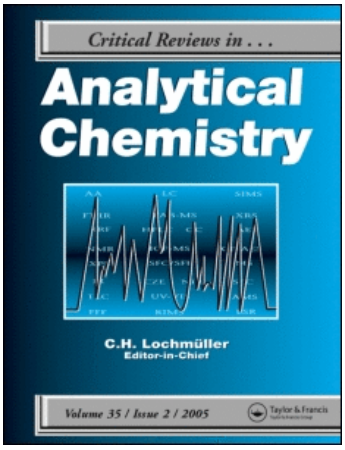

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ORGANIC REAGENTS IN PHOTOMETRIC ANALYSIS

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I. INTRODUCTION

One of the most remarkable properties widely used in chemical analysis is the ability of a metal ion solution or a chemical substance to change its color under the effect of

external factors, most often chemical reactions. Such reactions are known as color reactions. Color reactions of practical value have been found for almost all inorganic ions. It would hardly be an exaggeration to say that until recently almost half of all analyses, particularly in important branches of industry and in agriculture, were based on colorimetric and, later, photometric (or spectrophotometric) techniques.

An ultimate goal in many rapidly developing new branches of industry, such as extraction and processing of mineral raw materials, metallurgy, chemical, nuclear, and semiconductor industries, is the production of highly pure substances. The need to provide for rapid and effective analytical inspection at every stage of production, sometimes involving minute quantities and concentrations of substances, has given impetus to introduction and further development and refinement of spectrophotometric techniques. At a certain stage, these techniques are the only feasible ones.

A number of inorganic reagents are known which have long and successfully been used, and are still in use, as photometric reagents. However, the basic reagents in the photometric analysis of inorganic substances are organic reagents (OR) featuring a number of outstanding properties some of which will be discussed below.

The emergence of physical and physicochemical inspection techniques featuring high sensitivity, selectivity, and other valuable analytical properties (mass spectrometry, automatic quantometry, activation analysis, new methods of polarography, atomic absorption analysis, and others), and their further development have made it topical to evaluate the importance of chemical photometric analysis in general and the use of OR in particular. Such an evaluation of the importance of OR and the promise they hold will be instrumental in guiding chemical research workers in appropriate directions.

We should like to emphasize at this point that we are not going to discuss the use of OR in other fields of analytical chemistry (extraction, concentration, their application as organic ion exchangers and chelating resins, in physical analysis) or processing (fine methods of isolating, separating, and purifying substances). The effectiveness of their application in these fields is obvious, and the bright prospects of their future development are beyond any doubt. We shall consider the application of OR only in the context of photometric determination of inorganic substances.

The basic advantages of spectrophotometry are well known — high sensitivity, in some cases high selectivity, ease in application, simplicity of instrumentation, ready availability of reagents and instruments. At the same time, to enable the solution of many problems related to rapid and routine analyses as part of process control, some other requirements should be met, namely, the possibility of automating analysis in a flow of a liquid or air, obtaining the analysis results as soon as possible and, in some cases, exercising remote control. Spectrophotometry is precisely the technique that in principle solves these problems as well. Furthermore, the solutions should develop direct methods of determining traces of elements without separating them from the substrate. This is presently the main trend in the development of spectrophotometric techniques of determining elements.

The opportunity to develop direct and rapid analysis techniques depends mainly on two factors: selectivity and reliability of the reaction. Reliability, in this case, is meant to be the indifference of the obtained results to minor variations in the reaction conditions (pH, temperature, etc.), as well as the insignificant influence on the basic reaction of other substances present in the solution, such as weak oxidizers and reducers, organic solvents, and salts.

Most reliable results are expected when use is made of organic reagents interacting with elements in highly acidic media which do not require buffer solutions. In this case, apart from the whole procedure of preparing the photometric solution being simplified by directly diluting the solution to be analyzed with an acid (which, for

example, will permit conducting analysis in a liquid flow), the possible false signals associated with hydrolysis of ions, formation of polymer structures, etc. is minimized, which is particularly important in determining some rare and predominantly heavy elements, such as Ti, Zr, Hf, Nb, Ta, and Pa. In recent years, a number of effective ORs have been proposed for use in highly acidic media: arsenazo (III) and analogues, antipyrine and its numerous derivatives, reagents of the triphenylmethane series, etc. The use of these reagents has made it possible to solve most problems involved in determination of heavy elements.

The selectivity of ORs calls for closer scrutiny. We shall only point out that the most important feature of organic reagents, namely, the practically inexhaustible potential to form new analogues of colored compounds and compounds of new classes, gives enough reason to be optimistic about the possibility of synthesis of either absolutely specific reagents or reagents highly selective under certain conditions.

All the foregoing permits a sufficiently high estimate of the prospects of employing ORs in spectrophotometry. However, just like any other technique, spectrophotometry suffers from a number of limitations. One of these is precisely what determines the area of its rational application. Spectrophotometric techniques should preferably be used in determining elements in absolute amounts of from 100 to 0.01 μg or up to 10^{-3}% of an element's content in a substance without separation from the substrate, up to 10^{-4}% with quick separation procedures, and up to 10^{-6}% with preliminary concentration of a particular element.

The possibility of synthesis of new selective and sensitive ORs is determined primarily by the status of the theory of analytical action of ORs. Over the past 10 to 15 years, considerable advances have been made in this direction, which we shall discuss in greater detail. These advances have made it possible to predict reagents' properties, thereby enabling directed synthesis of new reagents exhibiting desired valuable analytical properties.

The works related to the development of the theory of action of organic reagents for spectrophotometry provide explanation, permit prediction, and lead to the creation of new highly effective organic reagents. Also, theories are of utmost importance for developing ORs for other analytical applications, including concentration and separation, i.e., extracting agents and polymer sorbents. The unifying concept is that these other reagents, as a rule, include individual atomic groups or molecular fragments of reagents used in photometry. Therefore, the basic properties of these groups of reagents coincide to some extent. This is often true with respect to the strength of complexes, conditions of their formation, selectivity, etc. Thus, reagents giving color reactions with elements provide an appropriate model for studying properties of ORs used for other analytical purposes. These models contribute to predicting and creating, for example, new polymer sorbents and organic reagents for other analytical applications.

The theory and practice of using organic reagents in photometry have been covered in a great number of exhaustive monographs. We shall make reference only to some of them, mainly those published in recent years, as well as to a number of earlier works that have become classics.[1-30] These works deal with the fundamentals of spectrophotometry, latest developments in theoretical studies of ORs, and synthesis of new reagents and their practical application. In this paper, we tried to avoid, so far as possible, duplication of the contents of the references cited.

II. CURRENT TRENDS IN THE DEVELOPMENT OF SPECTROPHOTOMETRIC TECHNIQUES

A. Literature of Organic Reagents

Certain information on the current status of a branch of science can be provided by

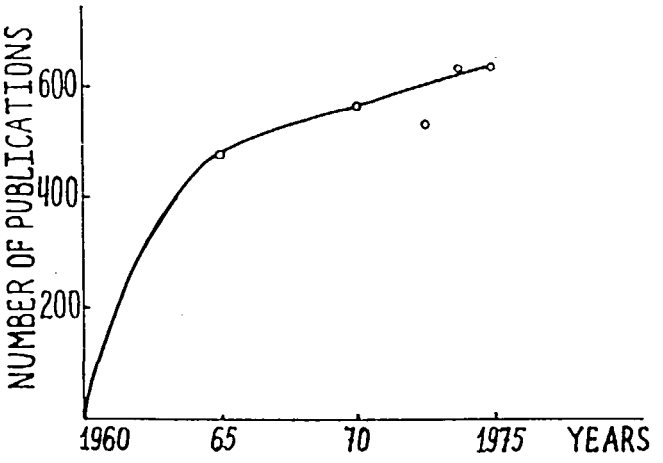


FIGURE 1. Proliferation of publications on organic reagents (according to the number of abstracts in *Analytical Abstracts*).

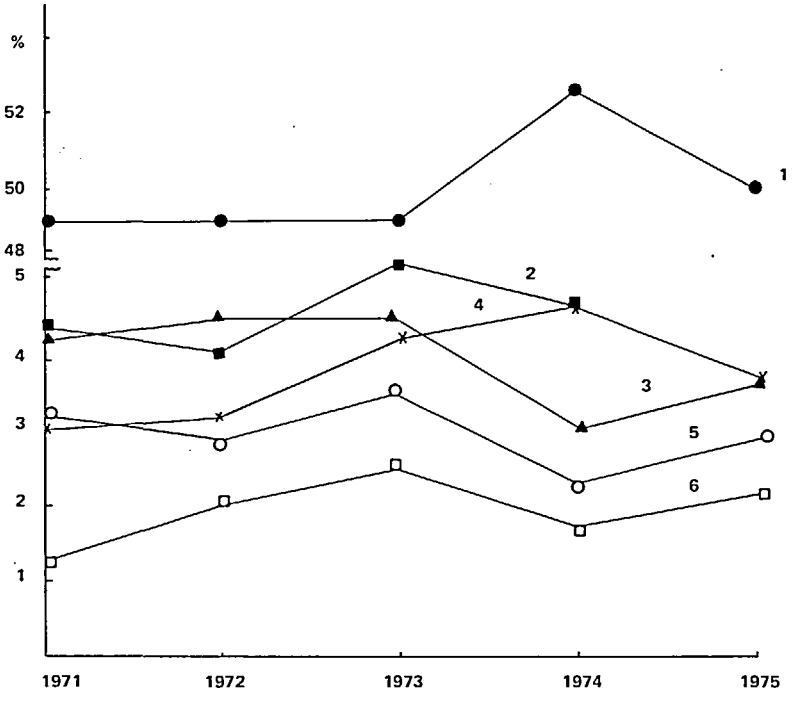


FIGURE 2. Publications on organic reagents in various fields of analytical chemistry: (1) photometry; (2) synthesis and properties of reagents; (3) fluorescence; (4) chelatometry; (5) indicators; (6) titrimetry.

scientometric analysis of the literature on the subject. Curves showing the progress in organic reagents from 1960 to 1975 are shown in Figure 1.[31] The number of publications dealing with studies and general analytical application of reagents varies from 465 to 610 per annum. According to other sources, the number of publications on organic reagents lies anywhere between 1329 (1971) and 944 (1975) with 4300 to 4750 (Reference 32) works being published annually in the field of analytical inorganic chemistry. Figure 2 (Reference 32) is a diagram showing the ratio of publications on

the application of organic reagents in different branches of analytical chemistry. The development of analytical chemistry and its individual branches can be graphically represented, on the basis of data available in the literature, in the form of curves of three types: recession, saturation, and exponential. As can be inferred from Figure 1, studies involving organic reagents have not yet reached the saturation stage and are on the rise. According to Reference 32, the works on ORs account for 22 to 28% of the literature on analytical chemistry.

Photometric analysis is one of the most widely used techniques, and until recently, the total number of publications on the subject was 35 to 40% of the literature on analytical chemistry.[34] By now, the number of works on photometric analysis has gone down to 25%, mainly because of the advent of atomic absorption analysis.[35]

All the above-cited figures, often varying from source to source, are only approximate, for it is impossible to take into account everything written on the subject and because it is not always easy to properly define the field of analytical chemistry to which an extensive treatise belongs. For example, ORs are often used at stages preceding the determination proper of a metal, which can be done using a physical method, etc. Nevertheless, the overall picture is clear enough: organic reagents and photometric analysis play a dominant role in the general subject of analytical chemistry. The development of physical and physicochemical methods does not materially affect the significance of photometric techniques, but this development requires a clearer definition of the areas of the most rational application of each technique.

B. Contrast in Color Reactions

Contrast is one of the most important characteristics of a color reaction, although this term is not yet clearly defined in analytical chemistry and is sometimes confused with sensitivity of a reaction. We say that a reaction has contrast when two solutions, under the same conditions except that one contains an OR and the other, a complex, differ substantially in color. When a new reagent is studied, visual observation is all that is done at the initial stage. If the reaction conditions under which a sufficient contrast is revealed by visual observation are not defined, the use of any advanced spectrophotometers with high resolution will, in most cases, produce no satisfactory results. This is due, first of all, to our eyes being a perfect optical instrument and, secondly, to the fact that the characteristic optical lines or absorption bands normally lie in the visible range of the spectrum, somewhere between 450 and 750 nm, and only in rare cases do analytically significant bands occur in a different spectral region.

The simplest quantitative expression of contrast $\Delta\lambda$, i.e., the difference between the maxima in the absorption spectra of the reaction product (MeR) and reagent (R), in nm, is

$$\Delta\lambda = \lambda_{\max}^{MeR} - \lambda_{\max}^{R} \qquad (1)$$

It is conventionally assumed that a reaction features a low contrast when $\Delta\lambda < 40$ nm, a medium contrast when $\Delta\lambda = 40$ to 80 nm, and a high contrast when $\Delta\lambda > 80$ nm. One should also take into consideration the spectrum shape or diffuseness, which is characterized by the absorption band half-widths. If the complex absorption spectrum has two or more maxima, the value of $\Delta\lambda$ is usually calculated using values of λ that will give the largest difference. The presence of two maxima is typical, for example, of reagents of the arsenazo (III) group. In some cases, the presence of two maxima may be due to the solution containing two complexes of different composition or structure. Many authors consider the principles of selecting the optimum or working wavelength λ in such a manner as to enhance the reaction sensitivity with minimum influence of the excess amount of the reagent, which is always present in excess as compared to

the metal under conditions of determination. Although there exists no rigorous quantitative criteria of selecting an optimum value of λ, investigators have been successfully doing this for a long time on the basis of spectrophotometric data. Therefore, without dwelling on this aspect, let us discuss the possible ways of increasing the contrast in color reactions.

One of such ways is through the use of organic solvents. It is known, for example, that the contrast-enhancing ability of a reagent of the ROH type can be more fully utilized by selecting a solvent promoting detachment of the proton from the hydroxyl groups present in the reagent molecule. Such solvents may be dimethylformamide and dimethylsulfoxide, both of which are sufficiently strong proton-acceptor solvents. They are used, for example, to enhance contrast in the reactions of phenylfluorone and its analogues.[35]

Another way to improve the contrast in color reactions is to change the structure of the reagent itself and, in the simplest case, introduce appropriate substituents into the molecule of the reagent. Usually, these are negative groups such as $-NO_2$, $-Cl$, $-Br$. Alizarin S and most monoazo compounds containing a *O,O'*-dihydroxyazo group react with elements with a higher contrast when $-NO_2$ is introduced.

More complex and less studied is the problem of creating new reagents to ensure contrast in reactions with elements. Solving the problem of predicting organic reagents means finding a mathematical relationship between the structural and the spectral-analytical characteristics of reagents and complexes. The most serious difficulty in solving this problem is the lack of a clear mathematical definition of the characteristics of contrast, sensitivity, selectivity, and other analytical characteristics of color reactions. Therefore, although attempts to elaborate a strict and comprehensive theory of prediction are still being made, the search for new and more promising reagents is, as a rule, carried out by way of comparison of the properties of organic reagents belonging to one or several chemical classes. A good example is provided by enhancement of contrast in color reactions of reagents of the arsenazo (III) group. It has been possible, while retaining the basic carbon skeleton, to synthesize more than 100 organic reagents by varying substituents in the benzene rings, some of these reagents ensuring high contrast in color reactions.[20]

For example, dicarboxybenzene S, a reagent containing two carboxy groups in ortho-positions to the azo groups, reacts with Cu, in aqua-organic media (acetone, propanol), with contrast $\Delta\lambda = 106$ nm and with Mn with contrast $\Delta\lambda = 180$ nm (Figure 3). In this case, two things are used to achieve high contrast: selection of an optimum reagent structure and nonaqueous solvents.[36]

The third and most commonly used way to enhance contrast in color reactions (as well as to improve other analytical characteristics) is the employment of mixed-ligand complexes, which will be described in greater detail in a following section.

C. Sensitivity or Detection Limit

Many relationships have been proposed on how to quantitatively express the sensitivity of color reactions.[37,38] The most universal characteristic seems to be molar absorptivity (or molar extinction coefficient) ε of the analytical product of the reaction. It is generally assumed that if $\varepsilon < 2 \times 10^4$, the reaction features low sensitivity, if $\varepsilon = (2 \text{ to } 6) \times 10^4$, the reaction features medium sensitivity, and if $\varepsilon > 6 \times 10^4$, the reaction is highly sensitive. There is a limit value of ε near 2×10^5, however, it is not yet precisely defined. Reactions are known where ε is assumed to be greater than 2×10^5; these, however, are mostly multiplication reactions where we deal with a sum of several ε. A good practical criterion of the sensitivity of a reaction is the value of "apparent" (or mean) molar absorptivity. Under optimum element determination conditions selected, for example, with a view to attaining maximum sensitivity of determination (pH, pres-

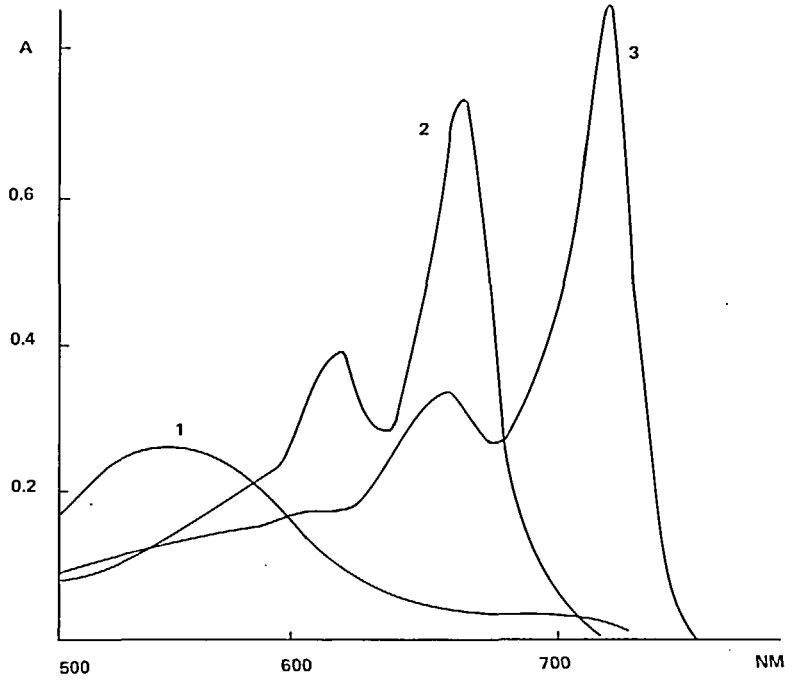


FIGURE 3. Absorption spectra of dicarboxybenzene S in acetone (1) and its complexes with Cu in propanol (2) and Mn in acetone (3).

ence of masking complexing agents, etc.), this value is calculated from well-known formula $\varepsilon = A/cl$. Therewith, we are not interested in the reaction mechanism, yield of the colored compound (which may be less than 100%), possibility of formation of ternary or other complexes, and the possible presence in the solution of several colored complexes of different compositions or structures. Hence, the apparent or mean molar absorptivity expressed in familiar units adequately represents the sensitivity of a particular analytical technique, while its comparison with the true molar extinction coefficient is indicative of the degree to which the sensitivity of determination drops with respect to the sensitivity of the reaction per se.

We can now consider possible ways to improve the sensitivity, distinguishing between the sensitivity of the analytical technique and that of the reaction proper. The sensitivity of analysis can be enhanced by way of concentration, for example, by extraction with organic solvents or by change of absorptivity measurement technique. Reactions of a drop of sample can be conducted by methods permitting the limit of detection of absolute quantities of a substance to be increased by one or two orders of magnitude.[22] The same holds true for microtechniques of quantitative determination of substances, for example, in a drop of solution under a microscope, developed by Alimarin and Petrikova.[4] These and other ways to raise the sensitivity of detecting and to determine an element (or the "detection limit" and "determined minimum" to use the commonly adopted terms) necessitate new techniques of preparing analytical solutions or special instrumentation, which complicates and slows down analysis. In cases where analysis has to be rapid and simple, this is not desirable.

The sensitivity of a reaction depends, first of all, on the molar absorptivity of the reaction product. As a rule, the reaction conditions (pH, type of solvent, temperature, etc.) affect the sensitivity insignificantly. They determine only the yield of the reaction product which, under selected optimum conditions of analysis, is seldom below 70 to 80%. However, the spectral curve (position of the maximum intensity and band half-

width) is known to undergo drastic changes when the reaction conditions (pH, solvent) are altered. These changes are due to the formation of complexes of a different composition or structure. For example, certain reagents, such as azo dyes, are known to interact with the metal by four different mechanisms depending on the reaction conditions.[39] Knowledge of these mechanisms and controlling the reaction conditions is one of the ways to raise the color reaction sensitivity.

Another way to increase the reaction sensitivity is to determine elements with mixed-ligand complexes. It is considered in more detail in Section II. E.

In conclusion we should like to point out that the prediction of sensitivity is one of the most complex problems in analytical chemistry. Chemists normally take an empirical approach in searching for new sensitive reagents, reaction conditions, and third components. The successful results of this search are then applied to other systems, analogues of the known and new reagents, and third components are studied, and so on. It should be noted that a significant advance has been made in the development of highly sensitive color reactions. For some elements, the upper sensitivity limit ($\varepsilon = 2 \times 10^5$) has been attained;[36] similar sensitivity for other elements is expected to be attained in the not too distant future.

D. Selectivity

The notions of specificity and selectivity as well as ways of expressing them are discussed at length in many publications.[40-43]Examination of these problems, however, are beyond the scope of this paper.

In what follows in this review, the term "selectivity" as applied to an OR will be used to imply that a limited number of elements can interact, in principle, with a given reagent, resulting in a color reaction. By the term "selectivity," as applied to a reaction, we mean a number of elements interacting with a given reagent under definite conditions of determination. The term "selectivity" can also be applied to an analysis technique, meaning the increase in selectivity provided by various steps preceding the photometric determination proper (various methods of isolation and separation of substances). We are not going to use this term in the latter context. When we say "higher" (or "improved") selectivity, we mean a decrease in the number of elements in various ionic forms and degrees of oxidation that will react with a given reagent.

Ways to increase the selectivity of a reaction are well known. Primarily, this can be done by varying the pH value. In accordance with some theoretical points of view[44] with oxygen-containing ORs of the R–OH type, color reactions in highly acidic media occur only with those elements whose cations display a strong tendency to hydrolysis, namely, B, Pa, Nb, Zr, Hf, U (IV), Pu (IV), and Th. In moderately acidic solutions, color reactions yield complexes in addition to those of the above-mentioned elements, for example, with Al, Ga, UO^{2+}_2, PuO^{2+}_2, Sc, and others; in weakly acidic and neutral media, they yield complexes of rare-earth elements, for example, VO^{2+}, Mo, Cu; and in alkali media, those of Zn, Ba, Sr, Ca, Mg, etc. This series, of course, has no absolute value. The reaction conditions are determined by the nature of OR and other factors. However, in most cases, determination of easily hydrolyzable elements in highly acidic media is more selective. Thus, taking into account the nature of ions of elements is an important factor in increasing the selectivity of reactions.

Another universal way of enhancing selectivity is through the use of masking agents, including chelates, which are steadily increasing in number and variety.[10,17] This way is also universal in that a situation is possible where a particular element is masked. By measuring the absorbance of a solution before and after adding the masking agent, one can evaluate the interference caused by the presence of other elements (for example, masking of UO^{2+}_2 with potassium hexametaphosphate in the case of its determination with the aid of reagents of the arsenazo type).

A promising method of increasing selectivity, which may eventually become universal, is determination of an element within a mixed-ligand complex. More and more publications are concerned with this particular approach. We shall make reference below only to one of the latest.[45]

The use of nonaqueous solvents also leads to higher selectivity of color reactions in some cases, but this method has not yet been properly studied, and therefore, its application is limited.

The selectivity of a reaction can also be improved by a reagent being used both for extraction and photometry rather than preliminary extraction followed by determination of an element. Evidently, one should distinguish between extraction of chelate compounds and that of ionic associates. Chelation[46] has been applied to practically all reagents of different classes, even those readily soluble in water.[47] This method resides in extraction of the diphenylguanidine salt of a respective chelate compound with butyl or amyl alcohol followed by photometry of the extract without any additional steps involved. It has become possible to use other heavy organic cations (for blocking sulfo groups) as well, plus organic solvents, which has substantially widened the scope of application of this method. The higher selectivity is due to the fact that complexes of only some metals, even if the latter were formed in the aqueous phase, are susceptible to extraction.

Basic dyes in extraction-photometric analysis based on extraction of an element taken as a complex anion and a basic dye taken as an ionic associate into an organic phase with subsequent photometry is an independent and broad field of analytical chemistry, equally related to extraction and photometric techniques of separation and determination. We will not dwell on this method in this review, limiting ourselves with reference to a few monographs.[14,18]

Above, methods of improvement of the selectivity based on chosen conditions and technique of determination have been considered. Selectivity of an organic reagent itself is determined by the structure of the reagent and by the nature of the functional-analytical group. This notion and its transformation are discussed below.

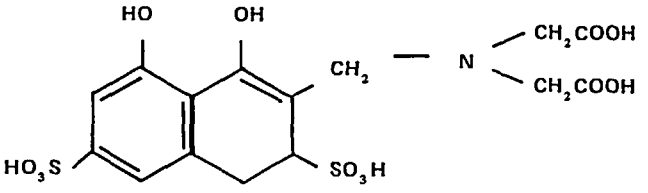
Since the number of possible functional groups is limited (only about a hundred groups have been described and adequately studied so far), a great deal of attention is being centered on increasing the selectivity of reagents with a particular group of interest. West[48] and others point out that one of the most common ways of enhancing the selectivity of a reagent is the introduction of substituents, or sterically hindering groups, into the molecule close to the chelation center. The introduction of various substituents such as analytically active groups into the molecule is another widely used approach to increase selectivity. However, theoretical studies throwing light upon but a few individual cases have not yet resulted in a general theory permitting the nature and position of the introduced substituents to be related to the selectivity of reagents, i.e., they have no predictive value.

In the work of Dziomko,[49] he notes that the main difficulty in attaining high selectivity with the use of chelates resides in the ability of metal ions to adapt to the coordination requirements of all ligands. In this connection, the Schwarzenbach principle (meeting the coordination requirements of a given ion so far as possible) will probably have to be additionally elucidated. Dziomko's newly proposed principle calls for at least minimum compliance with the geometric and donor-acceptor requirements of an ion with other metal ions meeting the same requirements.[50]

One of the most interesting and promising ways to attain high selectivity, or even specificity, is through synthesis and use of ORs with the molecule performing the function of a chelate ring that can accommodate only ions with particular coordination abilities. A good example is provided by West.[48]

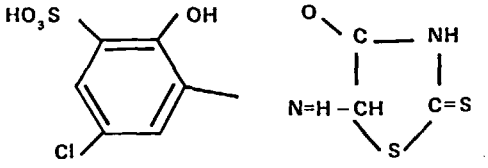
Another way to improve the selectivity of a reagent is to introduce into its molecule,

along with the basic functional-analytical group, another complexing group (e.g., of the imidodiacetic acid type) which would bind ions of other elements present in the solution. Such reagents are, for example, berillons III and IV[51] and HIMDY:[52,53]



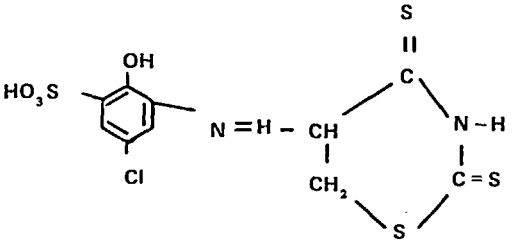
1,8–Dioxynaphthalene–3,6–disulfonic acid–2–methylimino–) acetic acid

A widely used technique to provide selective reagents is the synthesis of reagents with heterocyclic rings containing S, P, N, and other atoms, forming functional-analytical groups interacting with only some groups of elements. Consider just two examples from Reference 54:



Sulfochlorophenolazorhodanine

	Conditions	ε
Pt (IV) 3 *M*HCl		3.2×10^4
Pt (IV) 2 *M*H_3PO_4	+ 2 *M*H_2SO_4	1×10^5
Rh (III) 14 *M*H_2SO_4	+ 6 *M*CH_3COOH	3.5×10^4
Ir (IV) 10 *M*H_2SO_4	+ 6 *M*CH_3COOH	4×10^4
Pd (II) 5 *M*H_2SO_4	+ 8 *M*H_3PO_4	12×10^4
Au (III) 1 *M*HCl		5.2×10^4
Ag (I) pH 8 to 10		2×10^4



Sulfochlorophenolazothiopropiorhodanine (thirhodine)

	Conditions	ε
Pt (IV) 5 *M*H_3PO_4	+ 2 *M*CH_3COOH	6.5×10^4
Au (III) 3 *M*H_2SO_4	+ 3.5 *M*CH_3COOH	2.5×10^4
Ag (I) 10 *M*CH_3 COOH	+ 1 *M*H_3PO_4	5.3×10^4

Still another possible way to increase selectivity has nothing to do with changes in the chemical structure of the reagent molecule, but involves its various conformations.

TABLE 1

Development of Analytical Reactions — Types of Products and Their Approximate Time of First Usage

1955[55]	1965[56,57]	1970[58,59]	1975[45,60,61]
[MeB$_n$R$_n$]	[MeR$_n$R'$_n$]	[MeB$_n$] [Me'R$_n$]	[MeR$_n$] [Me'R'$_n$]
(BH)$_n$[MeR$_n$]	[MeB$_n$] R$_n$	[(BH)$_n$] [MeR$_n$R$_n$]	[Me(HR)$_n$] R$_n$R'$_n$
	[MeMe'R$_n$]	[MeR$_n$B$_n$] R'$_n$	[MeR$_n$R'$_n$] (H$_n$R)$^+$
	Ternary hetero-polyacids	[MeR$_n$R'$_n$] R"$_n$	[MeR$_n$R$_n$B$_n$] (BH)
		[MeR$_n$B$_n$B'$_n$]	[MeMe'R$_n$R'$_n$]
		[MeMe'R$_n$B$_n$] R'$_n$	[MeB$_n$R$_n$] [Me'R'$_n$]
		[MeR'$_n$R"$_n$R$_n$] (BH)	[MeR$_n$R'$_n$R"$_n$]

Note: Me, metal ion; B, organic base; R, electronegative reagent.

In fact, the above-mentioned four types of reactions between elements and azo dyes represent intereaction of elemental cations with various reagent conformers (or their formation in the process of complexing). Having studied an appropriate mechanism, one can select the right conditions for formation of a complex with the conformer whose reaction with a metal yields a most sensitive product.

Hence, it can be seen that there are many ways to enhance selectivity, some of which hold sufficient promise. At the same time, there has not yet been developed a universal approach that would offer an unambiguous solution of the problem of directed synthesis of OR specific to each element. All the above-mentioned methods of increasing selectivity require additional elaboration, accumulation, and generalization of data so that the established regularities could have a predictive value.

E. Heteroligand Complexes

Transition from binary Me-OR to ternary and more complex systems is one of the most effective ways to improve almost all analytical characteristics of color reactions. Since the early 1950s, this approach has been widely implemented in chemical analysis. By way of illustration, Table 1 shows the dynamics of this process.[45] The most widely used group of compounds in the acid dye-metal ion-organic base system are compounds of organic cations with metallochrome chelates.[45]

The role of cations in such compounds boils down to neutralization of excess electronegative charges in the reagent, due to the presence of sulfo groups.[48,58] or dissociated hydroxy groups which do not take any part in chelation.[62,63] A survey of the literature indicates that more than 40 dyes are used as the metallochrome reagents, about 20 organic cations are used for neutralizing the excess electronegative charges, and methods of determining more than 30 metal ions are known.[15,18,24,45,64,65]

Without dwelling on compounds of the above type, which are described in greater detail in numerous papers, let us now consider the application of surfactants in photometric analysis. It would be wrong to say that this approach is entirely new, but very interesting results were obtained and the mechanism of action of these compounds was revealed only recently. Earlier, descriptions appeared of such long-chain quaternary ammonium and pyridinium bases as cetyltrimethylammonium,[66,67] cetylpyridinium,[77-85] zephyramine,[86-89] and polyhydroxyethylated esters of alkyl phenol.[90] For analytical purposes, preference is given to water-soluble low-molecular surfactants, both ionogenic (cation- and anion-active) and nonionogenic.

Cation-active surfactants include salts of long-chain aliphatic primary, secondary and tertiary amines $R_1NH_2H^+Cl^-$, $R_1R_2NH^+HCl$, $R_1R_2R_3^+NHCl$, quaternary ammo-

TABLE 2

Some Characteristics of Color Reactions of Metals with OR and Cetylpyridinium

Reagent	Ion of interest	pH	Δλ (nm)	ε = n× 10⁴ MeR	ε = n× 10⁴ MeRsurfactant
Pyrocatechol violet	W	1—3	210	4	8
	Mo	2—4	220	3.7	15
	Ti	2—4	280	—	9.2
	Al	2—4	240	2.3	5.7
	Cu^{2+}	6—8	250	1.7	4.2
Chromazurol S	Cu^{2+}	6—8	180	3.5	7.1
	Al	5—7	190	4.6	15
	Fe (III)	4—7	190	1.2	5.7
Eriochromocyanine R	Cu^{2+}	6—8	150	1.6	3.5
	Al	4—8	140	3.1	3.8
Sulfochrome	Fe (III)	2—4	110	2.7	5.1
Disulfophenylfluorone	Ti	0.5—3	150	—	12
	Zr	1—3	130	—	10
Xylenol orange	REE	3—10	160	—	6.5
	Fe (III)	4—5	180	1.2	9.6
	V (IV)	2—4	160	0.3	4.6

nium bases $R_1R_2R_3R_4^+NCl^-$, salts of alkyl pyridinium and a number of other nitrous bases, such as imidazoline, imidazole, pyrimidine, oxazoline, and others. Also known are cation-active surfactants containing no nitrogen, such as sulfonium, phosphonium, and thiouronium compounds.

Anion-active surfactants include alkyl sulfonates RSO_3Na, alkylaryl sulfonates $RC_6H_5SO_3Na$, alkyl sulfates RSO_4Na, and related compounds containing, in their chain, additional polar groups (carbamide, ester, and other groups).

Nonionogenic surfactants include hydroxyethylated fatty acids, stearic and glyceric esters, esters of triethanolamine, organic acids and alkyl phenols, hydroxyethylated high-molecular alcohols, block copolymers of propylene and ethylene oxides, polyethylene derivatives of alcohols, polyethyleneglycol derivatives of acid amides, amines, propylene oxide, etc.

The introduction of cation-active surfactants, particularly those containing a quaternary nitrogen atom and a cetyl radical in the metal ion-reagent system, results in sharp changes in the reaction contrast at appropriate pH values, and, in some cases, in higher sensitivity. Table 2, according to Chernova,[91] lists certain studied systems, while Figures 4 to 6 show their absorption spectra. Note the high contrast and sensitivity of some reactions.

Another area of analytical application of surfactants is the determination of the OR percentage in their preparations. This method is based on formation of deeply colored ionic associates, base triarylmethane dyes, and anion-active surfactants. Analysis may be conducted by way of conventional spectrophotometric titration. The advantage over titration with metals is that the composition of the forming ionic associates is unambiguously determined by the condition of the reagent at a selected solution pH value. When use is made of cation-active surfactants, for example, cetylpyridinium (CP), analysis becomes universal owing to the uniformity of interaction of ORs with them. In other words, one titrant can be used to titrate a great number of organic reagents.

Literature offers certain considerations as to the chemical mechanism of these analytically interesting reactions.[71,72,91,92] As is known, surfactants, at certain concentrations (critical micellation concentration), form micelles which may be responsible for the observed effects. However, various types of surfactants and reagents exhibit dif-

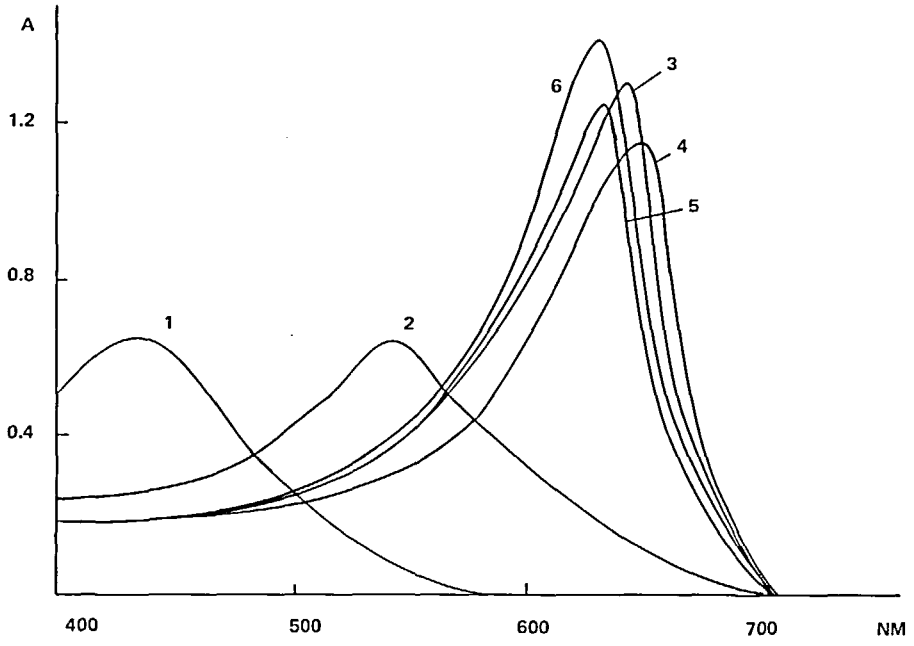


FIGURE 4. Absorption spectra of chromazurol S (1), its complexes with Al in the absence (2) and in the presence of nonionogenic surfactants: (3) OP-10; (4) syntanol DT-7; (5) syntanol DC-10; (6) OS-2P; pH 6.0; [OR] = 0.8×10^{-4} *M*; [Al] = 1.2×10^{-5} *M*.

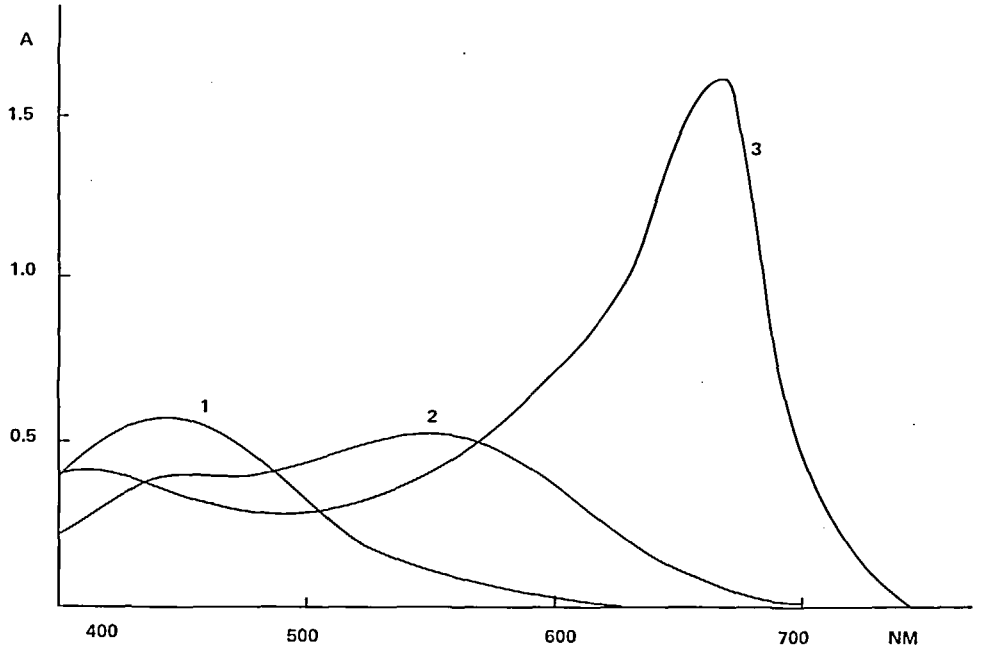


FIGURE 5. Absorption spectra of pyrocatechol violet (1), its binary complex with W (VI) (2) and its ternary complex with cetylpyridinium (3); [OR] = [W] = 4×10^{-5} *M*; [CP] = 2×10^{-4} *M*, pH 1.1.

ferent chemical mechanisms. It has been established, for example, that cation-active surfactants and OR of the pyrocatechnol violet type react at a surfactant concentration below the critical micellation concentration. It has been proposed that compounds

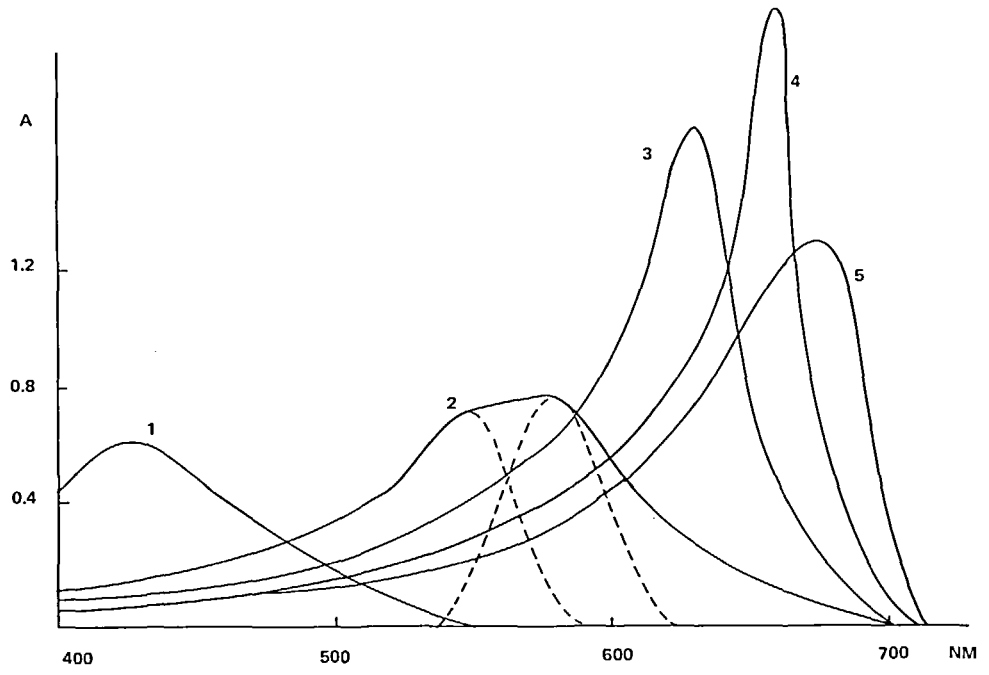
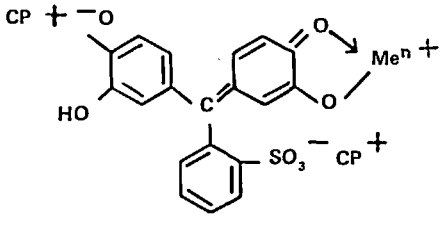


FIGURE 6. Absorption spectra of chromazurol S (1), its complexes with Be (2), Be and OP-7 (3), Sc and syntanol DS-10 (4), Fe^{3+} and OS-20 (5), and [OR] = 0.4×10^{-4} *M*; surfactant = 0.01%; [Me] = 0.8×10^{-5} *M*, pH 6.0.

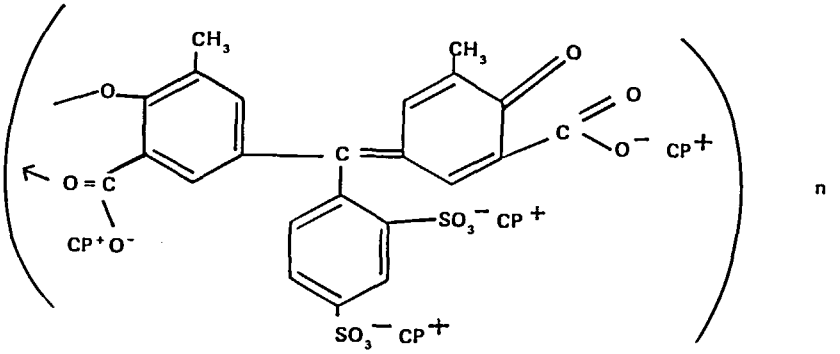
similar to ionic associates are formed, which are widely used in extraction-photometric analysis.[93] The sharp change in color, however, is indicative of interaction of cation-active surfactants with the OH- and COOH-groups of the reagent molecule, rather than with the sulfo groups. Associations of surfactants with reagents persist even in the case of complexing of the latter with metal ions, and the corresponding structure of the complex — associated with, for example, pyrocatechol violet — takes the following form:



In this and similar cases, the surfactant ions act as agents additionally affecting the π-electron system of reagents by forming associates with the hydroxyl oxygen symmetrical with the carbonyl oxygen which is an auxochrome, such an interaction leading to a bathochromic shift of the long-wave absorption band.

A somewhat different picture is observed in the case of chelates of phenol-carbonic acids of the triphenylmethane series. In the absence of surfactants, these reagents normally yield several products of interaction with metal ions, with carboxyl groups also participating in their formation.[94] The addition to such systems of cation-active surfactants leads to blocking of the carboxyl groups due to the formation of associates and transformation of phenol-carbonic acids from polyfunctional reagents to monofunctional ones, since only a single complexing group remains vacant, namely, the phenolic hydroxyl and the carbonyl oxygen of the −COOH group, which is in an ortho position

to the former. Thus, instead of several possible types of metal coordination, a single one remains, which results in formation of a heteroligand chelate of the following composition:



where n equals 1 to 3. Consequently, it may be assumed that in the case of phenolcarbonic acids of the triphenylmethane series, the role of surfactants resides not only in affecting the π-electron system of the reagent, but also changing the character of coordination of the metal atom in the presence of surfactants. The appearance of a narrow, high-resolution absorption band and the high molar absorptivity are determined by the peculiarities of this structure. The decisive factors seem to be the strong polarizing action of the metal, asymmetry of the molecule, and other features of the electronic structure of the complex.

In the case of nonionogenic surfactants, the mechanism of their reactions with both reagents and complexes is somewhat different. Respective color reactions are observed only after the critical micellation concentration of surfactants is attained, i.e., the corresponding processes probably occur in the micellar phase.[91,92,95-97]Such processes of shifting equilibrium as a result of local concentration of a substance on the surface of micelles are known under the general term "micellar catalysis." At present, these reactions are extensively studied by organic chemists and biochemists, for they simulate enzymatic processes. In this case, the essence of micellar-catalytic reactions boils down to the ability of nonionogenic surfactants to specifically interact with the reagent in a micella. In the case of chromazurol S, such interaction involves carboxyl groups and leads to their blocking. The latter materially affects complexing of chromazurol S with metal ions, since the interaction mechanism undergoes changes resulting in a reaction product featuring the longest wave absorption band.

The use of surfactants in combination with ORs is a good example of the fact that the analytical potentialities of even well-known reagents are far from being exhausted and that tapping of new ideas from related fields of science can substantially improve the principal analytical characteristics of entire classes of ORs.

F. Spot Analysis

Organic reagents form the basis of spot analysis techniques, the development of which an important contribution has been made by Tananaev and Feigl. The simplicity of spot analysis, which requires only rudimentary equipment and small amounts of chemicals (which can be selected in a great variety), as well as the possibility of conducting analysis under widely varying conditions on diverse substrates, have made it possible to develop selective techniques of detecting practically every element in the presence of a great number of different substances. These techniques also feature high sensitivity and rapidity that cannot be achieved by many other methods of chemical analysis.

The above features of spot analysis determine the areas of its preferable application.

These include, first of all, qualitative or semiquantitative analysis of materials under field conditions: minerals and ores found by geological field crews, soils, natural water, etc. Another area is inline monitoring of production processes (chemical or metallurgical), processing of mineral raw materials, etc., in other words, in cases where it is important to confirm the presence or absence of an element or compound at a particular stage of the process. Spot analysis may also be of value in environmental pollution control where individual or specially taken samples of water or air are checked for the presence of impurities. In our opinion, spot analysis will retain its importance in these particular cases and, despite the steady proliferation of physical techniques, deserves close attention.

Although all ORs suitable for spectrophotometric quantitative analysis can be used in spot analysis, some of their properties are particularly essential for the latter. They include: contrast in reactions, which determines the sensitivity of analysis; possibility of color reactions to be conducted under widely varying conditions, e.g., in highly acidic media; and, of course, selectivity. Note that such spot analysis techniques as the use of different substrates, various procedures of applying solutions, and others permit the number of possible ways to enhance selectivity to be considerably increased as compared with the above-mentioned ones. A more detailed description of spot analysis can be found in Reference 22.

G. Optimum Combination of Reagents for Determining Individual Elements

Owing to advances in synthesis, the number of ORs proposed for determining individual elements steadily increases and may be as high as several thousand, although it is difficult to give the precise figure. Therefore, the main difficulty for an analytical chemist, despite the availability of a number of reviews, is not to find an appropriate reagent for a particular element, but to choose the best of many. This difficulty is not merely technical, but stems from the fact that it is not always clear from literature sources whether a new compound under consideration is an effective reagent relative to a given ion or whether the author simply mentions it along with other compounds, often analogues of a known reagent, to provide a full picture of interaction of similarly structured reagents with ions of elements, which is of theoretical interest. Therefore, in recent years a great deal of attention has been focused by publications containing comparative analytical data on the efficiency of using ORs for individual element determinations.

The principal criteria governing the selection of a reagent are (1) sensitivity expressed in terms of the molar absorptivity, (2) stability of the reaction product, expressed in terms of the instability constant, (3) and limiting dilution associated with both criteria, selectivity relative to anions, and pH of the maximum complex yield (as a rule, more valuable reagents permit elements to be determined in a more acidic medium). No less important criteria are reaction contrast $\Delta\lambda$, effect of the reagent at the optimum (working) wavelength ($\varepsilon_{MeR} - \varepsilon_R$ or $\varepsilon_{MeR}/\varepsilon_R$ at λ_{opt}), selectivity relative to cations, and other characteristics, such as equilibrium restoration rate, stability of the reagent and reaction product to oxidants, reductants, and other external agents, extractability of the complex, etc.

The selectivity of an organic reagent is one of the most important criteria, as far as its analytical significance is concerned. At the same time, the number of specific or highly selective reagents known so far is very limited. Therefore, in most recent works, the problem of providing, for each element, a group of reagents complementing one another in selectivity is discussed more often. Depending on the anticipated content of other elements in a substance of interest, a particular reagent is used or, if possible, one of the reagents is used for separation and the other, for determining an element.

For example, in the case of Zr, the complementing reagents are arsenazo (III) and

TABLE 3

Group Reagents for Photometric and Extraction-Photometric Determination of Elements

Reagent	Elements entering into reactions
Chromazurol S	Be, Al, Ga, Zr, Th, Fe, V, Cu, Mn, Sn, Ti
Antipyrine S	Be, Ca, Cu, Ni, Zn, La, Ce, UO_2^{2+}, Th, Al, Ga, In, Zr, Sc
Arsenazo (I)	U, Th, Zr, Sc, REE, Al, Be, Ti, Nb, B, In
Arsenazo (III)	Th, Zr, Hf, Np, Pu, Pa, U, Sc, REE, Pd, Ca, Pb
Arsenazo M	REE, Cu, Pb, Ca, Sr, Th, Ba, Bi, Zr, Hf, Mg, Al, Zn, Cd, Ga, In, Mn, Ni, Ru, V
Dithizone	Pb, Zn, Cd, Hg, Ag, Cu, Bi, Pd, Mn, Fe, Co, Ni, Au
Sodium diethylthiocarbamate	Ti, V, Cr, Mo, Mn, Fe, Co, Ni, Cu, Ru, Rh, Ag, Os, Ir, Pt, Au, Ti, Bi, Pd
Xylenol orange	Al, Be, V, Bi, Ga, Zr, Fe, Cd, In, Cu, Mo, Nb, Sn, Pd, Pb, Tl, Ti, Th, U, Hf
Methylthymol blue	Al, V, Ga, Fe, In, REE, Ca, Mg, Mn, Cu, Ni, Pb, Ti, Th, Zn, Zr
Pyridylazoresorcin	Nb, Ta, Co, Pd, In, Ga, REE, Cu, Zn, Cd, Tl, Sc, Th, Pb, Bi, U
Sulfochlorophenol S	Nb, Zr, Sc, Mo, Al, Ga, In, Cu, V
Thoron (I)	Th, U (IV), Zr, Be, Sc, Pu, Np

sulfochlorophenol S. Arsenazo (III) enables Zr to be determined in the presence of Nb, Mo, and Cu with strong interference on the part of Th, U, and rare earths. Sulfochlorophenol S, on the other hand, permits Zr to be determined in the presence of Th, U, and REE with interference on the part of Nb, Mo, and Cu. Such pairs of reagents can be selected for many elements. If a solution is complex and all elements are present or if its composition is not known beforehand, one of the complementing reagents can be used for separating the element of interest (e.g., by extraction of Zr together with Nb, Mo, and Cu), whereafter Zr is determined in the extract with the aid of arsenazo (III). In this case, the elements extracted together with Zr do not interfere.

Implementation of this approach, i.e., selection of a group of reagents for determining each element, permits wide use of only a few synthesized reagents or group reagents. Each one is suitable, in principle, for determining several elements and forms part of the group of reagents intended for determining each element. Therewith, the required selectivity for each element is ensured by providing adequate determination conditions (pH), employing masking complexing agents, etc. Another advantage of using a limited number of group reagents in analysis resides in the fact that such widely used reagents are studied most extensively. This permits minor elaboration of an existing optimum procedure in order to determine each element even in new complex substances. Table 3 lists some of the most important group ORs used in spectrophotometric determination of elements, as well as elements with which they enter into specific color reactions. Reference can be made to a number of monographs and reviews[7,8,15,20,24,25,29] in which the properties of these reagents are described in greater detail and in which one can find exhaustive bibliography on their analytical application.

To provide an optimum combination of reagents for determining individual elements is a complex task involving tedious work, for a host of scientific and industrial factors must be taken into consideration. In the U.S.S.R., a number of institutions

and individual investigators are involved in this work. For example, the Institute of Chemical Reagents and High-Purity Compounds in cooperation with some universities conducts analytical testing and comparison of ORs of various analytical applications with a view to selecting the best. The results are published in the proceedings of the Institute and special brochures.[98] The Institute of Geochemistry and Analytical Chemistry publishes two series of monographs: *Analytical Reagents*[25,27] and *Analytical Chemistry of Elements.*[99] The data disclosed in these publications as well as in other papers, reviews, and books[6,7,15,18,20,21,24,29,100-115] are summarized in Table 4 which lists reagents recommended for determining individual elements.

TABLE 4

Organic Reagents Recommended for Spectrophotometric and Extraction-Photometric Determination of Elements

Element	Reagent	Reaction conditions	Molar Absorptivity or sensitivity (in Sandell units, $\mu g/cm^2$ or $\mu g/ml$)	Selectivity
Li	Quinolinazo	KOH	1.2×10^4	Low
	Thoron (I)	2% NaOH	1×10^4	Low
	Nitroanthranilazo	KOH	0.7×10^4	None
Cu (II)	Picramine M	0.1 *N*HCl	3.3×10^4	High
	Picramine R	0.7 *N*HCl	2.8×10^4	High
	Sodium diethyldithiocarbaminate	pH 4.5—11	0.004 $\mu g/cm^2$	High
	o-Tolidine	pH 5	0.004 $\mu g/cm^2$	Middle
Cu (I)	2,9-Dimethyl-1,10-phenanthroline	pH 4—6	0.008 $\mu g/cm^2$	High
	2,2-Diquinolyl	pH 6	0.01 $\mu g/cm^2$	High
Ag	Dithizon	0.5 *N*HNO_3	2.7×10^4	Low
	5-(*p*-Dimethylaminobenzylidene)-rhodanine	0.05 *N*HNO_3	2×10^4	Low
	Sulfochlorophenolazorhodanine	pH 2—6	2×10^4	Middle
	Thyrodine	10 *M* CH_3COOH + 1 *M* H_3PO_4	5.3×10^4	High
Au	5-(*p*-Dimethylaminobenzylidene)-rhodanine	0.1 *M*HCl	0.1—0.9 $\mu g/ml$	Low
	Sulfochlorophenolazorhodanine	5 *M*H_3PO_4 + 1 *M*HCl	5×10^4	Middle
Be	Chromazurol S + surfactant	pH 6	1.5×10^5	Middle
	Arsenazo (I)	pH 6—7	0.02 $\mu g/ml$	Low
	Sulfochlorophenol S	pH 6.3	3.5×10^4	Low
	Beryllon (IV)	pH 6—7.9	0.02 $\mu g/ml$	Low
	Alberon	pH 5	0.025 $\mu g/ml$	Low
	Beryllon (II)	pH 12—13	0.04 $\mu g/ml$	None
	Thoron	pH 9—12	0.5 $\mu g/ml$	None
Mg	Magneson	pH 9—12	3.4×10^4	None

TABLE 4 (continued)

Organic Reagents Recommended for Spectrophotometric and Extraction-Photometric Determination of Elements

Element	Reagent	Reaction conditions	Molar Absorptivity or sensitivity (in Sandell units)	Selectivity
	Chromotrope 2R	1—2 *N* NaOH	3.7×10^4	None
	Phenazo	1—2 *N* NaOH	3.5×10^4	Middle
	Titanium yellow	pH 12	3.6×10^4	Middle
Ca	Calcion	pH 12	0.8×10^4	Middle
	Glyoxal-bis-(2-hydroxyanil)	0.04 *N* NaOH	1.8×10^4	Middle
	Murexide	pH 12.5	1.4×10^4	Low
	Chlorophosphonazo (III)	pH 7	6.4×10^4	Low
	Arsenazo M	pH 4—6	5×10^4	Low
	Thymolphthalexon	pH 9—12	4×10^4	Low
Sr	Nitroorthanil S	pH 2.8	0.02 μg/m*l*	Low
	Orthanil S	pH3.5	0.01 μg/m*l*	Low
	Chlorophosphonazo (III)	pH 4.6	0.1μg/m*l*	Low
	Carboxynitrazo	pH 5	15×10^4	Low
	Arsenazo M	pH 4—6	4.4×10^4	Low
Ba	Carboxynitrazo	pH 5	1.5×10^4	Low
	Orthanil S	Ph 2—8	5.8×10^4	Low
	Orthanil B	pH 6	6.1×10^4	Low
	Nitroorthanil S	pH 2—6	6.3×10^4	Low
	Chlorophosphonazo (III)	pH 5.6	0.1 μg/m*l*	Low
	Arsenazo (III)	pH 4—6	3.8×10^4	Low
Zn	Dithizon	Ph 5—8	9.2×10^4	None
	Zincon	pH 8.5—9	1.4×10^4	Low
	n-Methylanabasine-*α*-azo-*β*-naphthol	pH 6—6.5	4×10^4	Low
	5-Nitrophenol-(2-axo)—2-(acetylhydrosino)-naphthalene	pH 6—9	3.8×10^4	Low
B	1,1′-Dianthrimide	95% H_2SO_4	3.3×10^4	Middle
	Curcumin	Concentrated H_2SO_4	1.8×10^4	Low
	Quinalizarin	94% H_2SO_4	1.1×10^4	Middle
	Carmine	Concentrated H_2SO_4	0.8×10^4	Middle
Al	Chromazurol S + surfactant	pH 6	1.4×10^5	Middle
	Aluminon	pH 4.4—5.5	1.7×10^4	Low
	Xylenol orange	pH 3.4	2.1×10^4	None
	Methylthymol blue	pH 3—3.5	1.9×10^4	None
	Pyrocatechol violet	pH 6—6.2	6.8×10^4	None
	Stilbazo	pH 5.4	3.4×10^4	Low
	Sulfochlorophenol S	pH 3.5—4	3.4×10^4	Low
	Eriochromocyanine K	pH 6—6.6	5.7×10^4	Low

TABLE 4 (continued)

Organic Reagents Recommended for Spectrophotometric and Extraction-Photometric Determination of Elements

Element	Reagent	Reaction conditions	Molar Absorptivity or sensitivity (in Sandell units)	Selectivity
Ga	Alizarin S	pH 4	0.8×10^4	Low
	Xylenol orange	pH 1—5	$1.6—2.6 \times 10^4$	Low
	Sulfochlorophenol S	pH 3	4.1×10^4	Low
In	Methylthymol blue	pH 3.6—4.3	2.1×10^4	Low
	Surface-active reagent	pH 4—5	—	Low
	Phenylfluoron	pH 3.5	4.9×10^4	Low
	Sulfochlorophenol S	pH 3.5	4.0×10^4	Low
Tl	Pyridylazonaphthol	pH 2.2, 50% methanol	2.2×10^4	Middle
	Pyridylazoresorcin	pH 2.2	1.9×10^4	Low
	Sodium 3,5 diphenyl-pyrazoline-1-dithio-carbomate	pH9	2×10^4	Low
	Bismuthol (II)	pH 2.3	2.8×10^4	Low
Sc	Xylenol orange	pH 4.6	3×10^4	None
	Arsenazo (III)	pH 2.2	1.5×10^4	Low
	Sulfochlorophenol S	pH 2.2	1.2×10^4	Low
	Chlorophosphonazo (III)	pH 2.5	1.2×10^4	Low
I	Arsenazo M	pH 3.3	6.7×10^4	Low
	Xylenol orange	pH 5.5—6	0.6×10^4	None
	Arsenazo (III)	pH 3	5.5×10^4	None
	Arsenazo (I)	pH 6—7	2.2×10^4	None
La and lanthanides	Arsenazo M	pH 3—4	$7.5—8.5 \times 10^4$	Low
	Arsenazo (III)	pH 1—4	$5.5—6.5 \times 10^4$	Low
	Xylenol orange	pH 4—7	$3.3—4.3 \times 10^4$	Low
	Carboxynitrazo (Ce)	pH 2—4	$1—1.6 \times 10^5$	Low
	Stilbazo	pH 7—8	1.2×10^4	
	Antipyrine S	pH 2.5	1×10^5	Low
Ti	Diantipyrylmethane	1—6 *N*HCl	1.8×10^4	Middle
	Dichlorochromotropic acid	pH 1—2	1.1×10^4	Middle
	Disulfophenylfluoron	pH 6	1×10^5	Middle
	4-Nitrobenzene C + H_2O_2	CH_3COOH	1×10^5	Middle
Ge	Phenylfluoron	1 *N*HCl	3.8×10^4	Middle
	Dihdroxyphenylbenzo-pyranol	0.1—0.6 *N* HCl	2.5×10^4	Middle
Mo	Dithiol	4—12 *N*HCl	2.1×10^4	High
	Sulfonitrophenol K	pH 2.5—4	5×10^4	Middle
	Pyridylazoresorcin	pH 6—7	2.7×10^4	Low
	Stilbazogall	pH 1.5	2.8×10^4	Middle
	Resarson	0.5-2.5 *N* HCl	1.3×10^4	Middle
	Lumogallion	pH 1—5	1.2×10^4	Middle

TABLE 4 (continued)

Organic Reagents Recommended for Spectrophotometric and Extraction-Photometric Determination of Elements

Element	Reagent	Reaction conditions	Molar Absorptivity or sensitivity (in Sandell units)	Selectivity
W	Pyrocatechol violet + surfactant (CP)	pH 1—1.5	4.4×10^4	High
	Dihydroxychrominols	pH 2	9.3×10^4	Low
	Sulfonitrophenol S	pH 1, H_2O_2	3.8×10^4	Middle
	Magneson XC + H_2O_2	1 *N*HCl	2×10^4	Middle
	Dithiol	6 *N*HCl	2×10^4	High
Ru	4-Nitrosodimethylaniline	pH 4.1	0.3 μg/m*l*	None
	Thiourea	HCl, ethanol	2μg/m*l*	Low
Rn	Pyridylazoresorcin	pH 6.2—6.5	4 g/m*l*	Low
	2-mercapto-4,5-dimethylthiazole	Concentrated HCl	1 g/m*l*	Middle
	Sulfochlorophenolazorhodanine	14 *M* H_2SO_4 + 6 M CH_3COOH	6.5×10^4	Middle
Pd	Sulfonitrophenol M	4 *N*$HClO_4$, pH 4	8.6×10^4	High
	Sulfochlorophenolazorhodanine	H_3PO_4 + HCl	1.2×10^5	Middle
	Palladiazo	3 *M* H_2SO_4	3.3×10^4	High
	Pyridylazoresorcin	10 *n* H_2SO_4	1.9×10^4	High
Zr	Phenylfluoron	pH 2	1.4×10^5	Middle
	Arsenazo (III)	9 *N*HCl	1.2×10^5	High
	Sulfonitrophenol S	1 *N*HCl	7.5×10^4	High
	Xylenol orange	pH 1.5	5.2×10^4	Middle
	Picramine R	1 *N*HCl	3.9×10^4	High
V	Sulfonitrophenol S	pH 1—4 NH_2OH	5.5×10^4	Low
	Sulfonazo	pH 4—5	3.6×10^4	Low
	Pyridylazoresoroin	pH 5—7	3.6×10^4	Low
	N-Benzoyl-N-phenylhydroxylamine	2—10 *N*HCl	0.5×10^4	Middle
Nb	Sulfonitrophenol M	1—3 *N*HCl	5.3×10^4	High
	Bromopyrogallol red	pH 5.8	5.3×10^4	Middle
	Pyridylazoresorcin	pH 5.8	$3.5—3.8 \times 10^4$	Middle
	Sulfochlorophenol S	1—3 *N*HCl	3.3×10^4	High
	Lumogallion	0.5—2 *N*HCl	1.68×10^4	Middle
	Picramine R	1—3 *N*HCl	1.5×10^4	High
Ta	Phenylfluoron	pH 4.5	6.4×10^4	Middle
	Dimethylfluoron	pH 1	4.2×10^4	Middle
	Methyl violet	pH 2.3	6.7×10^4	High
	Butylrhodamine	10 *N* H_2SO_4 $NH_2C_2O_4HF$	3×10^4	High
	Arsenazo (I)	pH 2	0.24×10^4	Middle
	Pyrogallol	pH 2—3	0.23×10^4	Middle

TABLE 4 (continued)

Organic Reagents Recommended for Spectrophotometric and Extraction-Photometric Determination of Elements

Element	Reagent	Reaction conditions	Molar Absorptivity or sensitivity (in Sandell units)	Selectivity
Os	Thiourea	0.5—4 *N* H_2SO_4	5 μg/m*l*	Low
Ir	*p*-Nitrosodimethylaniline	pH 7.2—7.3	1.5 μg/m*l*	None
	Pyridylazonaphthol	pH 4.6—5.9	1×10^4	Low
	Leuco base of crystal violet	pH 3.5—4.7	0.5 μg/m*l*	Low
Pt	Sulfochlorophenolazorhodanine	3 *M* HCl or	3.2×10^4	Middle
		H_3PO_4 + HCl	1×10^5	Middle
	Thyrodine	5 *M* H_2SO_4 2 *M* CH_3COOH	6.5×10^4	Middle
	p-Dimethylaminobenzylidenerhodanine	pH 2—4	1 μg/m*l*	None
	p-Nitrosodimethylaniline	2.2 *M*	1 μg/m*l*	None
Th	Arsenazo (II)	4.8 *M* HCl	1.2×10^5	High
	Thoron (I)	pH 0.7—1.2	1.2×10^4	High
Pa	Arsenazo (III)	7—8 *N* H_2SO_4	2.2×10^4	High
U (IV)	Arsenazo (III)	0.1—10 *N* HCl	1.3×10^5	High
	Chlorophosphonazo (III)	pH 0.7—3.0	6.5×10^4	High
	Thoron (I)	pH 0.8—2	1×10^4	High
UO^2_2	Arsenazo (III)	pH 1—3	5.3×10^4	High
	Arsenazo (I)	pH 4.5—8	2.3×10^4	Middle
Np (IV)	Arsenazo (III)	5—6 *N* HNO_3	1.2×10^5	Middle
	Thoron (I)	0.4 *N* HNO_3	1.4×10^4	Middle
	Arsenazo (*M*)	0.05 *N* HCl	0.9×10^5	Middle
Pu (IV)	Arsenazo (III)	0.1—10 *N* HCl	1.4×10^5	High
	Sulfonitrophenol S	0.1—3 *N* HCl or HNO_3	4.5×10^4	Middle
Am (III)	Arsenazo (III)	pH 3—3.5	8.2×10^4	Low
Am (II)	Arsenazo (II)	pH 4.5—5.2	2.7×10^4	Low
Cm (III)	Arsenazo (III)	pH 3—3.5	8.5×10^4	Low

H. Purity of Organic Reagents

When an analytical chemist relies completely on the OR specifications provided by

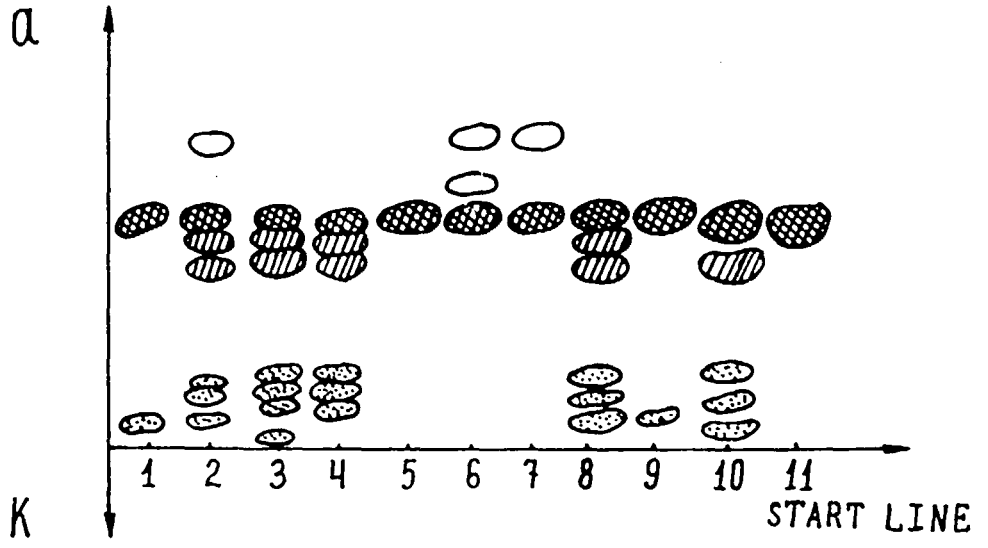


FIGURE 7. Electrophoretic separation of arsenazo (III) preparations produced by different manufacturers. (11) reference sample synthesized by a special technique with lithium salts.

the manufacturers, he may get into trouble. We have performed chromatographic and electrophoretic analysis of several samples of reagents, such as arsenazo (III), some triphenylmethane dyes, and pyridylazo compounds, manufactured by eight leading companies of different countries. These preparations turned out to contain up to seven colored fractions — various impurities — while the content of the basic compound varied from 40 to 90%. Some of the obtained electrophoregrams are given in Figures 7 and 8, without mentioning the manufacturers. If many of these compounds are suitable for practical analysis, they are not so for research purposes. This accounts for the discrepancies in the complex compositions as determined by different investigators (several-fold), as well as in calculations of complex stabilities (in some cases, involving several orders of magnitude), and so on.

The reasons why it is difficult to obtain pure samples of complex OR are obvious. They include the multistage nature of synthesis and side reactions resulting in isomers and other by-products of similar solubility and other properties. As a rule, complex OR cannot be separated in a macrocrystalline form, which is why it is difficult to render them pure. It is generally easier to synthesize a reagent anew, strictly maintaining the synthesis conditions and checking the quality of intermediate products at all stages, than to rid it of by-products. Some features of synthesis and analysis of azo compounds are discussed at length in References 20 and 116.

Analysis of any reagent preparation involves the following stages: (1) establishment of the individuality of a substance, (2) identification, and (3) determination of the basic substance percentage. As can be inferred from recent works, the most reliable ways to establish the individuality of a substance are chromatography[116,117] and electrophoresis.[116,118] There exist various chromatographic and electrophoretic techniques, and almost all of them are suitable for analyzing OR; therefore, we are not going to describe them in detail. For each group of reagents, depending on their solubility and other properties, there are selected an appropriate eluent, electrolyte, amperage, and other conditions for most effective separation of the basic substance from impurities, both colored and colorless. Normally, no serious difficulties arise in doing this. Rapid chromatographic and electrophoretic techniques should be preferable and in all cases be used in the course of reagent synthesis. In this case, purer preparations can be expected.

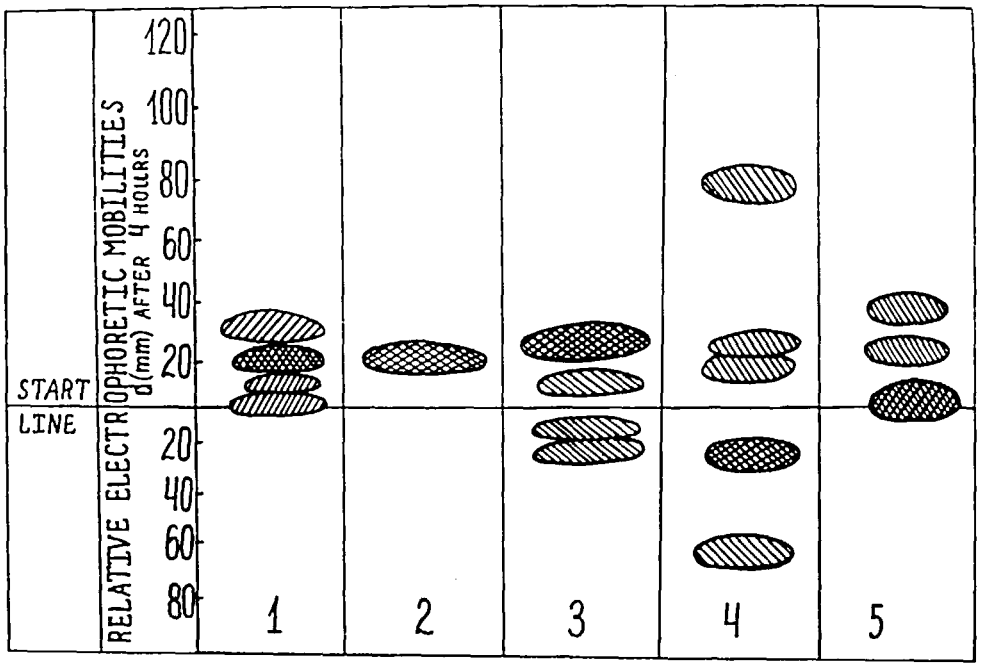


FIGURE 8. Electrophoretic separation of preparations of some triphenylmethane dyes: (1) methylthymol blue; (2) thymolphthalexon S separated from preparation I; (3) xylenol orange; (4) cresol red; (5) bromophenol red. The basic compound is cross-hatched.

Once the individuality of a substance has been established, the subsequent important stage is its identification or establishment of its actual structure. To identify known and previously studied compounds, it is sufficient to determine the principal physicochemical characteristics of a compound and compare them with the tabulated ones (λ_{max} of reagents and complexes, Rf, etc). In the case of new compounds, complete ultimate analysis is desirable,[119-121] or if possible, the countersynthesis method should be used.

After a substance has been purified and its individuality established, only salts of alkaline (or, in some cases, alkaline-earth) elements and crystal water may be present in the preparation. Generally, these impurities present no problems in studying and using a reagent, but for theoretical purposes, one should determine the basic substance percentage. The preparations available on the market more often than not lack such data.

Techniques of spectrophotometric titration using metal salts reacting with the reagent of interest are widely used or, as has been mentioned above, reacting with surfactants. Since the composition of the resulting compounds can be expressed in terms of an integer, such techniques are applicable to less known reactions as well. In many cases, potentiometric titration is highly effective. This technique is applicable if a reagent contains, in addition to acid groups titratable with an alkali as strong acids ($-SO_3H$, $-COOH$, $-AsO_3H_2$), groups titratable as weak acids at pH ranging from 7 to 10 (hydroxyl or dicarboxylic acid) if the differential titration curve features at least two well defined peaks. Sometimes, it is expedient to use potentiometric titration in the presence of copper salts, where a proton is produced when copper forms a complex with the reagents.[122]

Other methods worth attention include comparison of the absorbances of the preparations, at λ_{max}, with reference ones. Ultimate analysis will produce satisfactory results only with simultaneous determination of water of crystallization. More reliable estab-

lishment of elemental composition are the methods of determining As, P, S, total N, and N in azo groups.[119-121]

Analysis of reagents using at least two techniques at a time is most desirable. Of course, the purity of reagents substantially improves, and the analysis reliability is considerably enhanced if a reagent can be crystallized.

A practicing analytical chemist will save a lot of time if he subjects any OR preparation, prior to using it, to electrophoretic analysis and determines the percentage of the basic substance.

III. ADVANCES IN THE DEVELOPMENT OF THE THEORY OF ORGANIC REAGENTS

A. Chemical and Physicochemical Methods of Determining the Structure of Reagents and Complexes

Studies relating to the theory of organic reagents are generally pursued in three directions:

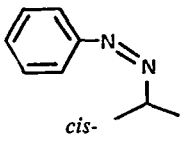
1. Obtaining valid thermodynamic characteristics of all processes leading to a particular analytical effect; kinetics of processes
2. Examination of the complexing mechanism, i.e., determining successive stages of formation of the reaction product, as well as the reagent structure under various conditions and the end product structure
3. Direct investigation of the effect determining the analytical value of a reagent, i.e., the nature of color reactions in the case of reagents for photometry, luminescence, etc.

The problem of structure of organic reagents and their complexes with elements underlies all subsequent theoretical postulates related both to interpretation of the analytical effects of a given reagent and to the possibility of predicting, in one way or another, the properties of new reagents. Progress in this direction has been marred by unsolved problems. Recently, Babko pointed out that very often structural formulas of complexes of elements with even well-known reagents exist merely because they have been around as long as anyone remembers and are transferred from one paper to another without good grounds. This was indicative of a certain lag in the development of a comprehensive theory of action of ORs, as compared to the advances in their practical application.

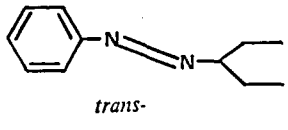
Physicochemical methods of studying the structure of chelate compounds of elements with ORs, such as spectrophotometry, EPR, potentiometry, and IR spectrometry, provide only indirect information on the structure of a compound. Direct physical methods (X-ray diffraction analysis) are not applicable in all cases, since a complex formed by a compound reagent cannot, in general, be separated in a crystalline form. Meanwhile, the processes of complexing are to a considerable degree determined by the structure and ionic states of the reagents, which, in turn, depend on the pH of the medium, type of solvent, temperature, etc. However, in the case of many reagents, establishing the classical structure is a nontrivial task.

Being in most cases polybasic acids with amphoteric properties, colored ORs change their ionic state in media of different acidity, detaching or attaching hydrogen ions, in some cases accompanied by characteristic variations in the OR properties, namely, chemical reactivity, electronic state, absorption spectra, and electrical conductance. These variations, however, may be caused not only by dissociation or protonization of reagents, but also by intramolecular migrations, e.g., spatial or tautomeric ones.[123] The difficulty of establishing the ionic state of reagents and the structure of their in-

dividual forms stems from the fact that all chemical and physical properties of reagents manifest themselves in an integrated manner, i.e., they may be determined by the presence of a number of equilibrium forms at a time. In this case, traditional chemical as well as spectrophotometric techniques do not always permit obtaining additional data. For example, in the case of a simple aromatic azo compound, namely, azobenzene, there exist two stereoforms: *cis*- and *trans*-azobenzene:[124,125]



cis-

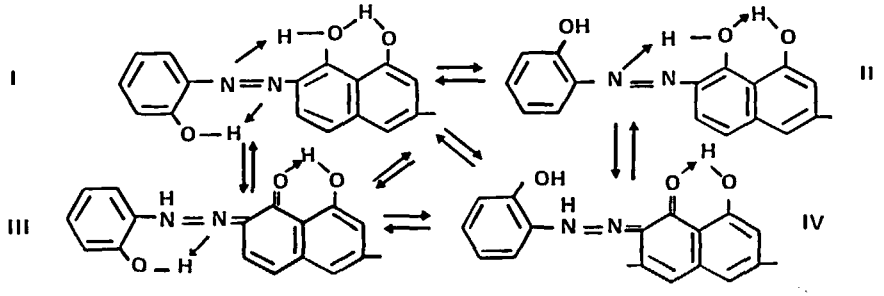


trans-

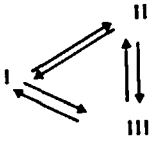
These forms differ in dipole moments,[126] melting points,[127] and their steric differences have been established by crystallographic examination.[128] Similar steric isomers have been found for some substituted azobenzenes and azonaphthalenes.[129] Such isomers lacking functional groups specific for each form are difficult to be chemically discerned.

In physicochemical studies of organic reagents, the existence of tautomers and isomers is often ignored, whereby the investigation is simplified. In some instances, this is justified — under certain conditions, one of the ionic and tautomeric forms of a reagent prevails. In this case, to establish the sequence of acid ionization, good results are obtained by simultaneous application of spectrophotometric and potentiometric techniques.[122] Even in this case, however, the obtained data should be regarded as preliminary prior to a more comprehensive study using other techniques. These data are not suitable for calculating the dissociation constants, for example.

In general, taking tautomerism into account, particularly for such reagents as azo compounds, is one of the most difficult problems and cannot always be solved by using classical chemical, viz., spectrophotometric techniques. Consider by way of example the structural characteristics of one of the most structurally simple reagents, namely, acid chrome dark blue (ACDB).[130,131] One can imagine the following four equilibrium forms of a single ionic state of this dye, for example, in 0.1 M H_2SO_4:



The existence of the reagent in a single form (II) is postulated,[130] and all spectrophotometric calculations of the dissociation constants are based on this postulate. Under the same conditions, the equilibrium state II⇌IV is postulated, too.[132] More recent quantum-chemical studies indicate that the state of the reagent in 0.1 M H_2SO_4 is best described as follows:[133]



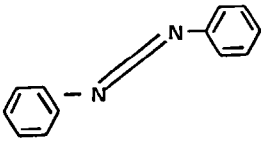
Although the phenomenon of tautomerism is widely known,[134-136] until recently only

very few investigators discussed their results in terms of tautomerism.[132,137-142] Therewith, it was normally assumed that the tautomeric equilibrium is almost completely shifted towards one of the forms. However, in defining the state and reactivity of a reagent, one should corroborate the existence of a single form or evaluate the concentration of other forms which, if they exist independently, may interact with metal ions. As is well known, the metal ion does not necessarily interact with the reagent form prevalent in the solution. The metal ion may shift the equilibrium towards the complex compound in the case of such a reagent form which was less stable in the absence of the metal and whose concentration in the solution was low. All this should be taken into consideration in trying to determine the complexing mechanism.

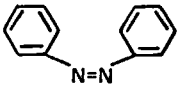
Traditional chemical and spectrophotometric techniques used for determining the composition of complexes are well known and amply covered in the literature, so there is no need to dwell on them here. Just as in studying reagents, good results are obtained by concurrent use of spectrophotometric and potentiometric techniques to determine the composition and number of protons evolved in reactions, which gives an idea of the nature of interaction between the metal ion and the reagent. At the same time, as in the case of reagents, these data are not sufficient to unambiguously establish the mechanism of the reactions and the structure of the reaction end product. Many examples can be given, showing that different investigators offer various structures for the same complex. Considered in what follows are some other methods developed in recent years and aimed at obtaining additional information on the structure of complexes and reaction mechanisms.

B. Atomic Model Method

The method of three-dimensional scale atomic models (long and widely used in theoretical organic chemistry), is, for all its simplicity, very useful in some cases of determining the structure of reagents and complexes. It is known, for example, that azobenzene may exist both in trans- and in cis-form:

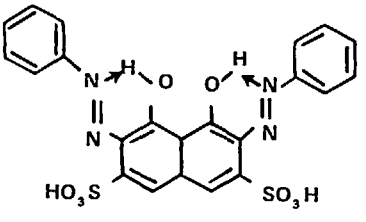


trans-



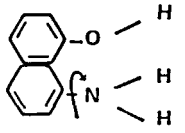
cis-

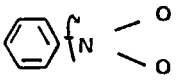
In the case of more complex OR containing these structural elements, atomic models show the only possible structures. For example, in the case of azo-substituted chromotropic acid, in view of the steric hindrances offered by the naphthalene ring sulfo groups, the only possible planar configuration is the trans-configuration of the reagents. Thus, the azo-form of the reagent known as benzene C may have only the following structure:



Note that the formation of hydrogen bonds in this case renders the structure denser and relieves the stress occurring as a result of steric hindrances in the arrangement of the hydroxy-group hydrogen, where the space charge increases as the H-bonds break.

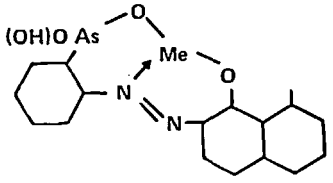
Sometimes, when calculations are made by the LCAO-MO method, difficulties arise in interpreting the results obtained for compounds containing, as substitutes, an NO_2 group on a benzene ring or an amino group in the peri position to one of the naphthalene ring hydroxyls (H-acid). The modeling of these groups in the above-mentioned rings indicates that, in the case of the H-acid, the plane of the amino group whose nitrogen is considered to be sp^2-hybridized does not coincide with that of the molecule, but is turned through a certain angle about the C–N bond:





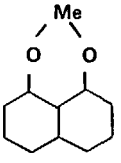
Here, the steric hindrances are caused by the hydroxyl group being sufficiently close to the amino group. As opposed to the amino group, the nitro group cannot, even in the absence of substituents in the ortho position, be arranged in the plane of the molecule because of the steric hindrances on the part of the nearest hydrogen atoms.

The atomic model method has made it possible to establish that the presence of voluminous groups in the ortho position to the azo group ($-ASO_3H_2$, $-PO_3H_2$, $-SO_3H$, and even $-COOH$) will not permit the metal cation to approach the azo group in the plane of the reagent's molecule; hence, in cases where such an interaction has been established, the metal ion is slightly above or below the plane of the molecule. For example, the commonly depicted structures of complexes of the following type:



are possible, in principle, provided the benzene and naphthalene rings are turned through an angle of about 25 to 30° and if the metal atom is above the plane of each ring. Only then is the metal atom closest (within the range of mean ionic radii), to the atoms of the salt-forming groups constituting the functional analytical groups of the reagent: O (OH-groups), O (AsO_3H_2-group) and N (azogroup).

The same arrangement of the metal atom, i.e., beyond the molecular plane, takes place in complexing with the participation of the peri-dihydroxy group (e.g., in chromotropic acid):



In the molecular plane, this structure is impossible because the oxygen atoms of the OH-groups are too close to one another and have bond directions which do not provide for coordination of any metal atom. At the same time, a metal atom lying beyond the molecular plane is possible at any coordination number of the metal. Three-dimensional atomic models have also made it possible to reveal other structural features of reagents and complexes.[131] For example, when a metal ion interacts with a reagent based on an R-salt, namely, chlorophosphonazo R (or trope I)

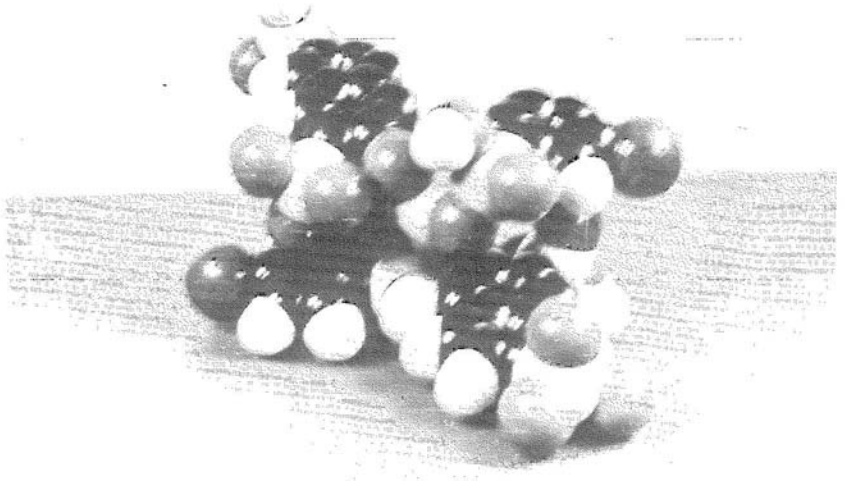
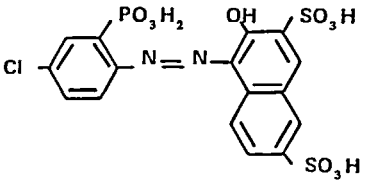


FIGURE 9. Three-dimensional model of metals with chlorophosphonazo P in the form of a propeller sandwich. Composition: 1:2.



within a MeR_2 complex, a possible structure will contain two molecules of this reagent surrounding the metal ion with coordination number 6.

In this case, the molecular structure is of the propeller type (Figure 9). The benzene and napthalene ring planes are parallel in pairs. In each reagent molecule, the angle between the planes of two rings is 25 to 30°. As can be seen from the drawing, the phospho groups are above the plane. The metal atom is beyond the benzene and naphthalene ring plane. At the same time, a structure is possible in which both azo groups lie in the same plane with the metal atom.

The above examples illustrate the usefulness of atomic models, particularly of perfect structures, for preliminary analysis of possible structures and for determining whether they are possible or not, in principle. Therewith, only quantitative methods of investigation provide complete data on the structure of reagents and complexes.

C. Quantum-Chemical Methods

The quantum-chemical methods of studying inorganic and organic substances have been extensively used in various branches of chemistry.[134,143-145] In a somewhat specific field of complex OR research, the quantum-chemical methods have been in use for about 10 years, enabling elucidation of many important aspects of the theory of action of ORs, which could not be studied by traditional methods.[146-150] Even in the relatively simple Huckel's version, the linear combination of atomic orbitals approximation method (LCAO-MO) enables calculation of the position of the reagent absorption bands, as well as an evaluation of the complete π-electron energy and relative band intensities. The obtained calculation data for a number of structures are compared

with the experimental ones (λ_{max}, I_n/I_{n+1}, where I_n is the absorption intensity of the nth absorption band at λ_{max}), which permits selection of an appropriate structure.

In addition, the LCAO-MO method provides additional information on the electronic structures of reagents and complexes, bond order (degree of double bonding), π-electron charges on atoms, and free valence indexes for individual atoms. In other words, it provides a molecular diagram of a reagent.

In recent years, much has been written on quantum-chemical studies of ORs of various classes and their complexes with elements. Apart from those mentioned above, we would also like to mention a few original papers,[151-155] reviews, and monographs.[20,26,156] In this paper, we should like to draw your attention to only some aspects of application of the quantum-chemical methods and their limitations and prospects for the future.

Earlier, the LCAO-MO method was applied to only a few simple azo compounds with appropriate calculations being made and molecular diagrams being obtained.[157,158] The structural complexity of many OR-azo compounds, for example, 2,7-bisazo-substituted chromotropic and H-acids which are polybasic acids, as well as the possibility of tautomeric transformations and steric isomerism along with the presence of several functional analytical groups, render the task of elucidating the complexing mechanism and the nature of color reactions extremely difficult. Therefore, in calculating the electronic and energy characteristics of both reagents and complexes, one should assume a simplified compound model. Since the S, As, and P atoms of acid groups $-SO_3H$, $-AsO_3H_2$, $-PO_3H_2$ and other similar groups lack lone-pair electrons, their π-system may be considered isolated, and they take practically no part in conjugation.[159] The effect of these groups may, therefore, be regarded as a disturbance affecting the Coulomb integral of the adjacent carbon atom. It may be assumed, according to Wheland and Pauling,[160] that $\alpha_{c'} = \alpha_c + 0.1\ \delta_x\beta_o$, where c′ is the carbon adjacent to the acid group and δ_x is a quantity representing, in β_o units, the deviation of the Coulomb integral of c′ from the standard value α_c.

The system of parameters for heteroatoms (S, AS, N, O) in different oxidation states may be selected or calculated according to References 143 and 161. The overlap integrals required for this calculation are taken from the tables of References[162 and 163], while the required ionization potentials are taken from Reference 164, the effective charges are calculated according to Slater,[165] and the interatomic distances are taken from the tables of Reference 166. The rest of heteroatoms are taken into account through the introduction of semiempirical parameters:

$$\alpha_x = \alpha_c + \delta_x\beta_o \quad (2)$$

$$\beta_{c-x} = h\beta_o \quad (3)$$

In studying structurally complex reagents, other approximations and semiempirical parameters are introduced as well, in view of the impossibility of calculating energy levels for an entire molecule. Therefore, just as any other technique, the quantum-chemical method, especially in the simple Huckel's version, has its limitations and can be applied only within certain limits, otherwise, its incorrect application will yield invalid results. This is precisely what sometimes happens when quantum-chemical methods are used.

Not being strictly absolute, the conclusions of quantum-chemical methods must be constantly checked by chemical analysis so as not to contradict well-established notions. A wrong presumption, an improperly selected model for calculations, which is inconsistent with all the accumulated knowledge in organic, coordination and analytical chemistry, will adversely affect the validity of quantum-chemical methods. One should not forget about the difficulties involved in the selection of parameters for

quantum-chemical calculations, the approximations typical of quantum-chemical methods, and the possible inaccuracies in experimental data which are used to some extent in quantum-chemical calculations. The famous adage in which mathematics is compared to a millstone that grinds everything put under it equally applies to quantum chemistry. Therefore, by way of calculation, a chemical investigator must foresee and analyze by way of calculation all theoretically possible structures (models) of reagents and complexes, as well as evaluate the obtained results from the standpoint of their consistency with the well-established experimental facts relating to the OR action theory. Selection of an adequate calculation technique is another difficult problem.

The simple Huckel's method, for all its limitations, has provided valuable information which is still considered reliable. The main reason is that the method had been rationally used. In selecting the right method, one should not be governed by the availability of appropriate software and computers, but by the chemical problems to be solved. Such a proper selection requires, of course, that the investigator should be equally skilled in both fields, i.e., in quantum and analytical chemistry.

The main problem of the organic reagent action theory is prediction of highly new sensitive and selective compounds. An ideal solution of this problem may be as follows: at the first stage, on the basis of general regularities of the structure of ORs belonging to certain classes, mathematical synthesis is performed of the structural formulas of all hypothetical molecules which may be of analytical value with a high degree of probability. In solving this problem, one should use the algorithms described in detail in References 167 and 168. Then, all of these structures are subjected to thorough quantum-chemical calculations during which the investigator not only finally establishes the possibility of their actual existence, but also determines whether they are capable of complexing metals, as well as the direction and amount of the occurring spectral changes, which in the final analysis, will determine the analytical value of the prospective reagent.

If such a theoretical prediction turns out to be successful, the reagent of interest is synthesized. In general, this approach is theoretically feasible. In practice, however, it will hardly become possible in the near future because of the enormous volume of calculations involved, to say nothing of the fact that the quantum-chemical theory and associated calculation techniques are far from being perfect and cannot, at present, guarantee absolutely reliable results. Therefore, theory (particularly, the quantum-chemical theory of structure and action of organic reagents), is primarily concerned with a more limited problem. It is necessary, first of all, to understand the nature of many already established facts, such as the effect of the type of substituents, their arrangement, etc. By using available data, for example, one can formulate recommendations for specific changes in the structure of a given reagent, which may eventually result in attaining the required properties: high sensitivity, selectivity, reaction contrast, complex strength, etc. These recommendations may then be used in synthesis of new reagents whose quality is checked by direct experiments.

If a new reagent turns out to be superior to those already in existence, additional calculations may help find ways of improving it. Such an approach would hardly yield fundamentally new reagents. However, known and related reagents can be improved much faster as compared to the purely empirical trial and error method. This is the direction in which calculation techniques related to the theory of structure and action of ORs are now developing.

Let us now dwell upon the present status of the quantum-chemical theory of polyatomic molecules and the range of problems solved by calculations related to this theory, which may be of interest in studying organic reagents.

Today, there exists a rather developed quantum-chemical theory of polyatomic molecules and their spectra, based on the variation principle and use of sample functions

in the form of linear combinations of atomic orbitals.[169,170] The most widely used calculation technique is the self-consistent field method, also known as the Hartree-Fock method, which enables solution of a great number of practically significant problems. This method, however, does not take into account some peculiarities of electron interaction, referred to as correlation effects. Then, there is an approach known as the configuration overlap method in which these effects are taken into consideration. In other words, investigators have at their disposal an intrinsically coherent theory on the basis of which it is possible to calculate, with a high degree of accuracy, the values of various characteristics of polyatomic molecules and their interactions.

Some extremely accurate calculations of relatively lame molecules have agreed well with experimental data. This indicates that the optimistic expectations expressed by physicists after the advent of quantum mechanics may finally come true. They hoped that all known chemical effects can be predicted, whereby the chemical problems will become purely theoretical, or physical. Unfortunately, these hopes are in general forlorn. In reality, calculations involve such enormous mathematical difficulties and the problem becomes so complicated that presently it can be solved with desired accuracy and theoretical strictness only in the case of very simple systems. Therefore, when investigators deal with large molecules, they have to resort to various approximations and trade strict theories for semiempirical variants. All these approximations differ in that they are evaluated in a different manner and use is made of various integrals appearing in strict theory.

It has also become standard practice to divide all valent electrons into localized and delocalized groups (σ- and π-approximation). Such a classification is quite satisfactory for calculations of most characteristics of molecules with a developed conjugate system. In the simple Huckel's method, only empirical, so called Coulomb and resonance integrals, are introduced. This allows for, in a most approximate fashion, not only interaction of an electron with a given atom or a pair of atoms in a bond, but also perturbations of its movement, caused by other electrons and nuclei. More sophisticated methods involve differentiation of the parameters used in such a manner that they start acquiring a definite physical significance. For example, in the Pariser-Parr-Pople method, these parameters include atomic ionization potentials and some others. In more advanced methods, due consideration is given to the dependence of matrix elements on the type of atomic functions and interatomic distances, various approximations are used for quantum-chemical integrals with some of them being accurately calculated, etc. It should be noted that, in general, the trend in the development of semiempirical methods is such that they gradually become nonempirical. These methods are definitely more complicated and require more computer time than, for example, Huckel's or Pariser-Parr-Popple methods. Nevertheless, advances in computers make their wide application possible. The greatest advantage of the semiempirical methods developed in recent years[171] lies in the possibility of calculating, within one set of parameters, various characteristics of molecules, such as total energies, geometry, dipole moments, heats of atomic linkage, dimeric structures, heats of reaction, etc. At present, it is theoretically possible to investigate the properties of very complex systems with an acceptable degree of accuracy. This, of course, cannot be ignored in solving specific problems of importance for analytical chemistry, since the development of analytical chemistry has entered a phase where work is usually productive only if the structure of already known compounds is studied in greater detail and if predictions can be made of the effect on various factors, in particular, substituents, on their properties.

It is now appropriate to point out certain conclusions that can be drawn from the experience of applying quantum methods in solving various problems related to the structure and properties of ORs. Note, first of all, the great benefit that can be derived

by theoretical analytical chemistry when, along with the common structural formulas, use is made of molecular diagrams based on the concepts of fractional charge on atoms and fractional bond order. Huckel's method alone permits constructing molecular diagrams representing the peculiarities of chemical bonds in complex molecules with conjugation much more accurately and vividly than conventional valence-line pictures. There are many examples[146-156] showing that molecular diagrams facilitate interpretation of analytical reactions. It is also important that such molecular diagrams remain practically the same when more complicated methods are used. In other words, Huckel's method, for all its simplicity, has not exhausted itself; it can and must be widely but specifically used in OR studies.

As far as ORs are concerned, one of the first problems being solved with the aid of quantum-chemical methods is their color and the reason why it changes during complexation. This problem is not only one of the most important per se, but also lends itself readily to solution by quantum-chemical methods. In fact, the color of a substance is determined by the long-wave band in the electronic absorption spectrum. Thus, analysis of the color of ORs and its changes during complexation and various intramolecular transformations constitutes one of the particular problems of the general theory of electronic spectra of polyatomic molecules, based on the concepts of quantum chemistry. The fact that the overwhelming majority of organic reagents feature a developed conjugate system and that the long-wave bands in the spectrum are associated with π-π-transitions (transitions between states of delocalized electrons) permit permits effective use of various methods based on the π-approximation. In early works, Huckel's method was mainly used, providing most valuable data. However, because of the limited application of this method and the difficulties involved in selecting parameters in systems with a great number of heteroatoms, preference is given to the Pariser-Parr-Popple method in combination with the configuration overlap method. This combination simplifies the problem of parameter selection and permits calculating not only singlet, but also triplet excited states. It also permits calculation of luminescence spectra, which is a most promising direction in the analytical application of organic reagents. For this purpose, Huckel's method is not suitable in principle.

As has already been mentioned, the problem involving analysis of a reagent in color changing during complexation or introduction of a substituent is purely physical and can be formulated on the basis of the contemporary theory of electronic spectra of polyatomic molecules. The main difficulty in calculating electronic spectra is that, since we use a semiempirical method, we should select a set of parameters that would not only adequately describe the spectrum of a given individual reagent (which is not difficult to do), but would also exhibit transferability with respect to molecules of a particular class, thus ensuring the possibility of predicting the spectral properties of a large group of reagents.

Such a selection of parameters is rather tedious work. However, if parameters have been selected for the basic structures, then by varying them one can predict the pattern of changes in the absorption bands. Each of the parameters being varied has a definite physical significance; for example, the Coulomb integrals are determined by the energy of the electrons near a given ring and by the energy of the Coulomb attraction of the atomic electron cloud to the other rings of the molecule; the resonance integral has approximately the same significance only for two centers forming a given bond, etc. By placing, near a particular atom, substituents whose effect on respective integrals is predictable, we can know in advance which substitute positions are favorable or not from the standpoint of subsequent spectral changes, as well as the nature of the substituents. By making appropriate calculations for both the reagent and the complex, it is possible to define the direction for the search of new reagents. Therewith, it is useful to produce graphs showing the sensitivity of the long-wave absorption band versus the substituent position. Such graphs may be found in Reference 172.

Having used this approach and compared the wave functions of the upper occupied and lower vacant orbitals of phenolazonaphthols, the authors of Reference 173 have arrived at the conclusion that azo derivatives of 1-naphthol must feature a higher contrast reaction than those of 2-naphthol. Synthesized dyes have corroborated this assumption. Theoretical analysis also suggests that the reaction contrast can be enhanced by introducing substituents onto the aromatic rings of dye molecules, preference being given to substituents producing only an inductive effect. As a result, a new reagent — "picramine E" — was created, reacting with zirconium and copper with a sensitivity twice as high than the previously used reagent "picramine R".[174]

Quantum-chemical calculations have established the feasibility of synthesis of new reagents containing a *O,O'*- aminohydroxyazo group and a *o,o'*-carboxyaminazo group. These reagents turned out to be highly sensitive and selective in reactions with palladium, rhodium, molybdenum, and platinum.[175] As a result of preliminary calculations, *N*-methylanabasine-*α'*-azo-4-cyclohexylresorcin was developed for photometric determination of indium.[176] Along with spectral examination, quantum methods are useful in other cases as well. They can be employed, for example, in studying charge transfers in redox reactions. For instance, as a result of quantum-chemical examination of the electronic structure of reagents, depending on the type of substituent, directed synthesis has been performed to produce new reagents, namely, 4-arsono- and 4-phosphophenylanthranilic acids, phosphonodiphenylamine, and diphosphonodiphenylamine, which are good redox reagents for determining iron, chromium and vanadium.[177]

There are few examples of directed syntheses of reagents, but it should be borne in mind that the number of known quantum-mechanical studies is limited, too. This is mainly due to the fact that analytical chemists do not yet extensively use quantum-chemical calculations in their work.

Another important problem in the solution of which quantum- chemical methods have played a significant role is that of tautomeric transformations of reagents or, in other words, the problem of intramolecular proton transfers. In this case, the methods of quantum chemistry permit calculations of the total energies of various tautomeric forms of reagents and the barriers of their mutual transformations, as well as the spectral characteristics of tautomers. Calculation of tautomer spectra in combination with methods of mathematical separation of overlapping absorption bands into components enables the tautomeric forms to be experimentally identified in various media. Solution of problems related to energy is required to draw conclusions as to the possibility of tautomeric transformations following changes in the properties of the medium.

In calculating the energy characteristics, one should take into account that they can be made in the π-approximation only if the energy of the σ-skeleton of the molecule is practically invariant during tautomeric transition. Although earlier (see, for example, Reference 26) even Huckel's method was successfully used for the purpose, it should be admitted, however, that neither this nor the PPP method is adequate for this problem; hence, neither method is promising. To solve energy problems one should use methods in which all valence electrons such as CNDO, INDO, and particularly MINDO/3[178] are taken into consideration. Therewith, it is possible to calculate not only the energy of tautomers, but also the potential curve of proton transfer. Unfortunately, such calculations are rather complicated and necessitate the use of BESM-6-type computers.

D. Conformational Analysis

One of the most important characteristics of reagents and complexes that can be adequately studied by methods of modern quantum chemistry is the system geometry.

Studying the geometric parameters is of particular significance because complexing reactions and spectral properties of compound molecules are, to a great extent, determined by the configuration, or geometry, of the molecule. Well known are such factors as steric hindrances, which impede a reaction because two reacting centers cannot come close to each other. Less well known is the effect of various conformational states of reagents and their different ionic forms on the course of reactions. It is anticipated that a reaction is strongly influenced by the electrostatic field created in the immediate proximity of the molecule of interest. Specific calculations suggest that these fields depend heavily on the geometric state of molecules.

To solve this problem, one can use theoretical conformational analysis based on the approximation of pair atom-atomic potentials. This technique, covered at length in References 179 and 180, is widely used in studying most diverse organic compounds including large biological objects.[181] Almost in every case where there was a possibility of checking such conformational calculations experimentally or with the aid of additional independent calculations, the method proved to yield good results. It can now be regarded as a highly reliable method of predicting value.

The method is composed of the following.[182] The total potential energy of a molecule is expressed in terms of the sum total of bond energies, valence angles which are allowed to slightly deviate from the standard values determined by the hybridization of atomic orbitals, energies of internal rotations, and energies of electron pair nonvalence interactions (in addition, for calculating energies of some compounds, components are introduced into the molecular potential energy corresponding to hydrogen bonds, electrostatic interactions, and solvation). In calculations of possible conformations, the bonds are assumed to be absolutely tight, the angle potentials are assumed to obey the square law with respect to the parameters of their deviation from the standard values (e.g., in the case of carbon, the standard angles are 180° for sp-hybridization, 120° for sp^2-hybridization, and 109° for sp^3 hybridization.). The potential of rotation around bonds is assumed to be periodic and having the form:

$$U = \frac{1}{2} U_0 (1 + \cos n\phi) \qquad (4)$$

The potential of all pair interactions is often written in the "6-exponent" form:

$$U = Ar^{-6} + B\exp(-Cr), \qquad (5)$$

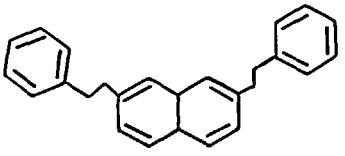
where r is the distance between atoms in a given pair and A, B, and C are empirical parameters which, as it turns out, are characteristic of atom combinations, and hence, can be used for various molecules without undergoing any changes. This is precisely what makes it possible to calculate complex systems with the aid of parameters that are empirically determined for some simple molecules.

The total potential energy of a molecule is, consequently, a function of interatomic distances. Corresponding to the known stable state are also other mutual atom arrangements for which the potential energy reaches a minimum. If a molecule can exist in various rotameric forms, there may be several such minima. The depth of a minimum determines whether a particular conformational state is energetically favored, while the height and width of the barrier between minima determine the probability of conformational transformations.

Thus, mathematically, the problem boils down to finding the minimum of the potential energy function with varying interatomic distances. It can be solved completely with the aid of well-known mathematical techniques. The simplicity of the potential function used permits the problem to be completely formalized and special computer programs to be written. These programs are powerful, on the one hand, and simple in presenting the initial data on the other. This feature facilitates theoretical conformational analysis in application.

Pair atom-atomic interactions can be calculated using a set of parameters proposed by Dashevsky, [180,183,184] whereas the set of parameters for a quantum calculation can be taken from Reference 185. This method permits evaluating the barriers of internal rotation of $-AsO_3H_2$, $-SO_3H$, $-COOH$, $-N=N$, and other groups.

The above-described method was used in calculating the conformation of some reagents of the arsenazo (III) group and related compounds. Therewith, consideration was given to the possibility of rotation around bonds $C_{ar}-N$, $N=N$, $C_{ar}-AsO_3H$, $C_{ar}-SO_3H$, $C_{ar}-COOH$, $C_{ar}-OH$, as well as to the possibility of deformation of the valence angles at the nitrogen atoms of the azo groups and oxygen atoms of the hydroxy groups.[182] As can be inferred from the calculations, the substituent-free skeleton of such reagents as arsenazo (III) is planar. This is obvious if it is borne in mind that *trans*-azobenzene is planar.[128] Rotation around the C_a-N bond of the naphthalene nucleus gives rise to steric isomers of different azo group orientation:

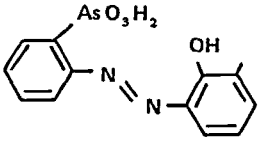


Despite the difference in geometry, both isomers (hence, the third, asymmetrical one) are energetically equivalent. Substitution of hydrogen atoms in positions 1 and 8 of the naphthalene ring by hydroxy groups results in a sharp differentiation of the possible conformers with respect to energy; conformations in which hydrogen bonds O–H...N are possible are energetically more expedient (approximately by the magnitude of the energy of the forming H-bonds) than those free of hydrogen bonds. In principle, conformers containing hydrogen bond O–H...O (asymmetrical conformations) may be formed as well. All possible conformations of such a molecule are planar.

The presence in this system of a rotating group considerably complicates the conformational picture and results in the main conformations of the molecule becoming nonplanar. The lowest energy is observed in those conformations in which two hydrogen bonds are formed. In equilibrium mixtures, at normal temperatures, only such forms seem to be present, since they are energetically more favored by 10 to 20 kcal/mol.

To elucidate the complexing mechanism or interpret experimental data on complexing of azo reagents with elements, it is not sufficient to know just the equilibrium geometry of conformers; it is also important to know how rigid a particular conformation is and approximately what energy expenditures are involved in the rotation around bonds to achieve an optimum geometry for complexing; it is equally important to evaluate the possibility of transition from one conformation to another.

Such calculations for arsenazo (I) indicate that the rotation around the bond $C_{benzene}-N=$



is sufficiently free (within about 30°, the energy amounts to approximately 1 kcal/mol), and the reagent may easily change its conformation during complexing. The barrier of transition to a neighboring (less stable) conformation is also small — 4 to 5 kcal/mol.

A similar approach was used in studying azo dyes of the same group but of more complex structure with various functional analytical groups and substituents.[185] Geometric and energy data have been obtained which enable definition of more stable conformers. Conformational maps were also obtained[180] permitting evaluation of the degree of "softness" or "rigidity" of a reagent and energies of transition from one transformation to another. It turned out that, although the statistical picture is rather complex, in analytical reactions there is normally present a single comformer (we are not discussing here tautomeric transformations and the possibility of several tautomeric forms being present at a time) whose structure is close to planar (the benzene ring leaves the plane of the naphthalene nucleus, depending on substituents, at angles ranging from 0 to 30°). The possible conformations of organic reagents are sufficiently flexible. This means that one and the same functional group, e.g., *o*-arsonazo-*o*-hydroxy or *o*-phosphonazo-*o*- hydroxy, will meet the coordination requirements of most metal cations, which may, in principle, interact with it.

This is one of the most significant conclusions of conformational analysis. The degree of flexibility or rigidity of a reagent is also indicative of its selectivity. As is known, reagents of the arsenazo (I) and arsenazo (III) groups are not selective — they interact with many elements. This agrees well with the obtained results as to the fexibility of conformation of this group of reagents.

No such conformational analysis has been carried out for reagents of other groups. If it is confirmed that the flexibility or rigidity of conformations of a reagent is directly associated with its selectivity, then conformational analysis of compounds of different classes will have a predictive value and serve as an effective means for theoretical finding of specific, selective, or group reagents.

Knowledge of the geometry of reagents and complexes is necessary for subsequent quantum-mechanical calculations, particularly in cases where semiempirical methods are used with separation of σ- and π-electrons. At present, the various versions of quantum-chemical methods and the atom-atomic potential method ensure effective and rapid calculation of the geometry of any ORs with an accuracy quite adequate for subsequent investigation of the reaction mechanism and, what is more important, provide necessary information in cases where direct experimental techniques such as electron diffraction analysis, X-ray diffraction analysis, and others cannot be used in principle because of the aggregate state of the compound, effect of the medium, etc. Therewith, appropriate calculations can be made within a relatively short period of time, which do not require, with the good service programs that are available, any particular skill on the investigator's part.

In recent years, quantum-chemical methods started being applied in studies of the reactivity of ORs and investigations of the mechanism of chemical complexing reactions. Every chemist is familiar with the experimental difficulties encountered when this problem is solved by purely chemical methods. This problem is no less difficult for quantum chemistry as well. Although it is possible to perceive a potential surface for a specific chemical reaction, or a so-called reaction tree, which would indicate the possible direction of the reaction, application of these calculation techniques to specific compounds in difficult. So far, we have not yet developed a universal approach which would permit these most important problems to be solved in a sufficiently systematic manner. However, a certain possibility is opened up as well if the following is taken into consideration.

As a rule, a complexing reaction, especially at the first stages when the metal cation or any other complex inorganic or organic ion is still relatively far from the molecule, has a pronounced ionic nature. At the first stage, the charged particle approaches the OR molecule which is electrically neutral as a whole. This approach or proximity creates a nonuniform electric field at the nearest periphery of the reagent molecule owing

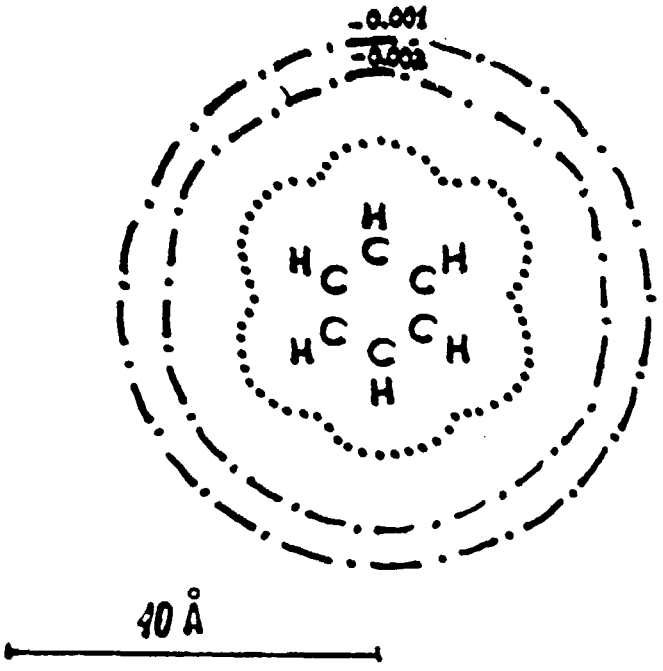


FIGURE 10. Molecular electrostatic potential of benzene.

to its intricate configuration and complex distribution of charges within it. The effect of this field is precisely what directs the initial approach of the attacking metal ion to the molecule. Evidently, this field may help the metal ion to approach the reaction center or, vice versa, prevent its movement, in which case the reaction either becomes impossible or slows down. Thus, there arises the problem of studying the type of the electric field surrounding the molecule at distances equal to those about two or three times the size of the molecule.

Theoretical estimates indicate that the solution to this problem will hardly require a particularly high accuracy and that it is quite sufficient to use various approximations similar to point-charge approximations calculated by the CNDO, INDO, and other methods. Methods based on the π- approximation are not suitable for the purpose. Consider some model examples demonstrating the dependence of the molecular electrostatic field on the substituent.

Figures 10 to 12 show different substituted benzenes. Dots define the area 2 A in radius from the peripheral atoms of the molecule, beyond which the potential was not calculated. The negative potential areas are indicated by dot-and-dash lines, while the positive potential areas are shown by solid lines. The zero potential lines are dashed. The potential is given in e/A. The distribution of the electric field in these molecules either promotes or hinders reactions of the nucleophilic or electrophilic type. In the former case, such reactions proceed, while in the latter case, they are impossible. Note that the electric potential picture is most illustrative and vividly demonstrates the role of substituents, particularly charged ones. It turns out that substituents are capable of substantially altering the nature of the external electric field practically without affecting the distribution of the electron density in direct proximity to the reaction center. Respective examples of model reagents are given in Figures 13 and 14.

This relatively new approach to the reactivity of organic compounds may equally apply to studying the interaction between OR and metal cations ultimately resulting in chelate compounds. Until recently, various methods were applied mainly to exam-

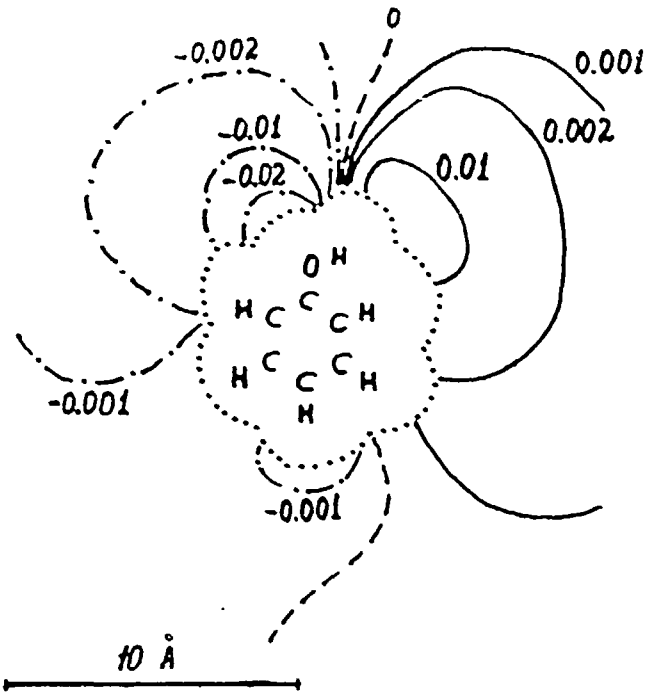


FIGURE 11. Molecular electrostatic potential of phenol.

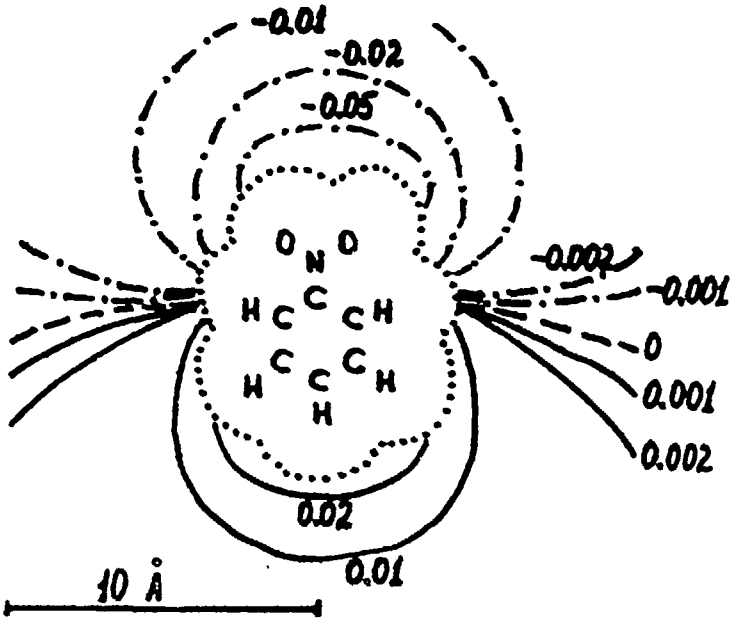


FIGURE 12. Molecular electrostatic potential of nitrobenzene.

ining static states such as the initial structure or structures of a reagent, the form in which the metal is present under given conditions, the structure of the end product of the reaction, and in some cases, possible structures of the intermediate products. Molecular electrostatic potential maps will, to some extent, make it possible to follow the path (or, to be more precise, most probable attack directions) of the metal ion towards

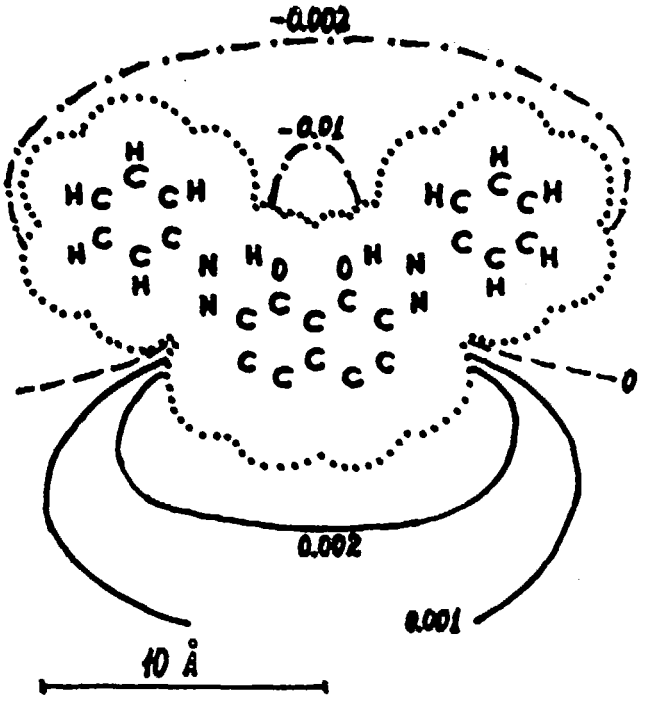


FIGURE 13. Molecular electrostatic potential for the benzene C model without the naphthalene ring sulfo groups.

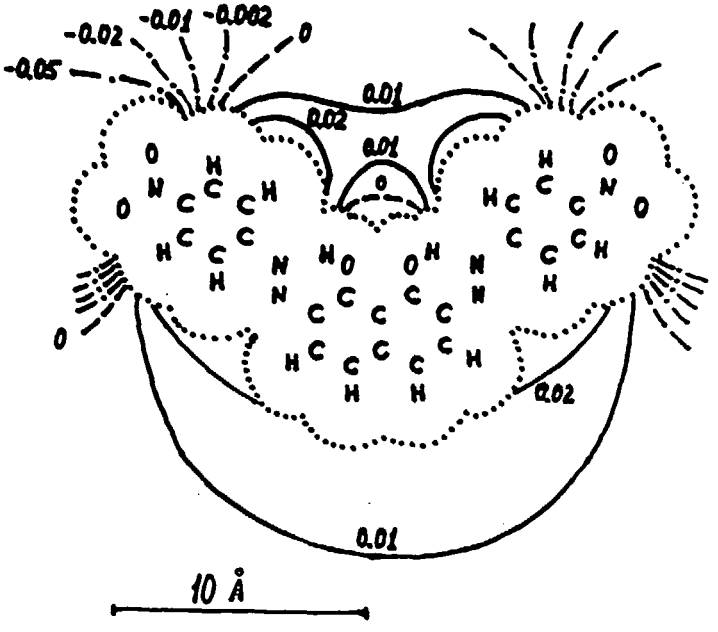


FIGURE 14. Molecular electrostatic potential for a model reagent containing two nitro groups in a p position to the azo groups.

the OR. This will probably permit the structure of the complex to be more clearly defined in cases where there are several possible sites of metal ion attachment. It is also possible that the selectivity of a reagent, reaction rates, and other analytical characteristics also depend, to some degree, on the distribution of the molecular electrostatic potential.

Experience, however limited, clearly suggests that further elaboration of the OR action theory and search for new classes of compounds suitable for analytical purposes is impossible without extensive use of calculation techniques developed in quantum chemistry and the theory of molecular structure and spectra.

E. Kinetics of Color Reactions

Studies of the rates of fast chemical reactions are highly important for both theoretical and practical analytical chemistry. Some chemical reactions which have long been considered fast become so slow under certain conditions that serious errors may be introduced into chemical analysis. Taking into consideration slowing down of reactions is especially important in designing automatic continuous-process control facilities, e.g., in-flow analysis systems. Until recently, little was known of the new practical ways to enhance sensitivity and selectivity. This is because the analytical forms are not intermediate products of reactions whose spectral characteristics can be determined with the aid of high-speed spectrophotometers, applying external action stopping, or by slowing down the reaction at a certain stage.

Obviously, studying the rates of reactions is essential in developing theory of action of OR. The mechanism of most chemical reactions of analytical value remains unknown so far. Even if the structure and composition of the starting components and end product of a reaction are known, little or nothing is known of the structure of intermediate products that form as an element's cation interacts with a structurally complex reagent.

Until recently, color reactions were classified as slow and instantaneous. The kinetics of the latter were hardly studied at all. However, to understand the mechanism of the process, instantaneous reactions are of great interest, since in this case, the complexing mechanism is manifest in its pure form. Slow reactions are normally encumbered by the processes of hydrolysis, dehydrolysis of metal ions, and other side processes.

The advances in studying fast reactions in complex fields of chemistry have made it possible to apply the methods used to the examination of color analytical reactions. Of late, new techniques of studying the kinetics of reactions have appeared, which are applicable to reactions with a transformation half-time ($t_{1/2}$) of 10^{-9} to 10 sec, [187-190] i.e., in a range much broader than for kinetics of reactions proceeding at "normal" rates (from 10 to 10^4 sec). With the advent of these techniques, fast reactions have become accessible to investigators. Earlier, methods of studying fast reactions were discussed at special symposia, [191,192] as well as in papers, [190,193-197] and individual works. [188,198-205]

The first studies of the mechanism of color reactions using the kinetic approach primarily involved model reactions. In almost every case, it was established that color reactions are not simple single-stage reactions, but yield one or several intermediate products. A study into the reaction of aluminum with xylenol orange and alumocreson[206] indicates that, in the first case, the reaction is in accordance with a second-order kinetic equation, whereas in the second case, it complies with a first-order equation. The monomolecular nature of the reaction of aluminum ions with alumocresol is explained by the fact that a limiting process of dissociation of polynuclear hydrated aluminum complexes takes place. Also studied was a slow reaction of niobium with xylenol orange; [207] the reaction was found to be first-order relative to xylenol orange.

Examination of complexing of gallium with methylthymol blue[208] revealed formation of an intermediate product, namely, $Ga(OR)_2$ along with the final complex of

composition GaOR. The first-order reaction was established with respect to the concentrations of both metal and reagent. The stage determining the rate of the process is that of interaction of the complex compound $Ga(OR)_2$ with cation $Ga(H_2O)_n$. Another study was made of interaction between the same reagent and Ni[209] as well as La;[210] the order of the reaction was found. Arsenazo (III) was studied in interaction with Zr.[211] In each of these cases, no quantitative data could be obtained except for establishing the reaction order.

Kinetic spectroscopy of fast reactions is very useful when analysis is made of a mixture of substances entering into similar reactions, but differing as far as the formation or dissociation of complexes is concerned. In analysis of alkaline-earth and some transition elements, the flow variant of this technique was used.[199,200,212] For quantitative determination of REE present in a combination, the kinetic approach was applied to the following reaction between complexon (III) and colored complexes formed by REE with xylenol orange:

$$LnX + EDTA \rightleftharpoons LnEDTA + X \qquad (6)$$

where Ln is the REE ion, X is the xylenol orange anion, and EDTA is ethylenediaminetetraacetic acid.[202] This is a first-order reaction relative to the colored LnX complex in the REE series, and the effective rate constant of this reaction in the REE series varies from 236 sec^{-1} for Ce(III) to 30 sec^{-1} for some REE.[213-215] The new method permits determining a rare-earth element with a tenfold excess of another rare-earth element.

The reaction between UO_2^{2+} and arsenazo (III), widely used in analytical chemistry, was also studied kinetically.[216] To this end, a specially designed spectrophotometer with electronic spectrum scanning was used to ensure registering optical absorption spectra in the range of 230 to 800 nm, as well as recording of kinetic curves at any one of these wavelengths.[188,205] The principle of operation of this spectrophotometer is illustrated in Figure 15 which represents a functional diagram of the instrument. Emission from a source of light with a continuous spectrum passes through the optical cell of a fast mixer operating on the stop-flow principle and on to a diffraction spectrograph in whose focal plane a special TV camera tube is arranged which is essentially an electrostatic slot dissector of the LI-602M type. The dissector transforms the optical spectrum to its electronic image and scans this image at the sweep frequency as a periodic sweep voltage is applied to its deflection plates. The amplified output of the dissector is fed to the input of a storage oscilloscope of the C8-1 type, used in this spectrophotometer as a storage device. The control unit of the instrument sets an appropriate mode of its operation, as well as produces the sweep voltage for the dis-

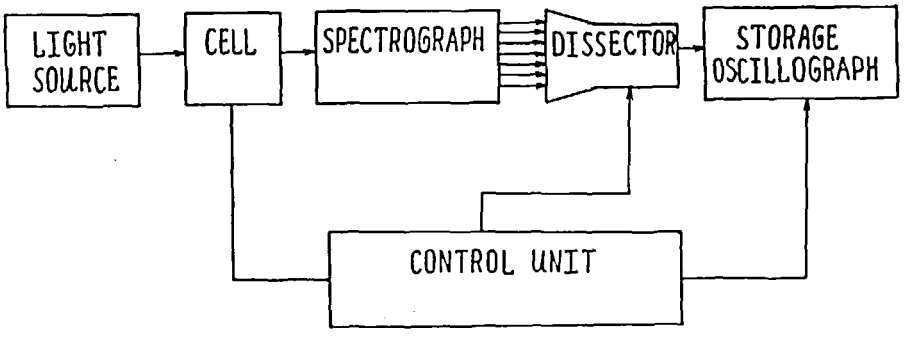


FIGURE 15. Schematic of a fast-response spectrophotometer with an oscilloscope output. See text for full explanation of components.

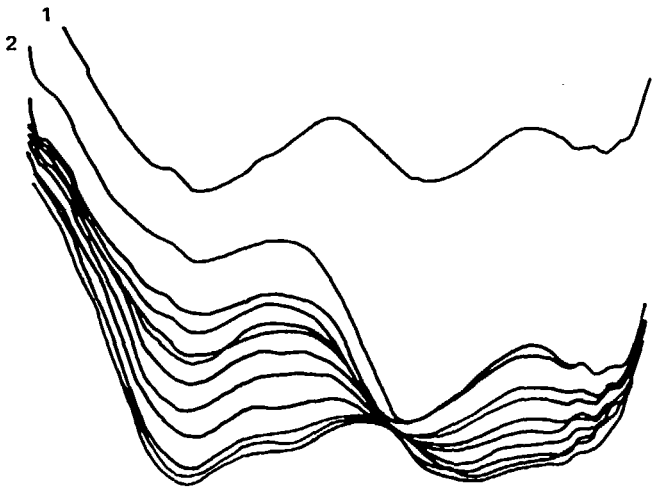


FIGURE 16. Transmission spectra of UO_2^{2+}-arsenazo (III) system. Initial reagent and metal concentrations: 2×10^{-5} *M*, pH 2.0. Curve 1 — Lamp's; Curve 2 — reagent's spectrum. The other spectra are those of UO_2^{2+} and arsenazo (III) and have been taken successively at 3.3-msec intervals (2, 3, 4, 5, 32, 64, 128, 256, 1023). The first minimum corresponds to 510 nm, the second, to 665 nm.

sector and CRT of the oscilloscope. Application of the sweep voltage to the deflection plates of the dissector and CRT of the oscilloscope in the parallel mode ensures linearity of the scale of wavelengths of the spectra of interest.

In the spectrophotometer, provision has been made for the following modes: recording of a single spectrum programmed recording of a group of spectra, continuous display, and recording of kinetic curves at a fixed wavelength. In the single spectrum recording mode, the spectra of the light source, substances under investigation, and the zero line are recorded. This mode may also be used for recording spectra at slow stages of a reaction. In the programmed recording mode, automatic recording is made of up to ten spectra with arbitrary numbers, preselected for recording out of 1023 spectra scanned successively at equal time intervals. In this mode, it is possible to automatically shift each of the spectra being recorded, along the ordinate, relative to a preceding one, which in some cases, is useful in determining the direction of variation in the absorbance. In the continuous recording mode, spectra are examined in advance, the instrument is calibrated, and the recording conditions are selected. The kinetic curve recording mode is effected with the sweep being discontinued and the oscilloscope being brought to the triggered mode. In this mode, the operation of the spectrophotometer is similar to that of standard Aminco® and Durrum® spectrophotometers intended for studying the kinetics of fast reactions. [217,218] This mode is suitable for studying reactions in the millisecond range, as well as reactions lasting several minutes, since the maximum sweep duration is 5 min.

Figures 16 and 17 represent typical curves that can be obtained and photographed from the oscilloscope. The new model permits interfacing the spectrophotometer with a computer, obtaining digital data, decoding the kinetic curves, and calculating respective kinetic reaction constants.

Analysis of absorption spectra and kinetic curves derived under various conditions (concentration, pH, third components, temperature, etc.) better elucidates the complexing mechanism. In the case of UO_2^{2+} reacting with arsenazo (III), the reaction was found to be close to first order, and its rate was found to vary directly with the concentration of one of the components, the most important being the concentration of the

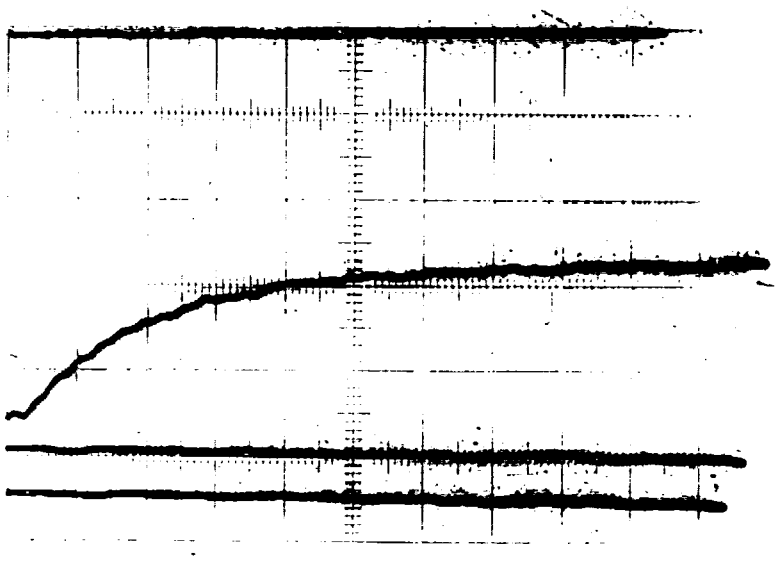


FIGURE 17. Kinetic curve of a reaction between UO_2^{2+} and arsenazo (III). Initial reagent and metal concentrations: 2×10^{-5} *M*, pH 2.0, λ = 510 nm. Upper straight line — 100% transmission; second straight line — transmission of the reagent; next — kinetic curve; at bottom — 0% transmission.

ionized form of the reagent. This means that, although one cannot rule out direct interaction of the uranyl ion with the nondissociated form of the reagent, the main process determining the reaction rate is the interaction between the uranyl ion and the active, dissociated form of the reagent.

At the same time, using conventional investigation techniques based on processing of the kinetic curve of formation of the end product, it is practically impossible to define the number of reaction stages and to calculate their rate constants, to say nothing of establishing the structure of the intermediate products. This is due to the fact that the kinetic curves based on variations in the optical properties of the system are not characteristic enough in the case of fast reactions. Even when fast-response spectrophotometers and mixing devices are used, by the time the first point of a kinetic curve is registered, the reaction is 30 to 40% complete and, in some cases, 50 to 60%. Substantially higher accuracy and reliability of the results are attained when a set of kinetic curves is studied and processed instead of just one curve, but with appropriately changed initial conditions. Again, even in this case, a full picture of the reaction mechanism cannot be obtained from the available kinetic curves.

More complete information on the mechanism of a complex color reaction can be provided by studying the spectra of the reaction products, recorded by the instrument as the reaction proceeds.

Both organic agents and their complexes with metal ions are colored substances; therefore, one may assume that the intermediate products formed in the course of a reaction will also be colored and exhibit their own absorption spectra in the visible region. Spectroscopic data or ORs and their complexes with metals indicate that their spectra are made up of a plurality of simple components; therefore, reaction product spectra recorded at different moments are composite spectral contours including bands belonging to the reagent, complex, and intermediate compounds.

At present, there exist elaborate methods of deconvoluting complicated spectral contours into basic components.[219-221] These methods enable the isolation of individual bands relating to the starting compounds as well as intermediate and end reaction

products. According to the Lambert-Beer law, the intensities in an absorption maximum of these individual bands vary directly with the concentrations of the substances to which these bands belong. Thus, we have a possible way of detecting changes in the concentration of individual compounds participating in a reaction or, in other words, obtaining their kinetic curves. The solution of this problem would enable the calculation of the rate constants of each elementary stage, which would have concrete meaning.

Experimentally, this problem is rather complex for it necessitates high accuracy of measurement and deconvolution of composite spectral curves into basic compounds and selection of optimum reaction conditions which would ensure that the reaction follows a definite pattern. It is also necessary to provide for adequate interpretation of the results.

One of the possible solutions of this problem, which is currently being sought, resides in combining experimental techniques with quantum-chemical calculations using a computer. First, on the basis of general chemical considerations, possible reaction patterns and the structure of intermediate products are assumed. Then, spectra of the system under study are experimentally obtained in the course of the reaction. These composite spectra are deconvoluted into a minimum number of Gaussian components. This is followed by relating the separated bands to their respective intermediate reaction products. This is done by comparing the absorption maxima of the experimentally discovered bands and those calculated by quantum-chemical methods.

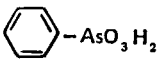
For each of these products, an appropriate kinetic curve is constructed. The presence of a maximum on this curve corroborates the existence of an intermediate product. The curves may be constructed not only experimentally, but also theoretically for an expected reaction pattern. To this end, model calculations are made with the aid of a program written in FORTRAN for a BESM-6 computer. The theoretical curves are compared with the experimental ones; on the basis of this comparison, one can judge the validity of the selected reaction pattern. Coincidence of the maxima of several bands is indicative of formation of only one intermediate product with a composite spectrum, which means that a different reaction pattern should be taken as the basis.

The foregoing is only one of the possible approaches to studying the reaction mechanism using kinetic, quantum-chemical and other data obtained as a result of experimental and theoretical examination of the complexing process. For the method to be considered reliably and finally proven, additional studies are required. Nevertheless, it is quite clear at present that studying reagents and complexes only under static conditions cannot provide full information on the mechanism of the occurring processes. Investigation into the dynamics of the process necessitates both experimental kinetic approach and theoretical analysis, including quantum-chemical and model calculations of the possible reaction patterns.

F. The Concept of Functional Analytical Groups of Organic Reagents

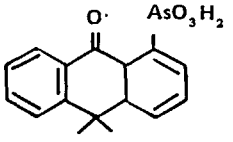
The concept of functional or specific atomic groups is most important in the OR theory. This notion was gradually put into use by Chugaev,[222] Feigl,[1,37] Belcher,[6] Kul'berg,[2] Kuznetsov, [44,223] and others. Initially, the notion of a functional (or functional analytical) group was used in the same sense as a group of atoms directly interacting with the metal cation within the molecule of an OR. Sometimes, this group of atoms was referred to as the analytical center of the molecule. At the same time, as the theory of ORs was being developed and new, more complex ORs were synthesized, this notion had to be more properly defined. It will be interesting to see in retrospect, using a simple atomic group such as AsO_3H_2 as an example, how the molecular functional group concept changes as the OR structure became more complicated.

Back in 1937, Alimarin and Frid proposed to use phenylarsonic acid for determining niobium and tantalum: [224]



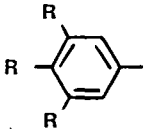
The presence of the arsono group is conducive to formation of particularly stable complexes with Zr, Ti, Sc, U, Th, rare-earths, and other elements. The products of reactions of these elements with phenylarsonic acid are colorless compounds; they find application, primarily, in gravimetric analysis and in separation of interfering elements. Phynylarsonic acid is also used for determining tin and thorium in monazite sands, as well as precipitation of zirconium by separating it from other elements.[225]

Afterwards, a great number of organic compounds of different classes were synthesized, containing an arsono group, which are also valuable organic reagents. Anthraquinone-*α*- arsonic acid (anthrahas) is employed to precipitate small amounts of Sn (IV), Zr, and Ti.[226]



Also used for precipitation and gravimetric determination of titanium and zirconium are *p*-hydroxyphenylarsonic and arsanilic acids.[227] The latter is most suitable for quantitative determination of cerium (the appearance of reddish brown color is due only to the chromoform action of cerium ions) and zirconium (appearance of a white residue). [228]

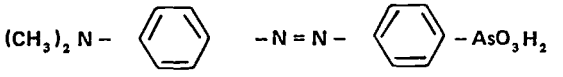
Zirconium is also precipitated by means of alcyl arsonic acids, such as propyl arsonic, allyl arsonic, and others. Reagents are known (mainly, precipitating agents) of the general formula:



where R is H, OH, NH_2, CH_3, Cl, NO_2, COOH, NH–CO–CH_3, NH–CH_2–COOH and other substituents. These reagents are suitable for precipitating Sn (IV), Zr, and Th.[229,230]

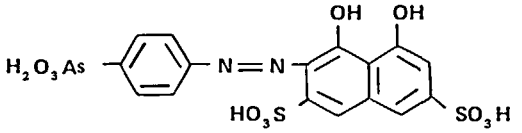
Consideration of this group of reagents-precipitators suggests that, with the exception of anthraquinone-*α*-arsonic acid where the carbonyl oxygen may participate in complexing with the element ion, the arsono group is the only group binding the metal ion, which leads to a particular analytical effect, namely, precipitation of the ions of interest with OR in the form of an ordinary salt through the participation of the arsono group.

Also attributed to the same category of reagents-precipitators are colored compounds containing an arsono group which is not in an ortho position to the azo group. In this case, the reaction mechanism also boils down to formation of ordinary salts with the participation of the $-AsO_3H_2-$ group; no chelate compounds with a sharp change in color are formed. For example, *p*-dimethylaminazophenylarsonic acid



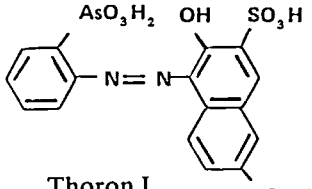
forms, together with zirconium ions, a slightly soluble precipitating reddish brown salt. [229,231] In this case, however, bearing in mind that the zirconium ions tend to interact

with the azo group, there is a possibility that the latter represents the functional analytical group. The same applies to azo dyes based on arsanilic acid and various azo derivatives such as chromotropic acid:

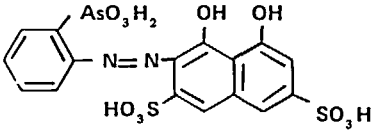


This compound also forms ordinary salts with certain elements and can be used for precipitating them. The molecule of this reagent contains more than one reaction center capable of binding the metal ions (arsono group, azo group, two hydroxy groups in positions 1 and 8 of the naphthalene ring, and an *o*-hydroxyazo group).

Further complication of the reaction center of the reagent, i.e., the appearance of a new functional analytical group, takes place in reagents such as thoron (I) and arsenazo (I):[232]

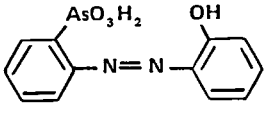


Thoron I

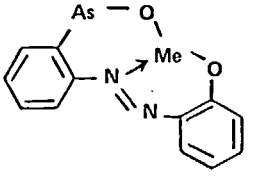


Arsenazo I

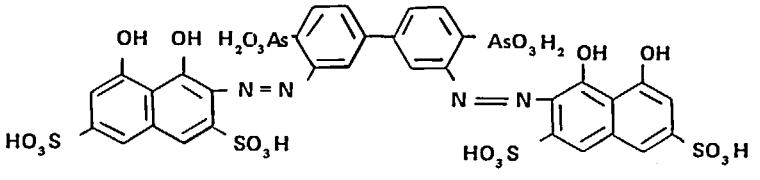
The mechanism of complexing reactions of elements with reagents containing an *o*-arsono-*o*-hydroxyazo group is well known. It has been established that the metal ions are bound by the *o*-arsono-*o*-hydroxyazo group



which is considered to be functionally analytical for this class of reagents. In its general form, the structure of a chelate compound is normally written as follows:



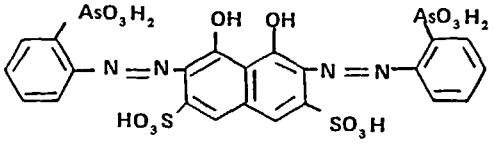
An analogue of arsenazo (I), namely, arsenazo (II), has been synthesized: [233]



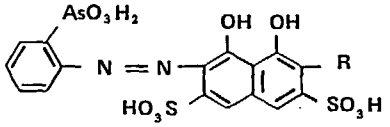
In this reagent, the functionally analytical group typical of arsenazo (I) occurs twice. Both parts of the arsenazo (II) molecule act as independent molecules of a respective monoazo compound. At the same time, the somewhat higher strength of complexes of elements with arsenazo (II) and the shift of the absorption band of the complex's

spectrum towards lower frequencies are indicative of a certain interaction between both parts of the molecule.[234]

The next large group of reagents includes 2,7-bis-azo- substitutes of chromotropic acid, such as arsenazo (III) and analogues: [235]

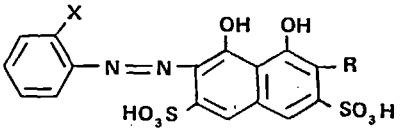


Arsenazo (III) contains the same functional analytical group as arsenazo (I), which occurs twice as in arsenazo (II). At the same time, the properties of arsenazo (III) sharply differ from those of arsenazo (I) and arsenazo (II). The difference resides in the much higher strength of complexes, a dramatic increase in the sensitivity and contrast of reactions, and changes in other properties (considered in greater detail in Reference 20, for example). Thus, neither the nature of a functionally analytical group nor their number in a reagent's molecule determines the most significant analytical properties of the reagent. The determining factor seems to be the reagent structure as a whole.[131] This is corroborated by consideration of reagents analogous to arsenazo (III), of the following structure:

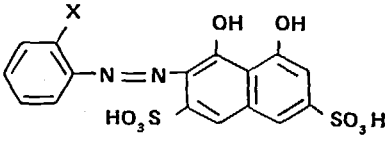


where R is the residue of any diazo component. These reagents enter into similar reactions with elements as arsenazo (III). According to some data, R is not necessarily a residue of a diazo component, but may be any other system with conjugated bonds, for example, $(CH{=}CH)_n{-}R_1$.

Examination of the principal analytical properties of reagents of a similar structure, which do not contain a single arsono group, of the type:



Where X is PO_3H_2, $-COOH$, $-OH$, $-SO_3H$ and other salt-forming and nonsalt-forming groups, suggests that they have the same feature as arsenazo (III), namely: 2,7-bisazo compounds of chromotropic acids sharply differ in properties from respective monoazo compounds of the type:



These examples indicate that the principal analytical properties of reagents are determined not only by the nature of those groups and atoms which directly coordinate the metal ion, but also by the molecular structure as a whole, which includes both coordinating and peripheral groups forming a single conjugated system. Some investigators distinguish between functional analytical groups directly coordinating the metal ion and analytically active groups, i.e., all other groups which affect the analytical properties of reagents. [2,6,12,236] Recent works show that in many cases the mechanism

of analytical reactions is more complicated than was previously assumed. Depending on the reaction conditions, different groups of reagents may participate in complexing with the element ion. In the case of coordination of the metal ion, the structure of the functionaly analytical group may change. The reaction mechanism within a functional analytical group depends on the nature of the metal ion. Dimer, mixed, and more compound complexes may be formed. In the case of dimer complexes, the reaction mechanism of two similar functional analytical groups may be different.

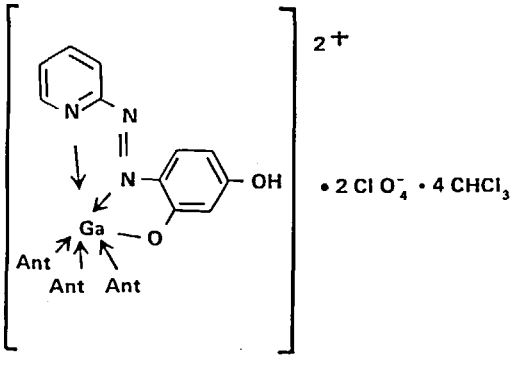
In this connection, it may be assumed that only a reagent's molecular structure as a whole, its carbon skeleton, and π-electron structure are fully representative of both known and unknown analytical properties of an OR. The nature of functional analytical and analytically active groups is but an additional important factor characterizing the analytical properties of individual reagents featuring similar carbon skeletons and π-electron structures.

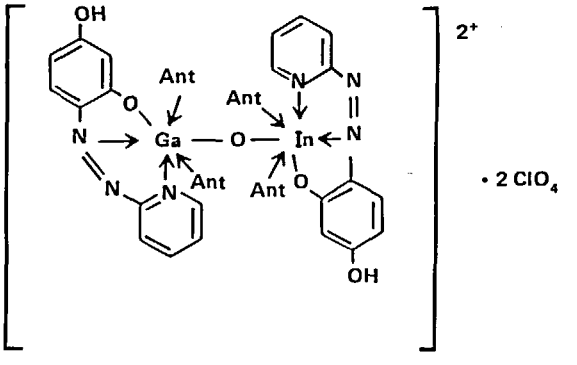
This principle of classification of certain structural features of ORs, into more and less important ones, insofar as their influence on the analytical properties of a reagent is concerned, may underlie classification of ORs in general. Such classification will be based on the general structure of a reagent, while secondary factors include the nature of functionally analytical and analytically active groups. An example of such classification of ORs namely, azo compounds, is given in Reference 20. Of course, this system does not exclude other possibilities of classification based, for example, on the analytical purpose of reagents.[2] The classification according to Reference 20 is in compliance with the quantum chemical concepts. Indeed, the action of the metal cation on similar π-electron systems brings about respective effects similar in a first approximation. This holds true even in the case where the functional analytical groups in two reagents differ in nature. Quantum-mechanical studies of the structure and properties of ORs with similar π-electron systems support the foregoing. [26,145-156]

In some cases, such a classification and approach to studying the properties of reagents may form the basis of research and directed synthesis of new reagents. We may sometimes predict such reagent properties as the conditions of their interaction with elements, sensitivity of the reaction, strength of complexes, solubility, extractability, etc. The reaction selectivity is predictable to a lesser degree.

The above regularities apply not only to azo compound-type ORs, but also to reagents of other classes: reagents of the triphenylmethane series and others. In all cases, selectivity, sensitivity, and other analytical properties are determined by a number of factors of which the most important are the π-electron structure of a molecule, its geometry, and the chemical nature of atoms and atomic groups which are in direct contact with the metal ion being coordinated.

Ternary (mixed-ligand) complexes also provide a vivid illustration of the determining role of the stereometry of reagent molecules and the coordination abilities of the central ion with respect to the analytical properties of the reagent and the reaction products. As an example, consider two assumed structures of multicomponent complexes of Ga and In with a surfactant and antipyrine: [237]





The decisive role of the geometric factors and coordination abilities of the metal ions with respect to the reaction selectivity follows from consideration of these structures. The same applies, for example, to multicomponent systems Nb, Ta-hydroxy acid OR.[238] Mo, V-NH_2OH-OR;[239] or W-H_2O_2-mono- or bis-azo compound.[240]

The main regularities of complexing of ORs remain true and can be applied to studying the mechanism of interaction of an element with polymer-chelating sorbents. In this case, the effect of geometric factors on the reactivity and selectivity becomes more significant for, apart from the geometry of the graft monomer unit, one should also take into account that of the polymer system as a whole.[241,242]

Thus, it can be seen that all basic properties of an OR are determined by the structure of the molecular carbon skeleton and its π-electron structure. These two factors define the stereometry of reagent molecules in a series of compounds of similar structure. A reagent's structure and π-electron structure determine the optical properties of the reagent and the products of its reaction with element ions, the strength of complexes, selectivity, and other properties.

The nature of the functionally analytical group of a reagent's molecule (the term being used to imply a group of associated atoms of the molecule, responsible for direct coordination of the element ion) is merely an additional but important factor affecting the reagent's selectivity. The same applies to other substitutes, both salt forming and nonsalt forming, which do not form part of the general conjugated π-electron system. They may affect the solubility, stability, and other reagent properties. The occasionally appearing notion of the chromoform center of a molecule seems to be already included in the general molecular π-electron system concept.

The term "analytical center of an organic reagent's molecule" is not clearly defined. If it is used to imply the most important part of an organic molecule, defining its principal analytical properties, one should include in this notion the OR molecule as a whole. If it denotes the site of attachment of the metal ion, then it is equivalent to the notion of a functionally analytical or specific group.

The notion of functional or specific groups should be preserved. It defines, at least in a first approximation, the group of elements which will preferably interact with a given reagent; it is also convenient in classifying reagents. However, it should be borne in mind that only the structure of a reagent's molecule as a whole completely defines the analytical properties of any OR.

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