric compounds with groups or reagents attached in one or another way, which can interact with metal ions or other compounds in the solution.

The mode of attachment can be based on both the sorption of the reagent molecules on the matrix and their covalent binding with the formation of a new polymer containing reactive fragments of the original reagent. It can be said that it is immobilisation of an organic reagent on the solid matrix that occurs in the former case, while in the latter case one deals with the formation of a new polymeric compound.

There are numerous examples of immobilisation of organic reagents on polymeric matrices.[103,104] One of the first developed methods was preparation of ion-exchange resins with absorbed reagents.[105] This consisted of common organic reagents containing sulfo or other acidic groups on an appropriate ion-exchange resin. The analytical functional groups in the sorbed reagent molecules do not lose their ability to bind metal ions. A wide range of different materials, *e.g.*, linear and network polymers

(ion-exchange resins based on styrene and divinylbenzene), polyurethane foams, activated charcoal, other organic and inorganic materials serve as solid matrices. The possibility of using ion-exchange resins in photometry was established [106] and reviewed.[107] A linear coloristic method was proposed for the determination of iron(III) and copper(II) with the use of hydrophobic silica gels with non-covalently immobilised Xylenol Orange or PAN as indicator powders.[108] Luminescent reagents can be immobilised as well, for example, luminol (3-aminophthalohydrazide), Rhodamine B {[9-(2-carboxyphenyl)-6-diethylamino-3*H*-xanthen-3-ylidene]diethylammonium chloride}, while glass, silica gel or organic polymers serve as the inert support.[109] For instance, it was proposed to use immobilised morine for the sorption-fluorimetric determination of zirconium and tin.[110] Polyurethane foams also present a considerable interest as sorbents due to their high efficiency in combination with versatility and high chemical and mechanical stability. Methods of concentration and determination were developed for more than 50 chemical elements.[111–116]

The detection of an analytical signal can be based on direct measurement of light absorption by the organic reagent modified by an ion-exchange resin, as well as on the application of reflectance spectroscopy. The former method called solid-phase spectrophotometry was proposed by Japanese researchers,[117] who were the first to establish a linear dependence of the light absorption by the solid phase on the concentration of the element in the initial solution. Different versions of this procedure were developed, including sorption of the metal–reagent complex by the ion-exchange resin and, *vice versa*, preliminary sorption of the reagent and its reaction with the metal in the sorbent phase.[118] Since the reagent is the active principle in both cases, it is possible to say that the organic reagent is immobilised on, and modified by, the ion-exchange resin.

2. Ion-exchange membranes

Yet another modern material that is used as a solid matrix is the ion-exchange membrane in a form of a thin film, plate or filter. It was established that the analytical efficiency of organic reagents increases upon immobilisation on such membranes. There are different versions of the practical implementation of this method of preconcentration and determination. Optically transparent membranes [for example, based on poly(vinyl chloride)], impregnated with trioctylamine in order to make them work as ion-exchange resins, are treated with a solution of a complex of a metal with an organic reagent (for example, Nb with PAR). The complex is adsorbed on the membrane and then the optical density is measured in a usual manner (in transmission mode).

As the interaction between the complex and the membrane active groups is mainly electrostatic in essence (formation of a salt or an ion associate), one can say that in such systems, *e.g.*, with polycaproamide membranes, the complex or the reagent incorporated in the matrix is modified (and immobilised). The equation of a reaction for a single unit can be written as follows:

$$\rangle\!\equiv\!N^+Cl^- + {}^-O_3SRM \longrightarrow \rangle\!\equiv\!NO_3SRM + Cl^-,$$

where $\rangle\!\equiv\!N^+Cl^-$ is a membrane polymer chain unit, ^-O_3SRM is an anion of metal complex with the reagent and $\rangle\!\equiv\!NO_3SRM$ is a polymer chain unit with an attached complex.

Other applications of membranes are also known.[119, 120] For instance, a cobalt complex with PAN was concentrated on thin ion-exchange films with subsequent determination of the metal directly in the sorbent phase. A number of reviews is devoted to the use of organic reagents in the sorption spectral methods.[121–124] Dynamic sorption preconcentration of elements with subsequent spectroscopic study has been surveyed.[125]

V. New classes of organic reagents

1. Receptor molecules

Macrocyclic ethers, the so-called crown ethers, are of considerable interest in many fields of chemistry, in particular, in analytical chemistry.[126] The molecules of crown ethers represent rings of nine or more atoms, at least three of them being oxygen atoms. 18-Crown-6 with six oxygen atoms in the ring is the most famous. A number of macrocyclic compounds containing secondary, tertiary, pyridinium-type, pyrrolium-type, azomethine, *etc*. nitrogen atoms (azacrown compounds), oxygen and nitrogen (oxazacrown compounds, cryptands), sulfur (thiacrown compounds), oxygen and sulfur (oxathiacrown compounds), nitrogen and sulfur (azathiacrowns) and so on were synthesised. Porphyrins belong to natural macrocycles.

The area of the use of macrocycles in the chemical analysis is extremely wide. They serve as reagents in photometry, in luminescence analysis (in conventional and extraction versions for ion pairs with the dye anion) and flow-injection analysis. They are also used as components of membranes for ion-selective electrodes, in sorption methods (following immobilisation on a surface), liquid and gas chromatography, extractive separation of alkali and alkaline-earth metals as well as radionuclides, *etc*.[126, 127]

The ability of macrocycles to form more stable complexes with metals with higher selectivity as compared to the acyclic ligands was called the macrocyclic effect.[90] This effect is caused by the fit of the macrocycle cavity to the size of the metal ion, as well as by the properties of the donor heteroatoms. In addition, a multicentre and multifunctional ion-to-ligand binding occurs, which forms the basis of the molecular recognition effect, or the host–guest correspondence principle. The multifunctional nature of the interaction is caused by the involvement of electrostatic (ion–ion, ion–dipole, dipole–dipole), donor–acceptor, π–π-stacking, van der Waals and hydrophobic interactions and hydrogen bonding. With account of the enthropy factor, such systems have much in common with biosystems.

3D Receptor molecules with cavities of definite size, such as cryptands, spherands, cryptospherands, cavitands in a form of a bowl, and also carcerands which have a form of coupled cups are the most efficient as regards both selectivity and the strength of binding to the analyte.[90, 126]

These receptor molecules exhibit quite unique properties.[128, 129] One of the spherands forms a stable complex with sodium ions ($\log K_{stab} = 14.1$) with the $Na^+ : K^+$ selectivity of 10^{10}! A photometric reagent for lithium ions of the torand family changes its colour upon replacement of the protons at the secondary nitrogen atom inside the ring. Molar extinction coefficients of such compounds (*e.g.*, metal porphyrins) are in the range of $n \times 10^5$.

The receptor molecules most widely used in different methods of analysis, separation and preconcentration are cyclodextrins (having the shape of a truncated cone) and calixarenes (having the shape of a basket).[71] The use of cyclodextrins in chemical analysis is reviewed.[130–135]

An important feature of the receptor molecules is the ability to bind not only metal cations, but also anions [90, 126, 128] or neutral organic molecules. In the case of organic compounds, the selectivity of receptors is manifested not only with respect to molecules of different sizes and nature, but also with respect to structural, geometrical and optical isomers. The separation and determination of enantiomers of pharmaceutical preparations, amino acids and other biologically active compounds by means of gas-liquid [130, 131, 134, 135] and liquid [136–138] chromatography, capillary electrophoresis,[138] extraction [131] and other methods [131, 136, 139] with the use of cyclodextrins as a mobile or stationary phase have become a common tool in the analytical practice. Cyclodextrins and calixarenes are widely employed in the luminescence analysis [130, 133] and in chemical sensors.[133, 140, 141] A series of receptor molecules for the anion determination were synthesised.[142] Aptamers belonging to the class of oligonucleotides [143]

represent a new type of analytical reagents the action of which is also based on molecular recognition.

2. Miscellaneous new classes of organic reagents

In recent years, the methods of determination of organic compounds both in the common objects (*e.g.*, in liquid media) and in biomaterials, were successfully developed. Enzymes used for the determination of metal ions,[144, 145] organometallic [146] and organic compounds [147, 148] both in solution and in the immobilised state are a new type of organic reagents. These reagents exhibit not only high sensitivity allowing the determination of many compounds on the nano- and picomolar levels, but also an extremely high selectivity that is characteristic of all enzymatic reactions. Fluoroimmunoassay based on the use of antigen – antibody interaction in different variants of registration of fluorescence as an analytical signal [149, 150] is closely related to this group of methods.

Many other organic reagents for determination of organic compounds are known, for example, widely used *o*-phthalaldehyde for primary and secondary amines and thiols,[151, 152] lophine derivatives (for a review, see Ref. 153) and other reagents (see reviews [154, 155]). Organic reagents are used for the determination of biological macromolecules,[10] the action of some reagents is based on the formation of charge-transfer complexes,[156, 157] metal diketonates can be used for the recognition of organic molecules.[158] Carbon tetrachloride can de determined by photochemical reactions.[159] New types of acyclic reagents for metals exhibit surprisingly high selectivity.[160]

Yet another method, the potential of which is not highly appreciated, is the determination of some metals and especially organic compounds by organic reagents in excited states. These analytical reactions are based on intra- and intermolecular transfer of excitation energy of molecules solubilised in different organised systems, which favours the concentration and close contact of the reactants. For example, in the widely known multicomponent system Eu(III) – thenoyltrifluoroacetone (TTA) – phenanthroline (or trioctylphosphine oxide) – surfactant, three TTA molecules excite to the singlet state as a result of light absorption, and then pass to the triplet state by intersystem crossing. Due to the relatively long lifetime and high energy of the excited state, the excitation energy is transferred intramolecularly from the TTA to the excited levels of Eu^{3+} (the antenna effect). As a result, the intensity of Eu^{3+} radiation increases virtually by an order of magnitude, and its detection limit drops to $10^{-9}-10^{-12}$ mol litre^{-1} (Refs 161 and 162).

An additional decrease in the europium detection limit by 1 – 2 orders of magnitude can be acquired on addition of a second rare-earth ion (for instance, gadolinium, terbium, yttrium), which serves as the intermediate unit in the energy transfer from ligand to the europium ion.[162, 163] In addition to TTA, a number of other types of reagents, including macrocycles, can be used as antenna ligands.[164] This method also allows determination of samarium, terbium, gadolinium, dysprosium, and curium.[165] The advantage of these multicomponent systems is that they provide a possibility of determination of not only metal, but also an organic ligand from quenching [166] as well as from enhancement of the sensitised fluorescence.[167]

Yet another implementation of organic reagents in the excited state is the determination of polycyclic aromatic hydrocarbons with the use of acridine dyes by means of sensibilised phosphorescence at room temperature in micelles.[168, 169] The method is selective, because the excitation of a dye takes place in the visible range. The dye molecule excites from the singlet to the triplet excited state under the influence of a heavy atom, and then a triplet-to-triplet energy transfer to the hydrocarbon molecule occurs (the triplet excitation energy for polycyclic aromatic hydrocarbon is lower than that for dye), and the hydrocarbon phosphorescence is detected. With the use of micelles, one can avoid liquid-nitrogen techniques and study the phosphorescence in solution at room temperature. Reagents based on self-organised supramolecular ensembles are also promising (for a review, see Ref. 170).

VI. Conclusion

The analysis of more than hundred years history of applications of the organic reagents in the analytical chemistry shows that they have played a significant role in both the development of the theoretical concepts in this area of science and the practical chemical analysis of many organic and inorganic subjects. Virtually each element of the Periodic Table in various concentrations, amounts and forms can be determined with the help of different classes of organic reagents. According to a rough estimate, more than 6000 organic compounds were proposed as analytical reagents. About 100 of them can be considered 'basic', *i.e.*, original as regards their chemical structures and analytical properties (sensitivity, selectivity, *etc.*), while others are in fact their derivatives exceeding them in the major analytical parameters. Usually, this excess is not higher than 2 – 3 times, so the replacement of the 'basic' reagents by their analogues (which often are much more expensive) is not always reasonable, taking into account the necessity of modifying the established protocols.

An intense development of physical methods of analysis, especially since the mid-20th century together with their obvious advantages (sensitivity, possibility of express analysis and automation, in many cases multielement analysis, *etc.*) was seemingly condemning the chemical methods (in particular, those with the use of organic reagents) to the gradual deprecation. However, new approaches and potentials emerged in the 1970 – 1980's and are actively implemented since then.

1. Automation of almost all stages of chemical analysis (from sampling, decomposition, component separation, concentration, *etc.* to the determination of compounds and elements) became possible. This allows quick analysis of a large number of samples, which is especially important in environmental monitoring, sanitary analysis and in many other cases.

2. Low cost of chemical methods of analysis as compared to physical ones plays an important role since the necessary equipment and reagents in the former are by orders of magnitude cheaper. A set of test methods have been developed (much of them with the use of organic reagents), which use quite a compact equipment and are low energy-consuming, and hence can be used in field analysis and are indispensable for environmental control, in extraordinary situations, *etc.*

3. In the last 20 – 30 years, the approach to the synthesis of new organic reagents has changed dramatically. Chemists engaged in analysis (as well as in synthesis) came to a conclusion that the infinite broadening of the assortment of related organic reagents containing the same analytical functional group and giving only a slight enhancement of the analytical properties as compared to the parent reagent is unreasonable. The use of modified and immobilised organic analytical reagents (or systems) appeared to be more promising. It is important that the reagents in use are basically the same, but their analytical characteristics are enhanced multiply due to their modification with auxiliary reagents. The efficiency of their analytical use grows in the same proportion. The same statement holds to even greater extent for the organised media and the receptor molecules that operate on the principle of molecular recognition.

4. Modern electronic techniques and small-sized measurement devices (pocket-type of third and fourth generations) open up broad perspectives of the use of chemical methods of analysis (including those usnig organic reagents) for extensive quick analyses in the environmental monitoring, medicine and other fields of science and technology. Further progress in this direction can provide us with the new measurable parameters for such systems and ways of their measurement, as well as with the new instrumental and computing methods, taking into account the intense development of the computing techniques and high technologies.

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