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Complexing Adsorption Chromatography and Its Prospects

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Investigations on complexing adsorption chromatography during its period of existence (1954-1970) are reviewed, and possible ways for its future development are considered.
The method was developed originally for preparing the extremely pure salts used in the production of phosphors, and then grew to be a general method of separating substances, enabling the most selective processes to be accomplished by simple procedures. However, widespread introduction of the method is hindered by the absence of published summaries covering technique, theory, and fields of application. The present review covers these aspects, and will enable research workers to apply the method correctly and to extend its field of use in the laboratory and in industry. A list of 80 references is included.

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I. INTRODUCTION

The problem of the selective extraction of substances from complicated mixtures has recently become especially important, as a consequence of the development of many branches of chemistry and technology which require the use of pure and ultrapure materials. Establishment of the most effective and economical methods for isolating, separating, and purifying substances is necessary to meet the demands of the development of nuclear energy, the manufacture of semiconductors, phosphors, and single crystals, the rational exploitation of combined ores, and many other branches of industry and fields of science.

Chromatography has played a considerable part in solving these problems, enabling pure substances to be obtained in various areas of chemical science and industry, including the selective extraction of substances from complicated mixtures.

The greatest difficulties arise in the development of procedures for obtaining pure and ultrapure materials and separating elements of closely similar properties. The practical solution of this problem requires the use of especially delicate and effective methods, since the usual chromatographic methods, based on the use of general-purpose sorbents (including ion exchangers), often prove ineffective. In this connection research workers have recently directed their efforts towards producing selective sorbents characterised not only by group but also by individual specificity towards particular elements. The development of such sorbents is extremely promising, since their practical use will enable the best separation to be obtained. Efforts to obtain such sorbents have been made for a long time, a particularly large number of papers having been published during recent years (see the reviews[1-3]).

It is well known that ordinary general-purpose ion exchangers possess some measure of selectivity, which is responsible for the sequential sorption of ions in so called "adsorption series". Selective exchangers, however, exhibit a more clearly pronounced selectivity, as a consequence of the presence in the polymer matrix of specific active groups, most often complex-forming.

General-purpose exchangers also often exhibit complexing properties, leading to a decrease in the degree of dissociation of ionogenic groups and hence an increase in selectivity. For example, cation-exchange resins containing carboxylate and phosphate groups, and also anion-exchange resins of low and medium basicity, absorb metal ions as a result of complex formation. Specially prepared selective exchangers usually contain ionogenic groups capable of forming inner complexes with metal cations. They are prepared by introducing an appropriate chelating agent into the polymer matrix. However, existing methods do not yet allow us to obtain selective exchangers having specified properties or with any active group, in spite of the varied range of specific reagents available to the modern analytical chemist. This explains the hitherto insignificant use which selective exchangers have found[1-10].

However, other opportunities for highly selective chromatographic separations can be realised by creating special conditions under which a rich variety of specific reagents of different kinds can be used for these processes.

The origin of this line of development was the use of precipitation chromatography[11-14] for many complicated separations by the simplest procedures. An almost unlimited number of chemical reagents can be used as precipitants in the columns. However, the broadest opportunities for selective separations are to be expected from the application of complexing agents by the method of complexing adsorption chromatography[15-20]. A great part in establishing this method and working out its physicochemical principles was played by Gurvich[15-20].

In contrast to precipitation chromatography, in which an inert support is used and the precipitates are frequently not attached to the carrier, but more along the column with the stream of solution, complexing adsorption chromatography uses as carrier a sorbent capable of retaining both the complexing agent and the products of its reaction with metal cations, which vary in solubility.

The complexing adsorption column consists of a sorbent carrier, which retains the complexing reagent sorbed on its surface. The term "modified" has recently been applied to such sorbents. When the solution of a mixture of substances is filtered through the column, separation occurs as a consequence of the differences in their capacity

for complex formation with the given reagent, in the stability of the complexes which are formed, and also in their sorbability on the given sorbent carrier. Separation is intensified also by the chromatographic method itself, a distinguishing feature of which is a multiplicity of elementary acts of separation. The reaction products are retained on the sorbent carrier in the column as sparingly soluble complex compounds (sometimes as soluble complexes). At the same time substances which do not react with the given complexing agent pass freely through the column into the filtrate.

Thus a selective process of separation can be realised most fully in the complexing adsorption method, the main factor in the present case being the selectivity of the complexing agent. Advances in the preparation of a large variety of such reagents opens up wide prospects for developing the method and extending its fields of application. Successful separation requires that the appropriate complexing agent and carrier should be matched, the properties of the modified sorbent studied, and also optimum conditions chosen. The conditions of separation include the most varied procedures used in chromatography—use of particular masking complexing agents, variation in solution pH, temperature, and rate of filtration—together with other procedures which may in some measure enhance the specificity of the reagent and the selectivity of the method. By this means columns possessing exceptional selectivity can be prepared by simple procedures using ordinary chemical reagents together with cheap and readily available sorbents.

The separation of substances by complexing adsorption chromatography is accomplished in several cases with only one filtration of the mixture through the column, whereas even complexing elution requires two stages—production of the primary chromatogram, followed by displacement by the eluent.

The procedures of complexing adsorption chromatography closely resemble those of precipitation chromatography, from which the method arose historically as a consequence of improving the latter by replacing the inert carrier by a sorbent actively involved in the process of separation[18]. The method was originally termed "adsorption–precipitation chromatography", but since in most cases sorbable reagents were used, which formed complexes with the separable substances, also sorbed to some extent on the carrier, the term "complexing adsorption chromatographic method" was adopted later[17,18].

Adsorption phenomena are secondary in precipitation chromatography; they always accompany separation to some extent. In the complexing adsorption method, however, adsorption phenomena are a factor determining the possibility of separation[19].

Since substances are more easily adsorbed from a given solvent the less soluble they are in it, the present method is applied most frequently to the separation of substances which react with the reagent to form products of limited solubility. It is interesting that sometimes, where several reactions are possible between a given substance and the complexing agent, reaction which leads to the formation of the most easily adsorbed product is accelerated under the conditions of a column. In this connection complex formation quite often involves different reaction mechanisms under static conditions and in the column[18,19]. Precipitation chromatography can be regarded as the limiting case of the adsorption—precipitation method in which, in view of the sparing solubility and the "tenacity" of all the compounds formed in the column, the adsorbent can be replaced by an inert support.

II. PHYSICOCHEMICAL PRINCIPLES OF COMPLEXING ADSORPTION CHROMATOGRAPHY

Detailed investigation of the processes accompanying the complexing adsorption of metals has revealed several specific features of this method[19]. It is distinguished from other methods of chromatographic analysis mainly by the conditions of application of complex formation, a reaction which is widely used for the separation of substances in both static and dynamic processes. Opportunities for the application of complex formation were especially broadened by the development of chromatography. Complexing processes became an important factor in separation both in ion-exchange and adsorption and in partition and precipitation chromatography.

The method of applying complexing agents most widely used in classical adsorption chromatography is development of the primary chromatogram. In this case the developer reacts with already separated substances, without taking part in their separation. Metals can be separated also by chromatographing mixtures of their soluble complexes on molecular sorbents, e.g. on aluminium oxide[21–23].

In ion-exchange chromatography a very widely used method for developing the primary chromatogram of the ions is the use of solutions of organic reagents which form readily soluble complexes with the separable cations. This procedure is especially valuable for the separation of rare-earth elements[24]. An analogous method is employed in partition chromatography[25]. In some cases the use of ion-exchange columns to separate complex ions obtained in solution or to segregate them from other substances is effective[26,27].

In isolated cases precipitation chromatography also makes use of sparingly soluble complexing agents in the form of chemisorbents together with carriers which are inert towards reactants and reaction products[11,27]. The fundamental process in precipitation chromatography is the formation of sparingly soluble compounds as a new phase, while adsorption processes, as already stated above, are secondary and may exert different and opposite effects on the separation.

In the method under review complex formation is invariably combined with sorption processes: no new solid phase is formed. The complexing agent is first attached to the sorbent carrier by sorption interaction, and then a solution of the mixture is introduced into the column. Separation in such a column is determined by the difference in the instability constants of the complexes formed by the cations with the complexing agent, these latter also being in some measure retained on the sorbent carrier by sorption forces. Under the most favourable conditions for separation some elements form complexes and are attached to the column, while others do not form such compounds and pass into the filtrate. One of the components can then be isolated in pure form, as has been achieved, for instance, in the thorough purification of salts used in the production of phosphors [15,16,19]. Thus in this method the possibility of separation is governed by the sorption interaction of the complexes with the sorbent carrier.

In this connection it is important to note also that, in the limiting case, the formation of sparingly soluble complexes takes place in the complexing adsorption method without isolation of a new solid phase: they are attached by van der Waals forces to the surface of the sorbent carrier at the instant of their formation, i.e. bypassing the precipitation stage, apparently becuase the bonding between

molecules of the complex and the surface of the sorbent is stronger than that between molecules of the complex in its crystals. It should be noted that the complexes which are formed may vary in solubility.

One condition for use of the complexing elution of chromatographic columns is that the reagent should be more or less soluble. This is a second stage, following formation of the primary chromatogram, and the ion forming the most stable compound is the first to pass into the filtrate. In contrast to this, the condition for application of the complexing adsorption method is that the reagent should be relatively sparingly soluble but readily adsorbed on the sorbent carrier, so that the reagent remains in the column and does not contaminate the solution of separable cations. Separation is accomplished by the application of only one process—filtration of the solution of separable substances through the column—and the cation forming the least stable complex is the first to pass through into the filtrate. This fact is responsible for the high selectivity of complexing adsorption columns and the possibility of using them to purify large quantities of substances, which do not react with the complexing agent, from impurities which form with the latter complex compounds that are sorbed on the carrier.

It is an extraordinarily complicated task to reveal the main laws and the mechanism of complexing adsorption, especially in view of the multiplicity of combinations in the preparation of modified sorbents, where both the properties of the carrier itself and of the complexing agent and also qualitatively new characteristics of the modified sorbent and those of the separable system may develop and influence the process.

One of the most important factors determining the mechanism of complexing adsorption is the nature of the sorbent carrier. The demands made on the latter by the essential nature of the method reduce basically to the following: the carrier should be insoluble in water or other solvent and possess a sufficiently large surface, the ability to sorb molecularly the complexing agents and their reaction products with the separable substances, good filtering ability, mechanical and chemical stability, and optimum kinetic characteristics. Existing sorbents may only partly satisfy these main requirements.

If the sorbent carrier contains any soluble components, they may be extracted during the process and further contaminate the solution of separable substances. The sorbents sometimes contain soluble components and mineral impurities, which are easily removed by careful preliminary washing.

The advisability of using a particular sorbent carrier depends in large measure on its adsorption capacity. In this connection sorbents having a maximum surface area, because of the presence either of pores or of a network structure, should be preferred. It is important that molecules of the modifier (i.e. of the already sorbed complexing agent) should be accessible for subsequent reaction with the separable ions.

The main type of sorption in the present method would be molecular sorption on to the carriers both of the complexing agents and of the metal complexes formed in the process of separation. Most sorbents contain various functional groups and energetically non-uniform centres, and one mechanism or another may predominate depending on the conditions of sorption. A study of the mechanism of sorption is therefore of great value in choosing the most suitable carrier–modifier system for a particular process.

The good filtering power, mechanical durability, and chemical resistance demanded of a sorbent carrier are governed by its operating conditions. Filtering power depends on the grain size of the sorbent, which is selected within optimum limits for a given size of column and a given rate of filtration of the solution. Adequate mechanical durability of the sorbent is important on prolonged operations, especially if it is desirable to regenerate the sorbent and use it many times. Various corrosive media may be employed during separation or sorbent regeneration, so that the chemical resistance of the sorbent is also quite important. Changes in the sorbent resulting from chemical reactions may lead not only to contamination of the solution but also to mechanical disintegration and loss of sorption capacity.

Modifying the surface of a sorbent carrier by the sorption of various complexing agents yields a qualitatively new sorbent: not only the chemical but also the physical properties of its surface have changed. The pore size and hence the total surface vary depending on the quantity of complexing agent sorbed by the carrier. The absorption of metal ions takes place on a modified sorbent, as a consequence of their chemical reaction with the complexing agent and the formation of new complexes. Other types of sorption, characteristic of the unmodified carrier, may be either partly or completely suppressed.

It must be borne in mind that the chemical reactions occurring in a complexing adsorption column may differ from those in solution[19]. For example, compounds which are unstable in solution under ordinary conditions are often formed in a column and exist for a long time[12–14]; in other cases certain reactions, which are not feasible under static conditions, may go to completion in a column[19]. These aspects of the accomplishment of reactions directly in columns may find the widest practical application, from the separation of different modifications of chemical compounds to reactions which occur with difficulty under static conditions, including catalytic processes for organic and for inorganic substances.

We have investigated the mechanism of the sorption of complexing agents and inorganic ions on active carbon[28,29], and shown that the former (e.g. dimethylglyoxime, 1-nitroso-2-naphthol, 8-hydroxyquinoline, tannin, xanthates, dithizone, diethyldithiocarbamates, derivatives of hydroxamic acids, phenylarsonic acid, thionalide, thiourea, etc.) undergo sorption of molecular type. Carbon is able to retain firmly 10–20% of the complexing agent, about 1.0–3.0 mg-equiv.g^{-1}, while the ion-exchange sorption of inorganic ions on active carbon is only 0.05 to 0.07 mg-equiv.g^{-1}. These results are consistent with those obtained by other workers[19,30]. It was established also that the sorption of the complexes formed with metal ions is molecular in character[28,29].

The fact that sorption can occur on active carbon by two mechanisms—molecular and ion-exchange—does not prevent its use as a carrier in the complexing adsorption method. Ion-exchange sorption has been shown[28,29] to predominate at low (up to 1%) surface coverage by the modifier. Above 1% coverage this is suppressed by sorption of the complexing agent, and the metal is absorbed by the complexing adsorption mechanism. We can therefore regard modified active carbon as monofunctional, corresponding in its action to the complexing modifier sorbed on it.

The optimum quantity of modifier on the carrier should be found empirically in each individual case. The total absorption capacity of the metal increases with increase in the coverage of carbon by the modifier[28,29], while the degree of utilisation of the complexing agent diminishes. However, the most complete exploitation of the modifier,

in some cases even ~100%, can be attained by selecting experimental conditions under which the metal ion is complexed to the maximum extent. This is usually achieved by choosing the optimum pH for the given system[22,28,29].

The temperature conditions are very important for separations by the complexing adsorption method. Rise in temperature tends to increase the rate of absorption of a metal cation. A considerable temperature effect can be used for intensifying complexing adsorption, since it tends to increase the productivity of the columns and permits higher rates of filtration.

All the above factors, influencing in some measure the separation of substances by complexing adsorption, must obviously be taken into account in determining optimum procedures for the chromatographic processes.

III. CONDITIONS OF APPLICATION OF SORBENT CARRIERS AND COMPLEXING AGENTS IN COMPLEXING ADSORPTION CHROMATOGRAPHY

Very few sorbent carriers at present available for complexing adsorption satisfy the above requirements. The most widely used for these purposes is active carbon, which was first employed by the originators of this method[15,17]. Subsequently technical conditions were developed for "active wood charcoal for chromatography" (DAUKh) [19], which was used in industry for obtaining high-purity salts employed in the manufacture of phosphors. In contrast to other carriers, charcoal, like most carbon sorbents, is a readily available and cheap material, possessing adequate sorption capacity, mechanical and thermal durability, and structural stability. The oblong grains of DAUKh charcoal have a cross-section of 0.2–0.6 mm. Carbon of such grain-size ensures a satisfactory rate of filtration when used in fairly large columns[19]. Complexing adsorption processes have been accomplished also on other brands of carbon[31-35].

Other sorbents, e.g. Wofatit E[36], whose capacity is several times greater than that of active carbon, have been used as carriers. Our investigations indicate that Wofatit E is useful as a sorbent carrier in processes where strong selective absorption is required. This resin is unsuitable for very fine separations, since with strong absorption substances of similar properties exhibit no differences in behaviour.

Among Soviet synthetic materials it is only recently that macroporous resins have been synthesised which are capable of both molecular and ion-exchange sorption. Such resins may be supposed to be good sorbent carriers for complexing agents.

Experience in the application of various complexing agents has enabled us to recommend several general and special procedures for modifying carbon in order to prepare selective sorbents. Charcoal can conveniently be freed from mineral impurities by pretreatment with 5–10% hydrochloric (or sulphuric) acid heated to 60–70°C.[16] The completeness of extraction of mineral impurities—mainly iron, copper, and potassium—must be checked by application of the most sensitive analytical methods to the filtrate. After treatment the excess acid must be washed out of the charcoal with distilled water until the washings are neutral to Methyl Orange, and the carbon brought to an air-dry state.

The method used to prepare the modified carbon may vary with the properties of the complexing agent. Sorption of sparingly soluble, non-volatile reagents (e.g. dimethylglyoxime, *N*-hydroxy-*N*-phenylbenzamide) is best accomplished by heating an aqueous suspension with carbon on a water-bath at 70°C. Heating is advisable to accelerate dissolution of the reagent and to remove air. As reagent is absorbed, fresh portions gradually dissolve and pass into the sorbed state. Soluble reagents (e.g. diethyldithiocarbamate, tannin, phenylarsonic acid) may be sorbed from aqueous suspension on shaking. It is advisable to preheat the suspension at 70°C for 5–10 min to remove air bubbles. Heating is inadvisable for the sorption of reagents which are volatile in steam (e.g. hydroxyquinoline). In this case saturation must be accomplished at ordinary temperatures, by shaking an aqueous suspension of carbon with the reagent. It is advisable to preheat an aqueous suspension of the carbon (without the reagent) at 70°C, and then cool it. Completion of sorption is assessed by disappearance of the corresponding colour from the solution when a sensitive qualitative test is applied for the given reagent.

The quantity of complexing reagent which can be retained in the sorbed state on DAUKh charcoal is usually 10–20% based on the weight of carbon.

Most complexing agents are firmly sorbed on the carbon surface, and hardly any desorption occurs on washing with water or on the passage of considerable volumes of solution. But in some cases, e.g. in the sorption of tannin, the reagent is not firmly retained on the carbon surface, and is gradually washed out of the column. In order to secure better attachment of such reagents, it is advisable after sorption to dry the modified carbon without washing it with water[29,37].

Some sorbents absorb well from solutions in organic solvents, e.g. dithizone from chloroform solution on to carbon[31]. The modified sorbent obtained sorbs heavy metals well from aqueous solutions.

An interesting method is to impregnate active carbons and other inert carriers with liquid organic reagents. McClaine and Noble[32,33] extracted uranium selectively on carbon treated with organophosphorus acid derivatives, which give stable chelate complexes with several metals, in particular uranium. Such sorbents have been employed in industry to extract rare metals.

In some cases a modifier is deposited from the vapour phase on to a carrier[38,39]. A carbon–titanium sorbent, which absorbs uranium selectively, has been obtained in this way.

The application of modified sorbents under dynamic conditions—in complexing adsorption chromatographic columns—is most effective, and we shall be concerned here mainly with this method.

Independently of column size (from laboratory to industrial dimensions) the modified sorbent is introduced as a suspension in an appropriate solvent (aqueous suspensions are mostly used). If the modified sorbent required is in a dry form, its aqueous suspension is first heated at 70°C. This is especially important in cases in which separation is effected at high temperatures, since dissolved air would be evolved from an unheated suspension, and might cause swelling of the sorbent layer.

If substances which do not react with the modifier are to be thoroughly freed from impurities that react with it to form stable sorbable compounds, it is advisable to place a layer of the pure sorbent carrier below the layer of modified sorbent, in order to prevent contamination of the filtrate with compounds that may be partly desorbed from the modified sorbent layer. The pure carrier is introduced into the column by the same procedures as the modified sorbent.

In the preparation of modified sorbents it must be borne in mind that the reactions of complexing agents on sorbent carriers with metal ions often occur differently from in a homogeneous medium. The special features of the process are exploited to intensify the separation effect (e.g. with dimethylglyoxime, 1-nitro-2-naphthol, xanthates, etc.). Sometimes, however, reactions in columns do not produce the expected separation, owing to the occurrence of undesired reactions.

An example of the complicating effect of the sorbent carrier is provided by columns containing carbon modified with sodium tetraphenylborate, a selective reagent for precipitation of the univalent ions K^+, Rb^+, Cs^+, NH_4^+, Ag^+, Hg_2^{2+}, and Tl^+. The solubility products of compounds of these metals with tetraphenylborate lie in the range 2×10^{-8}–5×10^{-10}. It would therefore appear promising to use such columns for the selective absorption of these ions from solutions of salts of other metals, especially for the thorough purification of sodium salts. However, our investigations of the sorption of potassium from aqueous salt solutions has revealed certain anomalies in this process. Potassium is completely absorbed on a carbon–tetraphenylborate column provided that sodium is absent from the solution: in the presence of sodium salts, however, the sorption of potassium is considerably weaker. Potassium absorbed by a column is displaced by sodium salts. A precipitate of potassium tetraphenylborate obtained in the absence of carbon is decomposed on addition of the latter to the system, with the liberation of K^+ and BO_3^{3-} ions. We explain this by the following decomposition of tetraphenylborate in the presence of carbon

$$(C_6H_5)_4BK + 4H_2O \rightleftarrows H_3BO_3 + KOH + 4C_6H_6 . \quad (1)$$

The decomposition of sodium tetraphenylborate occurs according to the equation[40]

$$(C_6H_5)_4BNa + 3H_2O \rightleftarrows C_6H_5B(OH)_2 + 3C_6H_6 + NaOH . \quad (2)$$

Detection of the BO_3^{3-} ion in solution indicates that reaction (1) takes place in the presence of carbon. It is interesting that displacement of the reaction to the right-hand side, i.e. liberation of the K^+ ion, does not take place from a precipitate of potassium tetraphenylborate in sodium iodide solution. Carbon evidently catalyses the decomposition of tetraphenylborate. For this reason sodium salts cannot be completely freed from contamination by potassium using a carbon–tetraphenylborate column. The maximum degree of purification achievable by this method does not exceed 0.0016%.

In some cases the sorption capacity is diminished when a sorbent is modified, owing to blocking of the active groups of the modifier. An example is provided by Dzhelassi and Egorov[41], who investigated the sorption of germanium on BAU carbon, alumina, and EDE-10P anion exchanger, all treated with dimethylaminophenylfluorone. It was found that after such treatment the sorption of germanium increased on the anion exchanger, but diminished on carbon and on alumina. The explanation offered[41] was that, when the modifier is sorbed on carbon and alumina, the *ortho*-dihydroxy-groups capable of reacting with germanium lose their activity.

The above examples show that a favourable effect cannot always be expected after modification of a sorbent. When the expected effect is not achieved, the reasons must be ascertained, and if possible another modifier–carrier system chosen.

Experience in the application of several complexing agents has shown that most selective isolations can be conducted more efficiently in complexing adsorption columns than in solution. The development of the theory of complex formation during recent years has revealed new opportunities for accomplishing many specific separations which can be successfully used in the complexing adsorption method. Complexes of the chelate type—hydroxyquinoline, dithizone, *N*-hydroxy-*N*-phenylbenzamide, diethyldithiocarbamate, pyridylazoresorcinol, pyridylazonaphthol, dimethylglyoxime, etc.—should play a special part here. If masking agents are used, chelate compounds provide the widest possibilities for the isolation and separation of pure elements. The number of chelate compounds studied is continually increasing, with an accompanying increase in the possibility of choosing systems having the maximum selectivity for extracting rare, trace, and other impurity elements[80].

IV. FIELDS OF APPLICATION OF COMPLEXING ADSORPTION CHROMATOGRAPHY

1. Production of Pure Salts

Complexing adsorption chromatography was developed during 1954–1957 in solving purely manufacturing problems[15,16,19,28]. The first field of application of this method was the production of high-purity salts used in the manufacture of phosphors. This problem was successfully solved for the purpose of purifying metals, which do not react with the complexing agent in the column, from impurity metals which form stable and firmly adsorbed compounds with it (e.g. the purification of zinc and cadmium sulphates from traces of copper, iron, nickel, and cobalt)[16,19]. The columns used consisted of two layers: the lower layer contained active carbon; the upper layer comprised active carbon and a complexing agent (e.g. dimethylglyoxime or 1-nitroso-2-naphthol) to react with impurities, in the proportions 10 : 1. The purpose of the lower layer was to prevent the partly water-soluble organic reagent from breaking through into the filtrate. The complex compounds formed in the column were firmly retained on the surface of the carbon. Purification of dissolved salts of zinc, cadmium, alkali metals, and alkaline-earth metals in the presence of hydrogen peroxide at pH 5.8–7.2 on such carbon–dimethylglyoxime and carbon–1-nitroso-2-naphthol columns lowered the concentration of copper, iron, nickel, and cobalt to 1×10^{-9}–4×10^{-8} g ml^{-1}.[16,19,28]

The fact that in this case the complexing agent does not react with the cations of the salts to be purified is responsible for the selective sorption of impurities by the columns, the lack of an effect of the initial impurity concentration on the degree of purification of the solutions (this can be assessed from colorimetric and luminescence analyses), and the extremely high operating capacity of such columns. In the purification of reagent salts with impurity contents exceeding the standard level by factors of 10–1000 the capacity of the column is measured in tons of solution for kilograms of sorbent. The use of carbon–dimethylglyoxime columns to purify the raw materials for the production of phosphors has been adopted by industry, and is applied successfully in both works and laboratory[15–18,20,42–44]. Carbon–*o*-hydroxyquinoline columns can be used to purify alkali-metal salts from heavy metals[15].

Cations which react with the complexing agent can also be separated by means of a complexing adsorption column. As in other applications of chromatography, it is important that there should be a sufficiently large difference in properties (stability constants of the complexes).

For example, a carbon–dimethylglyoxime column can be used to free cobalt salts from contamination by nickel[20]. Cobalt is the first to pass into the filtrate, as it forms a less stable compound with dimethylglyoxime in the column than does nickel. Chemical analysis does not detect nickel in the filtrate, and during purification the cobalt salt does not become contaminated with any substances which it did not contain before purification. In this case the lower layer of the column, which retains the cobalt dimethylglyoximine desorbed from the upper layer, should not be too small.

When the solutions to be purified contain cobalt, it is advisable to use carbon–1-nitroso-2-naphthol columns. These have some advantage over carbon–dimethylglyoxime columns, since they are able to free from cobalt more concentrated (20–25%) zinc sulphate solutions[17]. Furthermore, cobalt dimethylglyoximine begins to be desorbed relatively rapidly from the column, which is not observed when 1-nitroso-2-naphthol is used. In cases in which it is desirable to recover the absorbed nickel and cobalt, however, it is advisable to use dimethylglyoxime columns, since the reaction between dimethylglyoxime and metal cations is reversible in a column (unlike the reaction under static conditions), and the absorbed nickel and cobalt can be extracted with a small volume of aqueous hydrochloric acid[17].

Modified sorbents which bind the main substance but do not react with impurities can also be used to obtain high-purity products. We proposed a method of purifying radioactive niobium-95 from microquantities of antimony-125 on a carbon–*N*-hydroxy-*N*-phenylbenzamide column[29,44] from tartrate solutions buffered to pH 4.5–5.5 with ammoniacal ammonium acetate at 90°C. The column had first been washed with the same buffer mixture. The niobium complex of the modifier formed on filtration was retained in the column, whereas at this pH the antimony passed freely into the filtrate. The niobium sorbed in the column was then washed out with the buffer mixture at the same temperature. Analysis of the filtrates by means of a γ-ray spectrometer showed that the first portions of the filtrate contained the pure radioactive isotope ^{125}Sb, and subsequent fractions contained the pure radioactive isotope ^{95}Nb.

2. Group Separation or Isolation of One Component from a Mixture

The complexing adsorption method has recently become widely used for the separation of metals into groups and for the isolation of one component from a mixture. The application of modified sorbents is especially important when other methods prove ineffective (e.g. in the separation of rare-earth, rare, and trace elements).

We have recommended carbon–xanthate columns for the segregation of alkali and alkaline-earth metals from heavy metals and for the separation of metals which react with xanthates to form sparingly soluble compounds (e.g. Cu^{2+} from Zn^{2+}, Ni^{2+}, etc.)[43].

Conditions have been described for the separation and purification of metals by means of dithizone[31,43,45–47], sodium diethyldithiocarbamate[43,48], zinc and cadmium diethyldithiocarbamates[49], and several other complexing agents[50]. Aleksovskii[51,52] proposed a specially prepared zinc aluminosilicate as sorbent carrier for sodium diethyldithiocarbamate: after modification with a 1% solution of this salt a sorbent which is selective towards copper is obtained. Pierce and Peck[53] recommend that dithizone should be sorbed on acetylated cellulose, and the modified sorbent was used for the selective extraction of zinc, shown to be absorbed by the reaction $Zn^{2+} + 2HDz = ZnDz_2 + 2H^+$.

Hesford[54] recommends that active carbon should be saturated with bases—aqueous ammonia, methylamine, diethylamine, alkylamines, hexamines, pyridine, etc.—having different dissociation constants. Strong bases were used to segregate most cations, which form insoluble hydroxides, from alkali and alkaline-earth metals. Weak or complexing bases were used to isolate or separate certain cations.

Andreev et al.[31] applied the method for the selective isolation and concentration of lead, iron, copper, manganese, cobalt, and cadmium present in microconcentrations in natural waters. Active carbon of KAD and BAU brands was used as sorbent carrier. The dithizone modifier was sorbed from chloroform solution, and subsequently removed by the solvent. Carbon–dithizone columns containing an underlayer of pure carbon possess considerable capacity for the above elements, and are capable of multiple extraction and concentration of metals. The absorbed metals can be isolated into the filtrate with a small volume of weak hydrochloric acid, after which the column is ready for further use without additional regeneration.

3. Concentration of Metals

The complexing adsorption method makes it possible not only to isolate but also to concentrate metals from very dilute solutions ($\leq$ 0.2–0.3 mg litre^{-1}). The metal extracted by the column from a salt solution in which it occurred at a low concentration can be desorbed by decomposing the complex formed in the column and can be concentrated into a small volume of solution. For example, nickel can be segregated on a carbon–dimethylglyoxime column from excess of such a salt as zinc sulphate or sodium sulphate, and then extracted from the column with a small quantity of dilute hydrochloric acid; this increases the nickel concentration a hundredfold[17]. Similarly the reversibility of the reaction between cobalt and dimethylglyoxime in a column, in contrast to the reaction under static conditions, can be used to recover the cobalt removed in the purification of zinc sulphate solution.

4. Qualitative Analysis of Ions

The complexing adsorption method is no less effective for the qualitative analysis of mixtures of ions. Visual observation on colourless adsorbents is most suitable for this purpose. For example, aluminium oxide "for chromatography", after it has been wetted with water, is able to adsorb from aqueous solution metal complexes of dimethylglyoxime. The adsorption properties of aluminium oxide can be exploited by using water-saturated columns of the oxide mixed with dimethylglyoxime, e.g. in the proportions 10 : 1, for the qualitative determination of nickel and cobalt when present together[20]. In such a column nickel forms a pinkish-red zone, and cobalt forms a yellow zone below the nickel zone. It is possible in this way to detect 0.4 μg of nickel at a dilution of 250 000 : 1 in a 3700-fold excess of cobalt, and 2.9 μg cobalt at a dilution of 34 500 : 1 in a 500-fold excess of nickel. Mixtures of Co^{2+}, Ni^{2+}, and Fe^{2+} can also be separated on such columns[55].

The wide possibilities of combining various complexing agents with sorbent carriers has enabled a systematic qualitative analysis of ions to be based on this method[56,57]. It gives entirely reliable detection of micro-quantities of ions.

5. Study of Complex Formation under Dynamic Conditions

Gurvich showed the great possibilities of the method for investigating complex formation in a column[42,55]. Using as example a carbon–dimethylglyoxime column, he obtained new information on the properties of organic reagents, the structure and stability of their compounds with metals, the formation of compounds whose existence had not previously been detected, etc. Thus it has been established that in a carbon–dimethylglyoxime column bivalent nickel, cobalt, copper, and iron form compounds of general formula $M(HDm)_2$, and their relative stabilities have been determined. On such a column these cations form the sequence—$Cu^{2+} > Ni^{2+}$, $Co^{2+} > Fe^{2+}$—in order of diminishing sorbability. This coincides with the order of decreasing stability of their dimethylglyoximines of type $M(HDm)_2$. The order of diminishing stability—$Cu^{2+} > Ni^{2+} > Fe^{2+}$—has been found similarly for the 1-nitroso-2-naphtholates.

Study of the order of sorbability of Cu^{2+} and Fe^{3+} on a carbon–dimethylglyoxime column indicated[42] the existence of compounds—iron(III) copper dimethylglyoximines—in which dimethylglyoxime was combined with both metals. In fact, these compounds were subsequently detected when the reactions were conducted under static conditions. Iron(III) dimethylglyoximine was detected on a column formed by a mixture of aluminium oxide and dimethylglyoxime. This was later confirmed by conducting the reaction between an iron(III) salt and an aqueous solution of dimethylglyoxime under static conditions[55].

6. Extraction of Rare and Trace Elements

Complexing adsorption chromatography has a great future for the incidental extraction of rare and trace elements in the combined exploitation of ores. Appropriate choice of the sorbent carrier and also of the complexing agent will make it possible to extract completely valuable impurities present in minute quantities in the original raw material, and then to obtain them as concentrates. An example of such application is the industrial extraction of germanium from copper schists on columns of Wofatit E saturated with tannin[36]. Germanium was sorbed from 0.1 *N* sulphuric acid having a germanium content of 15 to 200 mg litre^{-1} and with a minimum ratio of germanium to the other elements in the lye of 1 : 10 000. Germanium was sorbed selectively, and the quantity remaining in the mixture did not exceed 0.1 mg litre^{-1}. It was desorbed by means of 9–10 *N* hydrochloric acid: the quantity of tannin thus extracted was so minute that only after 6–8 cycles did some diminution in the capacity of the column for germanium become appreciable. The amount of tannin required to regenerate the column was only 25% of the original quantity.

Other modified sorbents have been examined for the selective extraction of germanium[34,41,58–62]. Matveeva and Press[34] sorbed tannin on KAD–iodide carbon and on AN-1 anion exchanger. The sorption of germanium has been investigated also on KAD–ground carbon and on ASM silica gel modified with catechol, quinalizarin, and phenylfluorone[59], on EDE-10P anion exchanger modified with Tiron [disodium 4,5-dihydroxy benzene-1,3-disulphonate][58], and on BAU carbon modified with 8-hydroxyquinoline, tartaric and citric acids, and iron hydroxide[60–63]. In all cases modification of the sorbent led to increased sorption of germanium. However, the best results were obtained by Ziegenbalg and Scheffler on the Macroporous resin Wofatit E.[36] The use of macroporus resins as sorbent carriers is undoubtedly extremely promising for such processes. Further searches for optimum modified sorbents must be directed not only at new complexing agents but also at producing the best sorbent carriers.

Modified sorbents based on active carbons have been used to isolate uranium. A large-scale countercurrent scheme was proposed for the selective extraction of uranium from ore slurries and sulphuric-acid concentrates by walnut, coconut, and almond shell charcoals modified with di-2-ethylhexyl pyrophosphate and other organophosphorus compounds capable of chelating uranium[32,33]. These workers established also that the capacity of the modified sorbent depends on the nature of the complexing agent, its surface concentration, and the nature of the sorbent carrier.

The selective sorption of uranium from nitrate solutions containing zinc, thorium, iron, and vanadium has been accomplished[64] on BAU carbon modified with tributyl phosphate, and a method has been suggested[65] for separating uranium and iron on KAD carbon modified with 1-nitroso-2-naphthol. In the presence of trilon B at pH 4.5 to 5.5 and ratios of uranium to iron of 1 : 1–100, uranium undergoes almost complete absorption with insignificant sorption of iron. Variation in the ratio of uranium to iron within wide limits has no effect on the results of the separation.

"Alkaline A" carbon treated with phenylarsonic acid, and also arsenazo III and alkylphosphoric acids, was used for the quantitative isolation of protactinium from 1 M sulphuric acid in the presence of tin, titanium, chromium, aluminium, iron, thorium, zirconium, and uranium[35]. These sorbents were used to concentrate protactinium from uranium ores and from the products of their processing, and also to isolate protactinium from neutron-irradiated thorium.

Acetylcellulose and the vinyl chloride–acetate copolymer Corvic have been successfully used as supporting sorbents[66–68]. Microquantities of indium have been extracted on an acetylcellulose column modified with dithizone[66], and the Corvic copolymer modified with di-2-ethylhexyl hydrogen orthophosphate has been used to separate the rare-earth metals from lanthanum to lutetium. The separation was conducted from dilute perchloric acid at 60°C. Elements absorbed by the column were eluted separately in order of increasing atomic weight by perchloric acid of gradually increasing concentration[67,68].

The complexing adsorption method has been recommended also for the overall segregation of rare-earth elements from heavy metals[69,70].

7. Separation of Elements with Similar Properties

We have shown[29,43,44,71–73] that complexing adsorption chromatography offers the greatest opportunities for effecting highly selective processes in the separation of elements with closely similar properties. Niobium and tantalum, which possess similar chemical and physical

properties, were taken as the most difficult pair of elements to separate. The difficulty of separation is aggravated by the interaction of the elements, since they partly lose their individual properties when present in admixture. Aqueous solutions of their tartrate or oxalate complexes were used, with DAUKh charcoal as supporting sorbent. We find it useful to divide methods of separating niobium and tantalum into two groups, according to the complexing agents employed.

1. The modified sorbent binds mainly niobium, which is retained by the column, while tantalum passes into the filtrate with the stream of buffered solution. This enables spectroscopically pure tantalum to be isolated. Such separations have been developed by using sorbents modified with 8-hydrozyquinoline and *N*-hydroxy-*N*-phenylbenzamide. Quantitative separation of the elements can be achieved from tartrate solutions of pH 5.2–5.4 on a carbon–hydroxyquinoline sorbent at ~95°C. With a carbon–*N*-hydroxy-*N*-phenylbenzamide sorbent the best results are obtained from tartrate solutions of pH 4.5 at 95°C; a tantalum fraction free from niobium can be obtained in only ~80% yield.

2. The modified sorbent binds tantalum preferentially, while niobium passes into the filtrate with the stream of buffered solution. The niobium fraction contains the spectroscopically pure element. These results have been obtained on sorbents modified with phenylarsonic acid and tannin. Quantitative separation of the elements was obtained on both sorbents. On a carbon–phenylarsonic sorbent separation is achieved at ~95°C from oxalate media containing 0.65–1.0 *N* hydrochloric acid. On a carbon–tannin sorbent niobium and tantalum are separated from oxalate solutions of pH 2–3 at 95°C.

Complexing adsorption chromatography can be used to concentrate dilute solutions of niobium and tantalum and also for isolating these elements from a mixture. Such processes can be accomplished, for example, on a carbon–diethyldithiocarbamate sorbent, when the columns can be used many times without further regeneration.

The methods which we have proposed for isolating and separating niobium and tantalum have defined advantages over existing methods, mainly in their simplicity, the elimination of injurious and flammable organic solvents, of toxic and chemically corrosive fluorides, plus the possibility of obtaining spectroscopically pure components.

8. Separating Organic Substances and Effecting Chemical Reactions

The principle underlying complexing adsorption chromatography can obviously be used not only for the separation of inorganic substances but also in organic chemistry to accomplish certain chemical reactions and to separate organic compounds.

Forster and Rogers[74] separated amines on columns comprising silica gel or aluminium oxide treated with inorganic salts. Modification was shown to improve the selectivity and increase the capacity of the sorbents. As in the separation of inorganic products, sorption is described by the Langmuir equation. Balint[75] separated the aromatic components of solar distillates on an aluminosilicate treated with picric acid.

9. Use of Modified Sorbents under Static Conditions

We have been discussing the chief ways in which modified sorbents can be used chromatographically, i.e. on columns under dynamic conditions. Sometimes, however, it is desirable to apply them under static conditions, e.g. at the enrichment stage in the selective sorption of elements from slurries and lyes and in some other cases.

Lodeishchikov and Panchenko showed[76] that the isolation of gold and silver from the difficultly filterable slurries formed in the processing of an argillaceous ore can be suitably and economically accomplished by stirring the slurry vigorously with a suspension of carbon in the presence of thiourea. With gold and silver contents in the slurry of 7.8 and 3.2 g t^{-1} respectively the total content of noble metals after isolation on carbon was given as 240 to 250 kg t^{-1}.

Kuzin et al.[77] investigated the sorption of uranium, cerium, thorium, iron, and magnesium on SKT active carbon from acetic-acid solutions, and found that under these conditions uranium is sorbed selectively and can be separated from the other components of the mixture. Desorption of the uranium with 1 *N* hydrochloric acid enables a high degree of concentration to be achieved.

Similar results were obtained by Kogan and Evdokimov[78,79] for the sorption of germanium from oxalate solution on BAU active carbon. They found that the molecular proportions of germanium and oxalic acid sorbed approximated to the ratio in the complex $H_2[Ge(C_2O_4)_3]$.

It must be borne in mind, however, that in the static variant we lose the advantages of the chromatographic method, i.e. the possibility of separating sorbable substances on a column and maximum utilisation of the capacity of the sorbent.

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Study of the mechanism of the complexing adsorption of metals enables paths for its further development to be mapped out, and possible limits to and the advisability of its application for practical purposes to be assessed.

We have investigated the mechanism and the kinetics of the absorption of metal ions on modified sorbents in which the carrier was DAUKh charcoal[28,29]. Several regularities which were then established—the molecular character of the sorption of complexing agents and their reaction products with metal ions, the inner-diffusion kinetic mechanism, and the occurrence of a second-order chemical reaction—can be regarded as general features of the method, as is shown by the kinetics of the process. At the same time there are also specific features of the mechanism resulting from the properties of active carbon as a carrier—the simultaneous occurrence of two sorption mechanisms (ion exchange and molecular) and the effect of the character of the pores on the sorption processes, as evident in the dependence of the degree of utilisation of the complexing agent on coverage of the sorbent carrier by the agent, on the retention time of the modified sorbent, and on the temperature.

Investigations of the mechanism and the kinetics of absorption on other sorbents, which can subsequently be used as supports for complexing agents, should be of considerable interest for the development of complexing adsorption chromatography. A promising field is the application of the recently synthesised macroporous and isoporous resins, which are capable of the molecular sorption of organic compounds. Perhaps these carriers will yield modified sorbents with better kinetic characteristics and greater utilisation of the modifier than in the case of sorbents based on active carbon. However, the application of active carbon in the complexing adsorption

method is not yet exhausted, and continued examination of the properties of this extremely interesting sorbent is required, so that all its inherent possibilities can be more fully exploited.

Active carbon is most convenient in industrial and semi-industrial preparations because of its cheapness, mechanical durability, and chemical resistance. The radiation resistance of carbon enables it to be used to separate radioactive preparations at various stages in the processing of ores. For example, Davydov et al.[35] used active carbon saturated with phenylarsonic and alkylphosphoric acids to concentrate protactinium from uranium ores and their products, and also for isolating protactinium from neutron-irradiated thorium. The yield of protactinium exceeded 90%. Modified carbon can be used[44] to purify radioactive isotopes.

The complexing adsorption method should play a quite important part in the isolation of rare and trace elements and in the separation of elements having closely similar properties[29,43,44,71-73].

Study of a series of complexing adsorption systems has shown that an unlimited range of highly selective sorbents having specified properties can be prepared by the simplest methods, by exploiting for this purpose the rich opportunities provided by the different kinds of complexing agents available to the chemist[80]. Some ways of preparing such modified sorbents have been discussed above.

Even at this stage in the development of complexing adsorption chromatography the analytical chemist is already able to select a modified sorbent for the overwhelming majority of separation processes, by skilfully exploiting the properties of separable and complexing substances.

The practical application of complexing adsorption chromatography has shown that it is most suitably employed for purifying substances which are not sorbed in the column from impurities present in minute concentrations and retained by the modified sorbent. With other concentration relations of the elements to be separated the advisability of using this method would be determined by economic considerations taking into account the possibility of regenerating the modified sorbent.

The broad development of the complexing adsorption method and its introduction into industry require the production of special sorbent carriers possessing mechanical, chemical, and radiation stability, a high capacity for various kinds of organic compounds, good kinetic and hydrodynamic characteristics, and a structure which would ensure full utilisation of the modifier independently of its amount on the carrier.

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