U. D. C. 543.545

Precipitation Chromatography

A.A.Lur'e

CONTENTS

I.	Introduction	39
II.	Brief historical outline	39
III.	Precipitation-chromatographic media	40
IV.	Precipitation-chromatographic methods of separation	41
V.	Diffusional precipitation chromatography	42
VI.	Theory of precipitation chromatography	43
	1. Problems of precipitation sorption	43
	2. Conditions for the formation of precipitation chromatograms	44
	3. Structure of precipitation chromatograms	44
	4. Quantitative analysis by precipitation chromatography	45
	5. Secondary phenomena	46
	6. Theory of diffusional precipitation chromatography	46
VII.	Applications of the method	47

I. INTRODUCTION

In most cases the usual sorbents do not exhibit high selectivity with respect to substances (ions) which do not differ markedly in their properties. The combination of ion-exchange or other chromatographic methods with the phenomenon of complex-formation in solution proved extremely useful and led to the discovery of many new efficient procedures for the separation of substances. This is also the idea of precipitation chromatography, which is based on another powerful chemical interaction, the formation of sparingly soluble compounds, in combination with the usual chromatographic methods. The introduction into the chromatographic medium of suitable precipitants as well as complex-forming agents permits selective and very rigorous control of the behaviour of the individual components of mixtures in their separation. The wide possibilities in choice of precipitants, including complex-forming precipitants, make precipitation chromatography one of the most universal methods in chemistry.

A fairly large number of published studies, has accumulated, in which the principles of precipitation chromatography were used. However, the literature on this problem is widely scattered and has been little systematised, and this retards the development and improvement of the method which is essentially very promising. In most monographs on chromatography, precipitation chromatography is either not mentioned at all (although a number of studies using essentially this method is often noted[1-3]) or the method is described very briefly purely on the basis of the paper by Gapon and Gapon (1948).[4-6] The textbook of chromatography published in Poland is an exception[7]: in the chapter devoted to precipitation chromatography 33 papers are quoted, and demonstrate the extremely wide variety of applications of this method. The special monograph of Ol'shanova et al.[8], the only one so far, mentions only about 60 papers on precipitation chromatography. A few more references are quoted in the thorough review on hydrolytic and precipitation chromatography by Hayek[9], but the selection of papers appears somewhat one-sided, as a result of which a number of very interesting developments in the method are not brought to the notice of the investigator.

In view of the existing situation in this field, the author thought it useful to include, together with a review of the basic principles and trends in the development of precipitation chromatography, a scientific and patent bibliography as complete as possible.

II. BRIEF HISTORICAL OUTLINE

The first known study involving elements of precipitation chromatography is in all probability that of Runge[10]. With purely decorative aims, he carried out chemical colour reactions (including reactions with formation of precipitates), by treating with salt solutions filter paper impregnated with various substances. Runge published his own work in 1855 as an album of novel paper chromatograms.

Tsvet[11], the founder of the chromatographic method, noted in 1906 and in 1910 that in many cases of the Schönbein–Goppelsroeder[12] "capillary analysis", put forward in 1861, the formation of a chromatogram on impregnating papers with pigment solutions can be accounted for by the precipitation of the pigment as a result of a concentration gradient of alcohol in the solvent (due to evaporation of the alcohol). However, since precipitation from solutions in these experiments is not caused by the formation of a new substance by a chemical reaction, Goppelsroeder's "capillary" chromatograms cannot be classified as precipitation chromatograms in the generally accepted modern sense of this term (see below). On the other hand, one would be fully justified in classifying as precipitation-chromatographic many reactions carried out in spot analysis[13], particularly in the "fractional" method of analysis which Tananaev proposed in 1920.[14] There are many studies in this field.

For a long time the application of the principles of precipitation-chromatographic separation was only desultory. A certain breakthrough took place in the 1930's. At the beginning of the 1930's Tsvet's chromatographic method was revived, but it was used as before for the separation of organic and biological substances. Towards the end of the 1930's Schwab and coworkers[15,16] suggested that the method be applied also in inorganic chemistry and used alumina extensively as sorbent for this purpose. It was then noted[16-19] that the sorption of certain inorganic ions on alumina exhibits the features (at least partially) of precipitation sorption. Then, following Flood's suggestion[20], paper impregnated with aluminium or chromium hydroxide

began to be used in the analysis of heavy metals[21-27]. The work of Erlenmeyer and coworkers[28-30] stimulated the use as chemical sorbents of organic substances such as hydroxyquinoline, dimethylglyoxime, etc., which form insoluble complexes with many metals[31-36].

In 1948 precipitation chromatography was formulated as an independent chromatographic method. The credit for this is deservedly given to the Soviet physical chemist Gapon. Together with his coworkers, he introduced precipitation chromatography as one of the classified varieties of the chromatographic method[37,38], formulated the basic principles of the precipitation-chromatographic separation of substances[39], and began the first systematic studies in this field[40-46]. Immediately after the appearance of the first fundamental paper by Gapon and Gapon[39], a considerable increase in publications on precipitation chromatography took place both in the Soviet Union and abroad. Starting with 1953, the number of annual publications is not less than 15–20.

III. PRECIPITATION-CHROMATOGRAPHIC MEDIA

In order to separate substances by the precipitation-chromatographic method, a substance capable of reacting with them (or with some of them) to form sparingly soluble reaction products is introduced into the solid phase in the chromatographic medium. Such a substance or ion is called the precipitant. However, the main bulk of the solid phase usually consists of the "carrier". The functions of the latter include imparting the necessary filtering capacity to the system and localisation in the solid phase both of the precipitant and the precipitates produced.

Carriers. Various sorbents (ion exchanger, molecular sorbents) are usually employed as carriers. Frequently solids which are completely inert chemically and physicochemically are also employed as carriers; they serve as fillers, which are introduced mainly to improve the hydrodynamic conditions. In this case powders of sparingly soluble inorganic or organic substances, for example zinc sulphide, dimethylglyoxime, and hydroxyquinoline are used as precipitants. The powdered carriers and sparingly soluble precipitants usually have an average degree of dispersion equivalent to diameters of 0.01–0.1 mm.

The sorbent-carriers retain the precipitates in the form of ions (on ion-exchange resins, zeolites, alumina, and other exchangers), molecules (for example, various organic bases on activated charcoal[47]), or even colloidal particles (for example, the colloidal precipitate of aluminium hydroxide on filter paper[21-27]). One of the principal requirements which must be met by sorbent carriers is also that the carriers should retain the reaction products (precipitates) as well.

In column precipitation chromatography the following carriers are usually employed: alumina ("anhydrous" or "activated for chromatography" and also alumina converted into the anion-exchanger form by treatment with acid), silica gel[34,39,40,44,45,48-57], starch[29,30,32,34,35,48,49,51], Kieselguhr[28,29,34,58,59], glass powder[51-53,60-63], and activated charcoal[47,64-75]. Cellulose[42,49], barium sulphate[29,34,44], gypsum[52], calcium and magnesium carbonates[52,76,77], bentonite[48,78,79], certain metal oxides (zinc[73,75,80-82], magnesium[83,84], lead, lanthanum, and bismuth[82-85], and others), and even ordinary sand[52,53,79,86,87] have also been used.

Application of ion exchangers charged with precipitant ions. This process is interesting because it is thereby possible to remove from solution ions of both charge types at the same time, for example:

$$R^-Ag^+ + NaCl \rightarrow R^-Na^+ + AgCl\downarrow.$$

Gans[88] suggested in 1909 that processes of this kind be used in sorption techniques, referring to an even earlier suggestion by Rümpler[89]. Subsequently this idea was embodied in the so-called silver zeolites, which are widely used for the purification of seawater under special conditions[90]. With the introduction of the synthesis of ion-exchange resins, the application of a cation exchanger in the silver-form was suggested[91] for this purpose, by analogy with the silver zeolite. Somewhat later Gaddis[92] used a weakly basic anion exchanger in the sulphide form instead of gaseous hydrogen sulphides in systematic qualitative analysis. Gaddis's idea was supported and developed further by Kunin[93,94] in 1949, and this was followed by other suggestions concerning the application of ion-exchange resins in the precipitation-chromatographic method: by Aleskovskii and Kheifets[95-98], Glueckauf[99,100], and Kielczewski[101]. Recently ion-exchange resins have been increasingly used in studies on precipitation chromatography (Refs. 102–113 and others).

However, a drawback of such ion-exchange precipitation systems should be noted. This concerns those cases where the solution contains a mixture of ions not all of which form precipitates with the precipitant. In such cases, exchange with the counterions in the solution causes more of precipitant ions to be displaced from the resin than can be consumed in precipitation in the "working" part of the column bed. This can be made clearer by means of an example: suppose that a resin is charged with silver and that the solution contains sodium chloride and nitrate. Sodium displaces from the resin an equivalent amount of silver ions which precipitate chloride ions. Since the ionic concentrations are linked by the relation $[Ag^+]+[Na^+] = [Cl^-] + [NO_3^-]$, it follows that $[Ag^+] > [Cl^-]$. The excess of the unreacted precipitant is washed out of the column with the stream of solvent. Thus the higher is the amount of non-precipitable and non-exchangeable ions (in this example nitrate) the lower is the efficiency of the precipitation-chromatographic column. Ion exchangers are therefore completely ineffective for trapping (precipitating) micro-impurities, for example in the purification of salt solutions. For this purpose, sparingly soluble precipitants are employed.

Sparingly soluble precipitants. In the practical application of precipitation chromatography sparingly soluble precipitants are most frequently used, particularly in paper chromatography. To obtain a precipitate on filter paper, the latter is usually impregnated initially with a solution of one of the reactants, containing as a rule the cation of the precipitate to be formed (since the paper exhibits a higher sorption capacity with respect to cations than with respect to anions). Then the paper is immersed in the solution of the other reactant, whose anion forms the required sparingly soluble compound with the cation present on the paper. It is desirable to wash out the excess of the unreacted salts with pure solvents[20,27,114]. Sometimes the the paper is immediately immersed in a suspension of the previously prepared precipitate[22-27]. Paper is impregnated with sparingly soluble organic precipitants in alcoholic etc. solutions with subsequent drying to remove the solvent[115-118].

Powders of sparingly soluble precipitants are sometimes introduced into the column in a pure form[33,36,76,77,119-125] but most often they are introduced in a mixture with a

filler[28,34-36,60,68]. In most cases the mixture of powders is loaded into the columns in a dry form only ("dry columns"). A homogeneous material can be loaded into columns also in the form of an aqueous suspension (with heterogeneous mixtures there is a risk of layer formation in the preparation of suspensions). An advantage of "wet" columns over "dry" columns is that in the former there are no trapped air bubbles which prevent the operation of part of the charge.

In some cases more than one precipitant is introduced into the chromatographic medium in order to increase the number of absorbing substances[27,48]. On the other hand, certain properties of the chromatographic medium are sometimes improved by using a carrier of more complex composition. For example, Hopf[32] initially impregnated paper with starch and then with the precipitant (violuric acid), probably in order to increase the concentration of the precipitant on the paper. In another study[126] a mixture of finely ground alumina and cellulose pulp, obtained by boiling cotton wool in dilute nitric acid, was used to produce a sorbent with the highest possible surface area and a good filtering capacity. The alumina adhered satisfactorily to the cellulose pulp, the combined carriers being subsequently charged with the precipitant (phosphate).

The carrier (filler) can also take a more active part in the precipitation absorption process. Thus, according to Napol'skii[87,127], the addition of magnesium or calcium oxide to dimethylglyoxime helped maintain in the column the optimum acidity of the medium for the precipitation of nickel (pH $\geqslant$ 6):

$$\begin{cases} NiSO_4 + 2\,H_2Dm \rightleftarrows Ni(HDm)_2\downarrow + H_2SO_4\,, \\ H_2SO_4 + MgO \rightarrow MgSO_4 + H_2O\,. \end{cases}$$

In some cases columns consisting of several beds with different precipitants were used[30,87,97,128-131] to ensure selectivity of absorption and a clear-cut separation of a number of substances[132].

It is noteworthy that a fairly widely used method of preparation of the precipitation-chromatographic medium, in which a readily soluble precipitant is introduced into the carrier, is erroneous. For example, columns with mechanical mixtures of a carrier and a readily soluble precipitant are used fairly frequently, the fraction of the precipitant amounting sometimes to 10–50% of the charge[39,40,44,48,108,133-137], or paper is impregnated with a solution of a readily soluble salt and then dried without washing[138-145]. In experiments with the usual carriers having low sorption capacity (paper, alumina, etc.) such a technique is undesirable, since soon after the start of filtration of the solution the excess of the precipitant, not fixed on the carrier by sorption forces, is washed out of the latter. Only in rapid processes (for example in spot reactions) can the substance react more or less completely with the precipitant. On the other hand, under the usual conditions of the chromatographic process, such technique is ineffective. It is even less applicable in quantitative analysis based on the size of the precipitation bands, which requires uniform distribution of the precipitant in the chromatographic medium (see below). The advantages of sparingly soluble precipitants in systems resembling those used in precipitation chromatography were pointed out by Clarke[146,147] as early as 1937. Investigators who used the precipitation-chromatographic method for quantitative analysis arrived at the same conclusion[62,114].

Among other principles of carrier and precipitant selection, one may note the tendency (in those cases where it is possible) to choose white or pale coloured carriers and precipitants, which form coloured precipitates with the ions evolved. In most real cases this can be fairly readily achieved and the investigator then secures the valuable advantage of being able to follow the process during the separation period and to correct the operation as required. To make observations on precipitates whose colour does not differ from that of the background, a phosphor may be introduced into the column before the experiment[48].

IV. PRECIPITATION-CHROMATOGRAPHIC METHODS OF SEPARATION

A fairly wide variety of procedures for the separation, purification, and concentration of substances is already used in precipitation chromatography. However, the possibilities of precipitation chromatography are still far from being exhausted and eventually the number of methods should probably increase considerably. The present situation in this field must be regarded as merely the initial stage of development.

One of the simplest chromatographic procedures based on precipitation chromatography consists in selective absorption of one of several substances in a solution passed through a suitably prepared column or impregnated paper. This method is widely used both in the concentration of substances from dilute solutions[62,87,146-148] and for the removal from solutions of specific interfering impurities[64-68,71-75,80,104,105,149,150]. In both cases precipitation chromatography has significant advantages over other methods used for the same purposes. In the first case (concentration) the minimum concentration at which a given substance can be absorbed from solution is usually very low as a result of the very low solubility products of the precipitates formed. This permits virtually quantitative isolation from solutions of components present even at microconcentrations[103,151]. On the other hand, ion-exchange resins and the usual sorbents are not very suitable for the removal of microimpurities from salt solutions at high concentrations because of insufficient differences in sorbabilities[73], while precipitation systems readily overcome this difficulty.

The advantages of precipitation under chromatographic conditions compared with static conditions are evident: the technique is simpler, the number of operations required is smaller, the time needed is shorter, the efficiency of separation is higher, and the risk of losses and contamination during the separation process is lower. We may quote the following examples of the significant simplification of technique. It has been suggested that in partition paper chromatography of alkali and alkaline earth metals the interference of polyvalent ions be eliminated as follows[152]. Polyvalent anions are precipitated from the solution as sparingly soluble lead salts at the beginning of the chromatographic band (not far from the start), where two drops of lead acetate solution are deposited before the start of the experiment; at the same time the test cations pass freely through the lead spot and move further along the paper in the usual order. Precipitation in chromatographic columns and not under static conditions is particularly desirable in those by no means rare cases[153,154] where colloidal precipitates are formed, since precipitation-chromatographic media quite often show a satisfactory capacity for the retention of colloids.

Many studies have been described in the literature on the separation of two and more substances by the selective absorption of some and the free passage of other mixture components[47,101,112,155,156]; in this way it is possible to separate ions and substances with similar properties[44,47,54,59,76,77,87,127,157-161].

Adequate selectivity of absorption under real conditions can be ensured both by the selection of the appropriate precipitant and, in the case of ion-exchange carriers, by the choice of an ion exchanger with the required acidity or basicity [92,99,100]. For this purpose (to ensure the specificity of absorption), Hesford [47] suggested that activated charcoal be saturated with bases differing in their dissociation constants: aqueous ammonia, methylamine, diethylamine, urea, ethanolamines, alkylamines, hexamines, pyridine, and others. Strong bases were used to separate most of the cations, forming insoluble hydroxides, from alkali and alkaline earth metals, while weak or complex-forming bases were used for the isolation or separation of particular cations.

Substances retained in the columns are then eluted with solutions of acids, alkalies, or complex-forming agents. Another separation procedure is based on the choice of a selective solvent, which elutes only one or some of the components to be separated which are retained in the column [47,63,111]. For example, on the alumina and cellulose pulp columns [126] mentioned above, silver and iron(III) ions were absorbed in the form of the phosphates and then eluted successively with 0.1 *N* acetic acid (silver) and hot 2 *N* hydrochloric acid (iron). The separation was quantitative. Kielczewski used an unusual procedure [110] for the separation of silver and copper(II) on an anion-exchange resin saturated with arsenate. After both silver and copper had been absorbed on the resin, hydrochloric acid was passed through the column. This resulted in the elution of copper, while the silver arsenate precipitate was converted into silver chloride, so that silver remained in the column. Subsequently silver was eluted with aqueous ammonia (complex-forming solvent).

Precipitation-chromatographic methods on paper differ little from the usual paper chromatographic procedures. Both linear and circular chromatograms are produced. A definite volume of the test solution is usually deposited with a capillary on impregnated paper and the chromatogram is then eluted with a pure solvent until the stabilisation of the zone boundaries. Sometimes dilute solutions can be applied to the paper continuously, i.e. by simple impregnation of the paper with solution at one end [162,163]. The thin-layer precipitation chromatographic technique [55-57] is in many ways similar to paper chromatography.

When a clear-cut detection of all the zones is required on paper or in a column, the primary chromatogram obtained (as a result of the passage of the initial solution) is washed with water or weak aqueous solutions of mineral salts; sometimes it is washed also with organic solvents [54,118,164-166]. If necessary the zones can be revealed by means of solutions or vapours of the usual reagents [22-24,109,139-145,167], or, especially in columns, by means of adsorption indicators introduced with the test solution [137,168-171].

When the primary precipitation chromatogram is washed with organic solvents, the components of the mixture on impregnated paper are frequently separated by elution [115-117, 172,173]. Possibly, it is more correct to regard these as cases of partition rather than precipitation chromatography.

One of the varieties of precipitation chromatography is a separation procedure in which absorption in the solid phase is due to an oxidation–reduction reaction with formation of a sparingly soluble reaction product [8,109]. An example of the application of this method is the use of manganese zeolites [174] for the removal of iron(II) and manganese(II) from water (in cases where the possibility of the preliminary aeration of water is limited and in certain others). The manganese zeolite is a source of oxygen which oxidises the divalent iron and manganese ions to the trivalent state, this being accompanied by the precipitation of the hydroxides. Oxidant additives (sodium permanganate) were used earlier in [175] gas mask filters. A small amount of the oxidant in the gas mask (about 3%) served to oxidise certain gases, for example arsine, which are poorly sorbed by activated charcoal and soda lime (the principal components of the gas mask filter). It has recently been suggested [176] that precipiation-chromatographic columns with a silver precipitant be used to trap arsine (from the gas phase):

$$AsH_3 + Ag^+ \rightarrow Ag_3As\downarrow + Ag^0 + AsO_3^{3-}.$$

The reducing properties of certain ion exchangers, including electron-exchange resins, have found application in the extraction (concentration) of noble metals from solutions [106,107,177].

We may mention yet another method—the procedure for the preparation of stable sols with the aid of precipitation-chromatographic columns [43,44,94,178,179]. In general this method cannot be regarded entirely as precipitation chromatography, since for this purpose one selects a special carrier, which, while retaining the precipitant, should not retain in the column the resulting colloidal precipitate. For example, the following processes have been achieved on ion exchangers [179]:

$$R(OH)_3 + AlCl_3 \rightarrow RCl_3 + Al(OH)_3\downarrow,$$
$$R'H_2 + Na_2SiO_3 \rightarrow R'Na_2 + H_2SiO_3\downarrow.$$

The sols obtained are very pure.

Yet another application of precipitation chromatography is the procedure for the quantitative determination of organic acids on paper impregnated with a hydroxide [180,181]. The quantitative analysis is based on the measurement of the area (or weight) of the section of the paper freed from the hydroxide precipitate as a result of dissolution by the test acid.

V. DIFFUSIONAL PRECIPITATION CHROMATOGRAPHY

The difference between the unusual variety of precipitation chromatography and the normal procedure is that here the principal mass-transfer mechanism is diffusion and not filtration of the solution. The specificity of the reaction medium consists in the fact that the latter does not permit the filtration of the solution and convective mixing of the substances. Such media include moisture-saturated porous materials [44,130,182,183], solutions in capillaries [184-186], and gels. The last are used most often, and therefore such chromatograms are also called "precipitation chromatograms in gels" [185-188]. The brief, accurate, and general name given in the heading of this section was proposed by Olenovich et al. [189].

The technique of this method is very simple. A fused gel of gelatin, agar-agar, or a similar substance, to which the precipitant had been introduced earlier in the form of a solution, is poured into test tubes or Petri dishes. When the gel has set, the test solution is poured onto its surface (in Petri dishes in the form of individual drops). The diffusion of the components of the solution into the gel is accompanied by the precipitation of the various deposits, which results in the continuous development of the chromatogram [185-196].

Some investigators have used paper impregnated with gel together with the precipitant [197,198]. Diffusional precipitation chromatograms can also be obtained in capillary tubes sealed at one end and filled with a precipitant solution (without gel) [185,186,199]. Such capillaries are simply immersed in the test solution with their open ends downwards.

A modified technique is used for special purposes: counter-diffusion of reacting substances in a pure gel medium [182,183,200-202].

VI. THEORY OF PRECIPITATION CHROMATOGRAPHY

1. Problems of Precipitation Sorption

The term "precipitation sorption" includes any processes where the absorption of a substance in an already existing solid phase involves the formation of a new solid phase due to the production of a sparingly soluble compound by a chemical reaction. This precipitation sorption is a complex process. In one of its stages the solute reacts with the precipitant which leads to the precipitation of a sparingly soluble compound. The following, no less important stage is the fixation of the newly formed precipitant in the solid phase. The nature of this fixation can be extremely varied—ranging from mechanical retention to adhesion or molecular fixation. The successful absorption of a substance in a precipitation-chromatographic system depends not only on the correct choice of the precipitant but also on the choice of the carrier which is capable of firm retention of the precipitates formed.

The present author [203] derived an equation for the isotherm of ionic precipitation absorption taking into account only the solubility of the precipitate (i.e. assuming that the precipitate is completely and firmly retained in the solid phase). It was found that the isotherm exhibits virtually maximum convexity. According to the familiar postulates of chromatographic theory, a number of important conclusions follow from this finding. When the isotherm is convex, dynamic precipitation sorption takes place with the formation of the so-called steady-state front, i.e. under conditions of parallel transfer of the sorption front. In those cases where the influence of the sorption kinetics or various longitudinal flow perturbations is weak, the effect of the convexity of the isotherm (tending to sharpen the front of the sorption wave) is particularly pronounced. As a result, exceptionally distinct zone boundaries are particularly frequently observed in precipitation chromatography [8,39,44].

Precipitation sorption on sparingly soluble precipitants. Earlier it was noted that in the practical application of precipitation chromatography, substances which are sparingly soluble in the solvents used but can react with the ions subjected to chromatography, forming even less soluble products, are employed very often as precipitants (the present author suggests that such precipitants be referred to as sparingly soluble). For example, zinc sulphide can absorb copper, cadmium, silver, and other ions, since the sulphides of these metals are even less soluble in water than zinc sulphide. The inclusion of such heterogeneous displacement reactions in precipitation-sorption processes is consistent with the generally accepted definition of a bulk-phase chemisorption reaction: "the absorption process due to a heterogeneous chemical reaction gradually spreads throughout the bulk of the solid, ... producing a new substance in the form of a new phase" (Lepin' [204]).

The absorption of ions on sparingly soluble precipitants is sometimes difficult to distinguish formally from ion exchange. Hayek [9] suggested that two varieties of formal ion exchange be distinguished: ion exchange on relatively high-molecular weight substances without appreciable change of structure, for example:

$$Ca_5(PO_4)_3OH + F^- \rightleftarrows Ca_5(PO_4)_3F + OH^- ,$$

and with change of structure of the initial substance, for example:

$$AgCl + Br^- \rightarrow AgBr + Cl^- .$$

The present author believes that the inclusion only of reactions of the second kind (with change of structure, i.e. with formation of a new solid phase) among precipitation processes is quite acceptable. For example, on the basis of the same considerations, one is quite justified in including among precipitation chemisorbents also the large class of sparingly soluble complex-forming precipitants (of the type of dimethylglyoxime and hydroxyquinoline), despite the apparent complexity of their molecules.

Precipitation sorption on ion exchangers. The application of ion exchangers in precipitation chromatography is based on a three-stage process [8,205,206]: (1) displacement of the precipitant ion from the resin by ion exchange; (2) its reaction with the ion undergoing chromatography leading to the formation of sparingly soluble compounds; (3) fixation of the precipitate on the resin. It has been established [205,206] that on synthetic resins with a high exchange capacity, the ion exchange and formation of a sparingly soluble compound can be clearly distinguished both in time and in space. The ion-exchange displacement of the precipitant ion A linked to the resin matrix R:

$$R^-A^+ + B^- + M^+ \rightleftarrows (R^-M^+ + A^+) + B^- ,$$

results in the binding of the ion B in the precipitate,

$$A^+ + B^- \rightarrow AB\downarrow$$

only after the liberated ions A have diffused to the surface of the resin grain. The explanation is that, as a result of the Donnan potential, the free electrolyte BM virtually does not enter the resin phase [94,207]. Helfferich [208], who considered the problem of the kinetics of ion-exchange processes accompanied by any chemical reaction, recently arrived at similar conclusions. Thus the view that the precipitates are formed and fixed within resin grains [103,105,110] must be regarded as erroneous.

The problems of the equilibrium in the system ion exchanger—sparingly soluble electrolyte—water have been examined in a number of studies [207,210-215]. Grigorov and Tarshis [209] demonstrated the equivalence and the reversibility of ion exchange accompanied by a chemical precipitation reaction. To show this, three successive ion-exchange cycles, including the reaction of barium chloride (or potassium sulphate) solution with the ion exchanger in the silver (or barium) form and the regeneration of the resin with a solution of silver nitrate (or barium chloride), were carried out. Despite the increasing amount of the precipitate (silver chloride or barium sulphate), the amounts of the ions undergoing exchange remained virtually constant in all three cycles. In general the possibility of the regeneration of the column without eluting the absorbed substance [106,107,113] is one of the valuable features of precipitation chromatography. For example, after a number of repetitions of the absorption–regeneration cycles on an electron-exchange resin, it is possible to accumulate reduced silver in amounts up to 300–400% of the weight of the resin [107].

Koblyanskii and Kameneva [216] observed higher rates of ion exchange in a cation-exchange column if the exchange was accompanied by the formation of a precipitate; this is

explained by the displacement of the ion-exchange equilibrium to the right. On the other hand, the general form of the elution curves revealed a dependence both on the solubility product of the precipitate formed and on the constant for the exchange of the corresponding pair of ions. The present author[205,217] showed that conditions of parallel transfer are established in the motion of the precipitation-sorption wave in cation-exchange and anion-exchange columns regardless of the constants for the exchange of the corresponding ions. He also developed a mathematical theory of dynamic precipitation sorption on ion exchangers.

Elsewhere[205,206] he discussed the problem of the mechanism of the fixation of the precipitate on the surface of the resin grains. The following probable mechanism of the fixation by adhesion of the peptised precipitate AB on the resin R was proposed:

$$R^-A^+ + B^- + M^+ \rightarrow R^-M^+ \cdot (B_n^- \cdot AB) + nM^+ ,$$

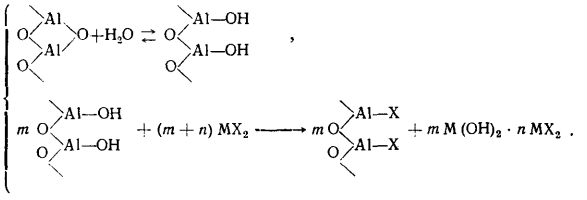
where part of the ions M remain in the diffusion layer at the precipitate particles.

Precipitation sorption on alumina and certain other inorganic sorbents. Because of its wide use in the chromatography of inorganic ions, alumina has attracted the attention of many investigators who attempted to elucidate the sorption mechanism. Gapon[38,218,219] believed that the absorption of cations on basic alumina and the absorption of anions on acid (treated with acid) alumina is due to ion exchange at the aluminate group:

$$(Al_2O_3)_mAlO_2 \cdot Na + A^+ + B^- \rightleftarrows (Al_2O_3)_mAlO_2 \cdot A + Na^+ + B^- ,$$
$$(Al_2O_3)_mAlO \cdot NO_3 + A^+ + B^- \rightleftarrows (Al_2O_3)_mAlO \cdot B + A^+ + NO_3^- .$$

The sorption of polyvalent anions on basic alumina and polyvalent cations on acid alumina was explained in the same papers[218,219] by the reversal of the charge on the sorbent surface by the polyvalent ions.

Without rejecting the possibility of the absorption of ions by ion exchange on alumina, most investigators nowadays believe that a hydrolytic absorption mechanism[9,17-19,84,85,220,221] is more likely for heavy metal salts on basic alumina, for example[81]:



Heavy metals are sorbed as precipitates of hydroxides or basic salts, for example $Cu_2(OH)_3Cl$ from $CuCl_2$ solutions[83,84,222,223], $Co_2(OH)_3Cl$ from $CoCl_2$ solutions[84], and $Cu_4(OH)_6SO_4$ from $CuSO_4$ solutions[84].

The capacity for hydration, which determines the absorption capacity of alumina, depends on the heat-treatment of the latter in its preparation from the hydroxide[223-225]. This capacity is a maximum for γ-alumina (the cubic form) obtained by heat treatment at about 600°C and is absent in the α-form (the rhombohedral form) formed on heating above 1200°C.

It has been noted[84,85] that the same hydrolytic mechanism accounts for the absorption of heavy metals on certain other basic substances, for example on magnesium or lanthanum oxides (as well as on anion exchangers in the hydroxide-form). The absorption of strong electrolytes from aqueous solutions on charcoals is regarded as hydrolytic[175,226-228]. This is indicated by the similarity (with certain unimportant exceptions) of the sorption series for heavy metals on basic alumina[15,16,19,85,133,221,229,230], lanthanum oxide[85], partially dehydrated ferric hydroxide[125], and on charcoal[231], both to one another and to the series of the solubility products of the hydroxides of these metals[232].

The sorption of heavy metals on alkaline silica gel is attributed to the formation of sparingly soluble polysilicates[233]. Here the polysilicate macroion of silica gel serves as a precipitant ion for certain metals. The same sorption series was obtained as for the solubilities of the silicates[233,234].

Certain anions are also sorbed on alumina by a precipitation mechanism[82]. In those cases where alumina is used as a carrier with a sorbed precipitant it is not always possible to observe the fixation of the newly formed precipitates on the carrier[39,43,44]. If the precipitate was nevertheless retained in the column, it was found[205,206] that the individual crystals of the precipitate are fixed on the surface of the grains of alumina (both basic and acid). Since the nature of these adhesion forces is not entirely clear, it is so far necessary to choose empirically the conditions under which the precipitation-chromatographic process can be successfully taken to completion (without loss of the precipitates).

2. Conditions for the Formation of Precipitation Chromatograms

The main factor which determines the separation of substances in precipitation chromatography is the difference between the solubilities of the precipitates formed[39]. Being a variety of the chromatographic method, precipitation chromatography is a dynamic process with multiple repetition of the fundamental step[8,53]. Schematically the formation of precipitation chromatograms can be described as follows[235]. When fresh portions of solutions enter a given element of the column (or impregnated paper), the component which reacts with the precipitant to yield the least soluble precipitate displaces the appropriate components from the previously formed more soluble precipitates. The displaced components move further with the solvent stream and are again precipitated in those layers of the column where there is either the free precipitant or a more soluble precipitate with other components. Frequent repetition of such redistribution of material in the direction of the stream leads to the formation of a developed precipitation chromatogram.

Two evident conditions must be satisfied for the formation of a precipitation chromatogram. In the first place the precipitate must be fixed in some way in the solid phase of the chromatographic medium and should not be eluted with the solvent stream[54,78,109,236] and in the second place the precipitates formed must be retained at the site of their precipitation[8,40,53,147,236-238].

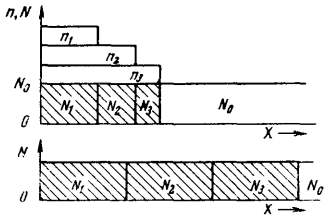
3. Structure of Precipitation Chromatograms

The sequence of the zones in precipitation chromatograms depends on the order of precipitation of the corresponding substances[8]. In the determination of the sequence of the zones one examines in the first place the relative solubility products of the precipitates and in addition the relative concentrations in the initial solution of the substances being separated[8,239]. The present author has given a rigorous mathematical derivation of the general

relations whereby the sequence of the zones in precipitation chromatograms can be predicted[240].

Gapon[43,44] proposed an approximate method for the determination of the zone sequence from reduced solubility products. Although this method is not quite rigorous (for this reason certain exceptions to the rule are observed)[44], in the majority of cases it gives a qualitatively correct picture. In Gapon's method the solubility products of the precipitates are compared after being raised to a power equal to the smallest common multiple of the number of precipitant ions in the precipitate molecule [the factor by which the number of precipitant ions in the precipitate molecule has to be multiplied to give the smallest integral common product (Ed. of Translation)]. For example, in the comparison of the solubilities of iron(III), copper(II), and silver(I) their solubility products are raised to the second, third, and sixth power respectively. The zone sequence (beginning at the start) should correspond to the sequence of increasing values of the quantities thus obtained.

In contrast to the other varieties of chromatography (molecular, ion-exchange), for precipitation chromatography with considerable differences between the solubilities of the resulting precipitates, theory predicts[205,239,241] a simple structure of the chromatogram with virtually only one component of the initial mixture (see Figure) in the solid phase of each zone. In the primary chromatogram some zones, in particular the first (at the start), may still contain admixtures of other components of the initial mixture in the form of a free solution, but in the washed chromatogram every zone contains only one component each. The zones follow one after another without discontinuities, usually with very distinct zone boundaries.



In the ideal case the ratios of the concentrations of the precipitant in the carrier (N_0) and the densities of precipitation (N_1, N_2, N_3, ...) should be equivalent. Under real conditions this requirement is satisfactorily met on finely dispersed sorbent-carriers[52,53,62,205,236].

The washing of the primary chromatogram with an indifferent solvent leads to the widening of the primary zones (particularly those further removed from the start), but only up to a certain limit, beyond which further washing virtually does not change the chromatogram[238,242]. This limit is determined by the amount of substance introduced and the precipitating capacity of the medium[235].

The distribution of the precipitates in the washed chromatogram has been little investigated by direct analysis. In some cases[78] insufficiently complete separation was observed in zones close to the start, although the zones were clearly distinguished by colour. The present author investigated[205,241] the reasons for the incomplete separation in certain specific systems. It was established that in highly dispersed inorganic ion exchangers charged with a precipitant ion, the contamination of initial zones by other components of the initial mixture can be accounted for by the adsorption coprecipitation of ions on the precipitates of the main substance; this occurs to a small extent. On sparingly soluble precipitants and in particular on ion-exchange resins charged with precipitants there is also a poor separation of mixtures in the chromatographic medium due to kinetic causes (continuing precipitation of impurity components from the free solution after formation of the primary chromatogram, when there is not sufficient time for the complete consumption of the precipitant during the brief period when the primary chromatogram is formed). To improve the separation in this last case, it is recommended that the primary chromatograms be washed immediately when the filtration of the initial solution is completed.

4. Quantitative Analysis by Precipitation Chromatography

In view of the very great simplicity of precipitation chromatograms (see Figure), simple quantitative determination of the components from the size of their zones in the chromatograms is possible. One of the conditions for quantitative analysis by precipitation chromatography, together with those enumerated above (see Section VI, Subsection 2), is the uniformity of distribution of the precipitant in the chromatographic medium[8,62,205,236,238].

Washed chromatograms. When washed chromatograms, which virtually do not contain the substances being analysed in a free form (see Figure), are used, a simple linear relation between the quantity of the component introduced and the size of its zone is obtained. The size of the zone is defined as follows: in column chromatography the volume or height of the zone[34,35,50,123,243], in paper or thin-layer linear chromatography the length[21,24-26,55,57,162,244-256], the area[166,257-273], or the weight of the zone[274-277] after the latter has been cut out, and in circular chromatography the area of the circular and annular zones[114,278,279].

Quantitative analysis by precipitation chromatography has proved so simple and convenient that in certain cases it has been used as a simple final step in analytical determinations. For example, it has been suggested[255,262] that partition and precipitation chromatography be combined, the first method being used to separate the ions and the second for their quantitative analysis, after the individual components have been transferred with the aid of appropriate solvents from the chromatograms where they had been separated to paper impregnated with the precipitants.

Although usually quantitative analysis by precipitation chromatography is used for the analysis of a single precipitable substance, there have also been studies on the quantitative determination of components in complex chromatograms[34,35,123,244,248,251,254,258,272,273]. The present author's investigation in this field[205,241] showed that, despite the partial retention of certain mixture components in zones other than their intrinsic zones (see above), the relations between the sizes of washed zones in complex chromatograms and the concentrations of the corresponding components in the initial solutions (for a constant sample volume)

remain linear or nearly so. As a result, quantitative analysis of complex mixtures by frontal precipitation chromatography is possible without preliminary separation.

In the chromatography of various ions on media with sparingly soluble precipitants a steady increase in the length (or area) of the zones with increasing solubility products of the precipitates was observed[62,78,114]. Kulaev[141,143,144] relates the velocity of the precipitation front directly to the solubility product, which of course is unjustified. The present author believes[205,241] that the above relation is due to differences in the rates of the reactions of the solution components with the precipitant. The rate of the displacement reaction is higher the greater is the difference between the solubility products of the starting material and the final product.

Primary chromatograms. Some investigators have used primary unwashed chromatograms for the quantitative analysis of a single precipitable component[51,78,135,137,168,170,280-285]. The zone size–concentration calibration graphs are then curves concave towards the zone size axis. The reason for the non-linearity of the calibration graphs is that part of the solution does not react with the precipitant, since it is retained by capillary forces behind the precipitation front in the free volume of the column[205,236]. Thus Stefkin[286] obtained a linear calibration graph over a fairly wide range of concentrations (0.016–0.5 M) even though he used unwashed chromatograms, but the latter were obtained by filtration at a reduced pressure: the solution was then drawn downwards in its entirety, without begin retained in the free volume of the column.

An equation for the relation between the size of the precipitate zone and the concentration of the initial solution and certain other factors was derived by Cetini and Ricca[238] and more rigorously by the present author[205,236]. The present author used this equation[205,236] as a basis for a more accurate and simpler method of quantitative determination of a single precipitable substance from the primary precipitation zone using linear calibration graphs in transformed coordinates (the reciprocal of zone size plotted against the reciprocal of concentration).

The present author[205] has also proposed a method of quantitative determination of a single precipitable substance from a primary circular zone, in which a very simple technique is employed. To determine the concentration of the solution, it is necessary to immerse a "wick" of impregnated paper into the test solution and then terminate the impregnation with solution at any convenient time: after drying the paper, it is necessary to measure the ratio of the radii of the solvent front and the precipitation zone (or the ratio of the areas of the corresponding circles). Mathematical analysis showed that linear calibration graphs are obtained when the square of the ratio of the radii or [the ratio of (Ed. of Translation)] the areas of the circles are plotted against the reciprocal of concentration. However, it should be noted that the use of primary chromatograms for quantitative analysis becomes ineffective at relatively high concentrations, and therefore in the general case it is more desirable to employ washed chromatograms.

The maximum dilution method. This method, proposed by Shemyakin and coworkers[5] is used in some cases for the quantitative determination of single precipitable substances[109,111,141,144,169,287-292]. The method consists in a number of successive dilutions of the test solution until the latter gives a negative qualitative response with respect to the ion being determined when tested on a precipitation-chromatographic medium. In preliminary experiments it is necessary to determine the minimum detectable amount and also an empirical "correction for losses", which is about 3–10%.[8] The method has very little accuracy[141], is laborious (particularly in the column version), and is suitable only for approximate determinations of microconcentrations[292].

5. Secondary Phenomena

The various processes involving changes in precipitation chromatograms after formation are combined under the common name "secondary phenomena in precipitation chromatography"[8,41-44,183,293-296]. In laboratory practice secondary phenomena are encountered very rarely (only in special cases) when washed chromatograms are obtained. However, in unwashed (primary) chromatograms, where the chromatographic layer contains free solutions at fairly high concentrations in addition to the precipitate, there is an extremely wide variety of secondary phenomena. In contrast to the requirements of analytical practice, where usually only washed chromatograms are dealt with, the study of secondary phenomena in precipitation-chromatographic processes under natural conditions (for example, in the investigation of certain ore-formation and soil-formation processes) is of exceptional importance.

The major proportion of secondary phenomena in precipitation chromatography consist in the effects of diffusion processes[294,295], which are frequently accompanied by various chemical reactions. In the precipitation chromatograms of the iodides of mercury, bismuth, and lead secondary complex-formation reactions combined with diffusion processes have been noted[43,44,295].

Very frequently (and both in washed and unwashed chromatograms) recrystallisation of the precipitates is observed, leading to the growth of bigger crystals at the expense of a large amount of small crystals[44,205,206]. The recrystallisation of precipitates is a favourable process from the standpoint of the firm fixation of the precipitate in the chromatographic media. Both the solubility and the extent to which the precipitates are dislodged are greatly reduced. However, the subsequent elution of the absorbed substance from the column becomes more difficult.

The disruptive effect of precipitates in porous media noted in some cases deserves attention[41,297].

6. Theory of Diffusional Precipitation Chromatography

In diffusional-precipitation systems the velocity of the precipitation front depends on a number of factors: the ratio of the diffusional capacities of the outer and inner electrolytes[298], the concentrations of the outer electrolyte[185,186,190,205,299,300], the inner electrolyte (precipitant)[205,300], and the gel[185], and also the solubility of the precipitate formed[198]. The relative contributions of all these factors in fact determine the form of the diffusional-precipitation chromatogram.

It has been shown[205,298,300] that analytical solutions available from the theory of diffusion[301] and thermal conductivity[302] cannot be applied directly to diffusional-precipitation systems. At the same time an adequate mathematical description of diffusion complicated by precipitation is so far lacking.

The simplest theoretical examination of precipitation diffusion, postulating a linear process[205,303], leads to the

conclusion that the ratio of the square of the depth of the precipitation zone to the time elapsed is constant if the concentration of the outer electrolyte remains constant. The validity of this hypothesis has been firmly established by numerous experimental investigations [303,304].

Diffusional precipitation with a non-constant source was investigated by Watanabe [305] and Mofávek [306]. The equations obtained by Mofavek describe the process more accurately [205,300].

Krishnamurti and Dhareshwar [198] observed empirically a relation between the height of the precipitation zone x and the solubility of the precipitate S. Using the diffusional precipitation (in an agar gel) of silver salts with ten anions of different valence types as an example, the relation was found to be of the form

$$x = k + k' \lg S \ ,$$

where k and k' are constants characterising a number of precipitation systems with a common precipitant ion.

In his study of the rate of penetration into the gel of the precipitation front for different (constant in time) concentrations of the outer solution c_0 the present author observed the following relation [205,300]:

$$x = (a + b \lg c_0) \sqrt{t} \ ,$$

where a and b are constants which depend on the concentration of the precipitant in the gel and t is the time. Using this equation, it is possible to improve the accuracy of, and make more convenient the quantitative analysis of solutions by the diffusional-precipitation method [196,299], which is simple and not at all laborious [205,300].

It has been noted [185] that the change in the density of the gel has little effect on the velocity of the precipitation front. Probably the Traube–Shikata rule [307], first established for the diffusion of dyes in gels, namely $\sqrt[3]{c_g D} =$ const. (c_g is the concentration of the gel and D the diffusion coefficient), holds in diffusional-precipitation systems.

Since a washed chromatogram cannot be obtained in diffusional-precipitation systems, one cannot expect the separation of the mixture components into individual zones: the liquid phase of the gel will contain all other initial-solution components, which form with the precipitant more soluble reaction products. Here we have the same situation as in the usual primary chromatograms: the visual separation of the chromatogram into zones (according to the colour of the precipitates) is not by itself evidence of sufficiently complete separation of the mixture.

The distribution of concentrations in diffusional-precipitation chromatograms is much more complex than in the usual chromatograms. The distribution along the column of precipitate of even a single substance is fairly complex, the chromatogram including bands of different colour and degree of transparency (depending on the size and amount of the precipitate crystals [308]). The zones of adjacent precipitates are sometimes separated by a region of the gel free from precipitate [185–187,192,195]. The effect of the precipitant concentration and the concentrations in the outer solutions, and the gel on the size of this region was investigated by Milone et al. [192].

Various repetitive structures, the so-called Liesegang rings [309,310], are fairly frequently superimposed onto the general pattern. However, it has been shown [205,298,311,312] that the presence or form of such structures in no way affect the principal features of the motion of the diffusional-precipitation zone front.

VII. APPLICATIONS OF THE METHOD

Examples of various applications of precipitation chromatography have already been noted above. Certain common precipitates for the separation of inorganic ions are indicated in the bibliography [327–355].

Among the traditional ways of using the precipitation-chromatographic method, one of the most important is qualitative chemical analysis [13,14,92,102,117,133,136,142,146,147,195,313,314]. A classical example of sensitivity and specificity is the qualitative test for nickel, which is carried out on a dimethylglyoxime column: the minimum detectable amount is 0.2 μg in the presence of a ten thousand-fold excess of cobalt [76,77].

Quantitative analysis by precipitation chromatography is used mainly for inorganic ions. The method has been employed for the analysis of metals and alloys [34,35,86,119,120,140,245,246,249,250,271], minerals [119,120,196], natural waters [163], various biological materials [86,152], and food products and materials used in the food industry [109,134,168,169,287–290,315]. Apart from inorganic ions, the substances separated and analysed have included organic acids [165], lower aliphatic amines [54], phenols [267,273], reducing sugars [261], and various pharmaceutical preparations [48,187,188,316].

Precipitation chromatography has found wide application in the thorough purification of salt solutions (removal of microimpurities), for example in the purification of salts for the preparation of phosphors [64–66,68,72,73,80,104,105,149,150,317–319]. The residual content of heavy metals in the products does not exceed 10^{-5}–10^{-6}%. The methods proposed are very economical, simple, and convenient. For example, it is possible to purify hundreds of kilograms of zinc or cadmium sulphates, giving "chemically pure" materials, by simple filtration through 1 kg of sorbent containing about 48 g of dimethylglyoxime [75].

James and Welch [103] used successfully anion-exchange resin columns charged with precipitant ions for trapping fragment elements from solutions without carriers, and they have noted that the method is superior to the usual coprecipitation procedure as regards efficiency and selectivity. Golovatyi and coworkers [62] demonstrated the possibility of the quantitative concentration of inorganic ions from solutions diluted by a factor of 75–100 relative to the minimum detectable amount (as shown by the colour reaction). The principles of precipitation chromatography have been used for a long time in the purification of water [90,91,174].

Precipitation and diffusional-precipitation chromatography are used to elucidate and model ore-formation processes [182,183,190,297,320–326].

After this article had been submitted to the editors, new papers have been published on precipitation chromatography in the column version [356–363], in particular in ion-exchange resin columns [364–371], and also on paper precipitation chromatography [372–391]. The above publications include also certain earlier papers, which the present author missed previously.

As before, the greatest number of publications deal with the quantitative analysis of inorganic ions on impregnated paper [373–384,389–391]. Small amounts of substances can be detected with the aid of columns [358,361,364]. Precipitation chromatography is used for quantitative inorganic analysis [388], purification of salts [356], quantitative separation of inorganic ions [366–368,386], and radiochemical separation on ion-exchange resins [369–371], including the separation of genetic isotope pairs (for example, $^{90}Sr + {}^{90}Y$, $^{140}Ba + {}^{140}La$). Some papers also deal with the problem of the theory of precipitation sorption [359,360,362,363,365].

REFERENCES

1. I.M.Hais and K.Macek (Editors), "Paper Chromatography" (Translated into Russian), Inostr.Lit., Moscow, 1962.
2. E.Lederer and M.Lederer, "Chromatography", Elsevier Publn.Co., Amsterdam, 1957.
3. F.H.Pollard and J.F.W.McOmie, "Chromatographic Methods of Inorganic Analysis", London, 1953.
4. V.V.Rachinskii and T.B.Gapon, "Khromatografiya v Biologii" (Chromatography in Biology), Izv.Akad.Nauk SSSR, Moscow, 1953.
5. F.M.Shemyakin, E.S.Mitselovskii, and D.V.Romanov, "Khromatograficheskii Analiz" (Chromatographic Analysis), Goskhimizdat, Moscow, 1955.
6. N.F.Ermolenko, "Khromatograficheskii Adsorbtsionnyi Analiz i Ego Razvitie" (Chromatographic Adsorption Analysis and Its Development), Izv.Akad.Nauk Beloruss.SSR, Minsk, 1955.
7. J.Opienska-Blauth, A.Waksmundzki, and M.Kanski, (Editors), "Chromatografia", Warsaw, 1957.
8. K.M.Ol'shanova, V.D.Kapylova, and N.M.Morozova, "Osadochnaya Khromatografiya" (Precipitation Chromatography), Izv.Akad.Nauk SSSR, Moscow, 1963.
9. E.Hayek, J.Chromatog., **2**, 334 (1959).
10. F.F.Runge, "Der Bildungstieb der Stoffe", Selbstverlag, Oranienburg, 1855.
11. M.S.Tsvet, "Khromatograficheskii Adsorbtsionnyi Analiz" (Chromatographic Adsorption Analysis), Izv.Akad.Nauk SSSR, 1946.
12. F.Goppelsroeder, "Über Capillar-Analyse", Vienna, 1889.
13. F.Feigl, "Qualitative Analysis by Spot Tests" (Translated into Russian), ONTI, Moscow, 1937.
14. N.A.Tananaev, "Kapel'nyi Metod" (Spot Tests), Goskhimizdat, Moscow–Leningrad, 1954.
15. G.M.Schwab and K.Jockers, Naturwiss., **25**, 44 (1937).
16. G.M.Schwab and K.Jockers, Angew.Chem., **50**, 546 (1937).
17. G.M.Schwab and A.Issidoridis, Z.phys.Chem.(Frankfurt), B **53**, 1 (1942).
18. G.M.Schwab, Discuss.Faraday Soc., No.7, 170 (1949).
19. L.Sacconi, Discuss.Faraday Soc., No.7, 173 (1949).
20. H.Flood, Z.analyt.Chem., **120**, 327 (1940).
21. H.Flood, Discuss Faraday Soc., No.7, 190 (1949).
22. H.Goto and Y.Kakita, J.Chem.Soc.Japan, **63**, 120 (1942); Chem.Abs., **41**, 3010 (1947).
23. Y.Kakita and H.Goto, Sci.Reports Res.Inst., Tôhoku Univ., ser.A, **2**, 837 (1950); Chem.Abs., **46**, 4947 (1952).
24. S.Iijima, T.Sato, and T.Kamoshita, Bull.Inst.Phys.Chem. Res., Tokyo, Chem.Edn., **23**, 181 (1944); Chem.Abs., **42**, 7197 (1948).
25. S.Iijima and T.Sato, Bull.Inst.Phys.Chem.Res., Tokyo, Chem.Edn., **23**, 233, (1944); Chem.Abs., **42**, 7198 (1948).
26. S.Iijima and T.Sato, Bull.Inst.Phys.Chem.Res., Tokyo, Chem.Edn., **23**, 284 (1944); Chem.Abs., **42**, 7198 (1948).
27. F.M.Shemyakin and I.P.Kharlamov, USSR P. 87210 (1949).
28. H.Erlenmeyer and H.Dahn, Helv.Chim.Acta, **22**, 1369 (1939).
29. H.Erlenmeyer and W.Schoenauer, Helv.Chim.Acta, **24**, 878 (1941).
30. H.Erlenmeyer and J.Schmidlin, Helv.Chim.Acta, **24**, 1213 (1941).
31. P.P.Hopf, C.G.Lynam, and H.Weil, B.P. 585224 (1944); Chem.Abs., **44**, 3750 (1950).
32. P.P.Hopf, J.Chem.Soc., 785 (1946).
33. J.A.Bishop, J.Chem.Educ., **22**, 524 (1945).
34. G.Robinson, Metallurgia, **37**, 45, 107 (1947).
35. G.Robinson, Discuss.Faraday Soc., No.7, 195 (1949).
36. F.M.Shemyakin and E.S.Mitselovskii, Zhur.Anal.Khim., **3**, 349 (1948).
37. E.N.Gapon and T.B.Gapon, Dokl.Akad.Nauk SSSR, **59**, 921 (1948).
38. T.B.Gapon and E.N.Gapon, Zhur.Anal.Khim., **3**, 203 (1948).
39. T.B.Gapon and E.N.Gapon, Dokl.Akad.Nauk SSSR, **60**, 401 (1948).
40. T.B.Gapon, Candidate's Thesis, Moscow Technical Institute of Agriculture and Fisheries, 1948.
41. I.M.Belen'kaya, Candidate's Thesis, Timiryazev Agricultural Academy, Moscow, 1948.
42. E.N.Gapon and I.M.Belen'kaya, "Referaty Dokladov na Soveshchanii po Khromatografii" (Abstracts of Reports at the Conference on Chromatography), Izv.Akad.Nauk SSSR, Moscow, 1960, p.35.
43. E.N.Gapon and I.M.Belen'kaya, "Issledovaniya v Oblasti Khromatografii" (Studies in Chromatography), Izv.Akad. Nauk SSSR, Moscow, 1952, p.35.
44. E.N.Gapon and I.M.Belen'kaya, Kolloid Zhur., **14**, 323 (1952).
45. I.M.Belen'kaya and M.A.Shilo, Nauch.Zap.Uzhgorod.Gos. Univ., **12**, 52 (1955).
46. I.M.Belen'kaya, Nauch.Zap.Uzhgorod.Gos.Univ., **22**, 35 (1957).
47. E.Hesford, "The Use of Adsorption Columns for Effecting Precipitation Separations", Report AERE C/M 222, UK Atomic Energy Authority, Harwell, 1957.
48. F.M.Shemyakin, V.S.Andreev, L.L.Gumanov, and V.I.Mokrova, Aptechnoe Delo, **2**, 33 (1953).
49. G.Cetini and F.Ricca, Gazzetta, **84**, 674 (1954).
50. G.Cetini and F.Ricca, Gazzetta, **85**, 419 (1955).
51. K.M.Ol'shanova and N.M.Morozova, Trudy Moskov.Tekhnol.Inst.Myasn. i Mol.Prom., **8**, 119 (1958).
52. V.D.Kopylova, Trudy Moskov.Tekhnol.Inst.Myasn.i Mol. Prom., **8**, 127 (1958).
53. V.D.Kopylova and K.M.Ol'shanova, "Issledovaniya v Oblasti Ionoobmennoi, Raspredelitel'noi i Osadochnoi Khromatografii" (Studies in Ion-Exchange, Partition, and Precipitation Chromatography), Izv.Akad.Nauk SSSR, Moscow, 1959, p.105.
54. J.L.Forstner and L.B.Rogers, Analyt.Chem., **31**, 365 (1959).
55. M.Muto, Nippon Kagaku Zasshi, **85**, A 11, 147 (1964).
56. M.Muto, Nippon Kagaku Zasshi, **85**, A 60, 782 (1964).
57. M.Muto, Nippon Kagaku Zasshi, **86**, A 5, 91 (1965).
58. R.O.Rach, Anales Asoc.quim.argentina, **37**, 274 (1949); Chem.Abs., **45**, 2361 (1951).
59. H.H.Strain, Analyt.Chem., **22**, 41 (1950).
60. V.V.Oshchapovskii, Zhur.Anal.Khim., **11**, 170 (1956).
61. R.N.Golovatyi, V.V.Oshchapovskii, and L.I.Zemlyanskaya, Ukrain.Khim.Zhur., **26**, 117 (1960).
62. R.N.Golovatyi, V.V.Oshchapovskii, and Z.S.Grin'kiv, Ukrain.Khim.Zhur., **28**, 245 (1962).
63. O.I.Komlev and N.A.Snitsar, Visnik L'viv.Univ., Ser. Khim., 79, 1964.
64. T.B.Gapon, A.M.Gurvich, A.A.Mettsler, M.S.Rabinovich, V.V.Strukov, and L.A.Usatova, USSR P. 101671 (1953).
65. T.B.Gapon, A.A.Mettsler, M.A.Rabinovich, E.I.Strukova, V.V.Strukov, and A.A.Usatova, USSR P. (Contingent Patent) 105942 (1953); USSR P. (Principal Patent) 99924 (1954).
66. T.B.Gapon, A.M.Gurvich, M.S.Rabinovich, V.V.Strukov, and L.A.Usatova, USSR P. 99924 (1954).
67. A.M.Gurvich, Zhur.Anal.Khim., **11**, 437 (1956).
68. A.M.Gurvich, T.B.Gapon, and M.S.Rabinovich, Khim. Prom., **1**, 31 (1956).
69. A.M.Gurvich, Zhur.Obshch.Khim., **27**, 40 (1957).
70. A.M.Gurvich, Zhur.Obshch.Khim., **27**, 316 (1957).
71. A.M.Gurvich and T.B.Gapon, Zavod.Lab., **23**, 1037 (1957).
72. A.M.Gurvich, T.B.Gapon, and M.S.Rabinovich, Izv.Akad. Nauk SSSR, Ser.Fiz., **21**, 656 (1957).

73. A.M.Gurvich, T.B.Gapon, and M.S.Rabinovich, "Materialy V Soveshchaniya po Lyuminestsentsii" (Proceedings of the Fifth Conference on Luminescence), Tartu, 1957, p.363.
74. A.M.Gurvich and T.B.Gapon, "Materialy Soveshchaniya po Primenenii Ionnogo Obmena v Tsvetnoi Metallurgii" (Proceedings of the Conference on the Application of Ion Exchange in Non-Ferrous Metallurgy), Izd.TsNIItsvetmet, Moscow, 1957, p.91.
75. A.M.Gurvich, Candidate's Thesis, Institute of Physical Chemistry of the USSR Academy of Sciences, Moscow, 1957.
76. F.Burriel and F.Pino Pérez, Anales real Soc.españ.Fis. Quim., **45B**, 749 (1949); Chem.Abs., **44**, 3837 (1950).
77. F.Burriel-Marti and F.Pino Pérez, Analyt.Chim.Acta, **3**, 468 (1949).
78. V.D.Kopylova, Trudy Moskov.Tekhnol.Inst.Myasn.i Mol. Prom., **6**, 170 (1956).
79. M.S.Fortunatov and N.O.Vartapetova, Dopovidi Akad.Nauk Ukrain.RSR, 1088 (1964).
80. T.B.Gapon, A.M.Gurvich, A.A.Mettsler, M.S.Rabinovich, V.V.Strukov, and L.A.Usatova, USSR P. 101183 (1953).
81. A.M.Gurvich, Zhur.Fiz.Khim., **32**, 1597 (1958).
82. E.Hayek and H.Schimann, Monatsh., **88**, 686 (1957).
83. H.Schäfer and W.Neugebauer, Naturwiss., **38**, 561 (1951).
84. H.Schäfer and W.Neugebauer, Z.anorg.Chem., **274**, 114 (1953).
85. E.Hayek, F.Lorenz, H.Schimann, and H.Ude, Monatsh., **90**, 49 (1959).
86. L.M.Provotorova, Candidate's Thesis, Moscow Pharmaceutical Institute, 1957.
87. S.A.Napol'skii, Uch.Zap.Kirov.Gos.Ped.Inst., **14**, 10 (1958).
88. R.Gans, Chem.Ind.(Dusseldorf), **32**, 197 (1909).
89. A.Rümpler, "Intern.Kongr.f.angew.Chemie", Berlin, 1903, Vol.3, p.59.
90. H.L.Tiger and S.Sussman, "Ion Exchange" (Translated into Russian), Inostr.Lit., Moscow, 1951, p.168.
91. N.V.Octrooien Maatschappij–"Activit", French P. 805 092 (1935).
92. S.Gaddis, J.Chem.Educ., **17**, 327 (1942).
93. R.Kunin, Analyt.Chem., **21**, 87 (1949).
94. R.Kunin and R.J.Myers, "Ion-Exchange Resins" (Translated into Russian), Inostr.Lit., Moscow, 1952.
95. V.B.Aleskovskii and Z.I.Kheifets, "Tezisy Dokladov Nauchno-Tekhnicheskoi Konferentsii Leningradskogo Tekhnologicheskogo Instituta Imeni Lensoveta" (Abstracts of Reports at the Science and Engineering Conference at the Lensovet Leningrad Technological Institute), 1951, p.42.
96. V.B.Aleskovskii and Z.I.Kheifets, Trudy Leningrad.Tekhnol.Inst.im.Lensoveta, **27**, 51 (1953).
97. V.B.Aleskovskii and Z.I.Kheifets, Trudy Leningrad.Tekhnol.Inst.im.Lensoveta, **35**, 108 (1956).
98. V.B.Aleskovskii and Z.I.Kheifets, Trudy Leningrad.Tekhnol.Inst.im.Lensoveta, **35**, 120 (1956).
99. E.Glueckauf and P.J.P.Roberts, B.P. 781 726 (1954).
100. E.Glueckauf and P.J.P.Roberts, "Precipitation Separations without Filtration", Report AERE C/R 1443, UK Atomic Energy Authority, Harwell, 1954.
101. W.Kielczewski, Roczniki Chem., **28**, 493 (1954).
102. A.I.Komlev and L.I.Tsimbalista, Zhur.Anal.Khim., **8**, 217 (1953).
103. R.H.James and G.A.Welch, Nature, **177**, 183 (1956).
104. E.A.Bozhevol'nov and V.V.Trusov, "Materialy V Soveshchaniya po Lyuminestsentsii" (Proceedings of the Fifth Conference on Luminescence), Tartu, 1957, p.347.
105. E.A.Bozhevol'nov and V.V.Trusov, Izv.Akad.Nauk SSSR, Ser.Fiz., **21**, 655 (1957).
106. A.B.Davankov, V.M.Laufer, and L.A.Shits, Zhur.Prikl. Khim., **30**, 839 (1957).
107. A.B.Davankov, T.A.Aptova, and Z.M.Giterman, Zhur. Prikl.Khim., **34**, 1852 (1961).
108. R.N.Golovatyi, V.V.Oshchapovskii, and N.N.Khudyakova, Ukrain.Khim.Zhur., **24**, 491 (1958).
109. N.M.Morozova, Candidate's Thesis, Moscow Technological Institute of the Meat and Milk Industry, 1960.
110. W.Kiełczewski, Chem.Analit., **8**, 691 (1963).
111. E.I.Zubkova and A.S.Konishcheva, "Primenenie Khromatograficheskogo Metoda pri Kontrole Kachestva Materialov" (Application of the Chromatographic Method in the Quality Control of Materials), Izd.Moskov.Doma NTP, 1964, No.1, p.114.
112. J.Gera, Chem.Analit., **9**, 541 (1964).
113. T.V.Ionatamishvili and Ts.S.Nachkebiya, Soobshch.Akad. Nauk Gruz.SSR, **37**, 595 (1965).
114. A.M.Liimatta and J.D.Spain, Analyt.Chem., **35**, 1898 (1963).
115. D.E.Laskowski and W.C.McCrone, Analyt.Chem., **23**, 1579 (1951).
116. Q.Fernando and J.P.Phillips, Analyt.Chem., **25**, 819 (1953).
117. Q.Fernando and M.de Silva, Analyst, **79**, 711 (1954).
118. E.S.Boichikova and V.B.Aleskovskii, Trudy Leningrad, Tekhnol.Inst.im.Lensoveta, **48**, 94 (1958).
119. R.O.Bach, Anales Asoc.quim.argentina, **37**, 55 (1949); Chem.Abs., **43**, 7859 (1949).
120. R.O.Bach, Anales Asoc.quim.argentina, **37**, 69 (1949); Chem.Abs., **43**, 7859 (1949).
121. A.V.Moskvin, "Katodolyuminestsentsiya" (Cathodoluminescence), GITTL, Moscow–Leningrad, 1949, Part.2.
122. A.Kutzelnigg, Z.Erzbergbau u.Metallhüettenw., **3**, 77 (1950); Chem.Abs., **44**, 6332 (1950).
123. B.Miličevič, Bull.Soc.chim.Belgrade, **15**, 167 (1950); Chem.Abs., **46**, 6038 (1952).
124. V.V.Oshchapovskii, Zhur.Anal.Khim., **11**, 606 (1956).
125. A.Lewandowski, W.Czemplik, and A.Dzik, Zeszyty Nauk Uniw.Poznaniu, **28**, 3 (1960).
126. D.V.Bezuglyi, I.A.Petrusevich, and N.K.Senyuta, Trudy Khar'kov.Politekh.Inst., **4**, 111 (1954).
127. S.A.Napol'skii, USSR P. 99 066 (1951).
128. S.A.Napol'skii, USSR P. 92 156 (1950).
129. S.A.Napol'skii, "Issledovaniya v Oblasti Khromatografii" (Studies in Chromatography), Izv.Akad.Nauk SSSR, Moscow, 1952, p.147.
130. S.A.Napol'skii, Candidate's Thesis, Kirov, 1953.
131. L.M.Provotorova, "Voprosy Sudebno-Medintsinskoi Ekspertizy" (Problems of Forensic Medicine), Gosyurizdat, Moscow, 1955, No.2, p.121.
132. L.Zechmeister and L.v.Cholnoky, "Die Chromatographische Adsorptionsmethode", Vienna, 1938.
133. K.M.Ol'shanova, Doctoral Thesis, Institute of Physical Chemistry of the USSR Academy of Sciences, Moscow, 1955.
134. K.M.Ol'shanova, Trudy Moskov.Tekhnol.Inst.Myasn.i Mol. Prom., **5**, 48 (1955).
135. V.D.Kopylova, K.M.Ol'shanova, and K.V.Chmutov, Zhur. Anal.Khim., **11**, 167 (1956).
136. K.M.Ol'shanova and K.V.Chmutov, Zhur.Anal.Khim., **13**, 162 (1958).
137. K.M.Ol'shanova and N.M.Morozova, "Issledovaniya v Oblasti Ionoobmennoi, Raspredelitel'noi i Osadochnoi Khromatografii" (Studies in Ion-Exchange, Partition, and Precipitation Chromatography), Izv.Akad.Nauk SSSR, Moscow, 1959, p.124.
138. V.L.Zolotavin and V.A.Ryabov, "Metody Analiza Chernykh i Tsvetnykh Metallov" (Methods of Analysis of Ferrous and Non-Ferrous Metals), Sverdlovsk–Moscow, 1953, p.17.
139. D.A.Vyakhirev and F.N.Kulaev, Trudy Kom.Anal.Khim. Akad.Nauk SSSR, **6**, (9), 527 (1955).
140. F.N.Kulaev, Candidate's Thesis, Gorky State Pedagogic Institute, 1956.

141. F.N.Kulaev, Zhur.Anal.Khim., **13**, 172 (1958).
142. F.N.Kulaev, Khimiya v Shkole, **6**, 63 (1958).
143. F.N.Kulaev, Zhur.Anal.Khim., **14**, 278 (1959).
144. F.N.Kulaev, "Khromatografiya, Ee Teoriya i Primenenie" (The Theory and Applications of Chromatography), Izv. Akad.Nauk SSSR, Moscow, 1960, p.450.
145. F.N.Kulaev, Izv.Vys.Ucheb.Zaved., Khim.i Khim.Tekhnol., **7**, 904 (1964).
146. B.I.Clarke and H.W.Hermance, Ind.Eng.Chem., Analyt., **9**, 292 (1937).
147. B.I.Clarke and H.W.Hermance, Ind.Eng.Chem., Analyt., **10**, 591 (1938).
148. E.B.Sandell, "Colorimetric Determination of Traces of Metals" (Translated into Russian), Izd.Mir, Moscow, 1964, p.38.
149. E.Tiede, Z.Elektrochem., **44**, 586 (1938).
150. W.Schikore and E.G.Müller, Z.anorg.Chem., **255**, 327 (1948).
151. C.Mahr and H.Klamberg, Arch.Eisenhüttenws., **28**, 795 (1957).
152. H.T.Gordon and C.A.Hewel, Analyt.Chem., **27**, 1471 (1955).
153. L.S.Aleksandrova and K.V.Chmutov, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 801 (1960).
154. L.S.Aleksandrova, T.B.Gapon, and K.V.Chmutov, "Ionnyi Obmen i Khromatografiya" (Ion Exchange and Chromatography), Izd.Voronezh.Gos.Univ., Voronezh, 1965, p.124.
155. H.Specker and H.Hartkamp, Z.analyt.Chem., **140**, 167 (1953).
156. H.Specker, M.Kuchtner, and H.Hartkamp, Z.analyt. Chem., **141**, 33 (1954).
157. St.A.Ivanov, D.Maneva, P.Toleva, and N.P.Mashev, Nauch.Trudove na VIKhVP, Plovdiv, **5**, 353 (1959).
158. D.Maneva, Nauch.Trudove na VIKhVP, Plovdiv, **11**, 135 (1964).
159. D.Maneva, Nauch.Trudove na VIKhVP, Plovdiv, **11**, 238 (1964).
160. H.Nagai, Bull.Chem.Soc.Japan, **33**, 715 (1960).
161. H.Nagai, Bull.Chem.Soc.Japan, **37**, 1076 (1964).
162. M.Milone, G.Cetini, and F.Ricca, Ann.Chim.(Italy), **43**, 652 (1953).
163. N.Ganchev and K.Koev, Zhur.Anal.Khim., **17**, 166 (1962).
164. R.O.Bach, Industria y Quimica (Buenos Aires), **12**, 283 (1950); Chem.Abs., **45**, 7463 (1951).
165. E.R.Reichl and J.E.Löffler, Mikrochim.Acta, 226 (1954).
166. A.Lewandowski and W.Kielczewski, Roczniki Chem., **30**, 275 (1956).
167. St.A.Ivanov, A.S.Petkov, and A.G.Toneva, Nauch.Trudove na VIKhVP, Plovdiv, **5**, 347 (1959).
168. K.M.Ol'shanova, V.Kopylova, and A.Bat-Ochir, Myasnaya Ind.SSSR, **29**, (5), 51 (1958).
169. N.M.Morozova and K.M.Ol'shanova, Izv.Vys.Ucheb. Zaved., Pishch.Tekhnol., 1, 130 (1961).
170. K.M.Ol'shanova, V.D.Kopylova, and N.M.Morozova, Izv. Vys.Ucheb.Zaved., Khim.i Khim.Tekhnol., **4**, 923 (1961).
171. V.D.Kopylova, N.M.Morozova, and K.M.Ol'shanova, Izv.Vys.Ucheb.Zaved., Khim.i Khim.Tekhnol., **5**,22 (1962).
172. M.S.Ivanova, Trudy Kom.Anal.Khim.Akad.Nauk SSSR, **7**, (10), 77 (1956).
173. S.Yokota and J.Shimada, Nippon Kagaky Zasshi, **79**, 1144 (1958); Chem.Abs., **53**, 8927 (1959).
174. C.Calmon, "Ion Exchange" (Translated into Russian), Inostr.Lit., Moscow, 1951, p.107.
175. M.M.Dubinin, "Fiziko-Khimicheskie Osnovy Sorbtsionnoi Tekhniki" (Physicochemical Foundations of Sorption Techniques), ONTI, 1935.
176. V.D.Kopylova and K.M.Ol'shanova, Izv.Vys.Ucheb.Zaved., Pishch.Tekhnol., 3, 158 (1961).
177. R.Grissbach, "Theory and Practive of Ion Exchange" (Translated into Russian), Inostr.Lit., Moscow, 1963.
178. R.G.Bird, U.S.P. 2 244 325 (1940).
179. J.W.Ryznar, Ind.Eng.Chem., **36**, 821 (1944).
180. N.Ganchev, Compt.Rend.Acad.Bulgare Sci., **14**, 495 (1961).
181. N.Ganchev and C.Todorova, Compt.Rend.Acad.Bulgare Sci., **14**, 591 (1961).
182. G.L.Pospelov, P.I.Kaushanskaya, and D.D.Saratovkin, Zap.Vses.Mineralogich Obshch., Second Series, **90**, 382 (1961).
183. P.I.Kaushanskaya, Candidate's Thesis, Siberian Division of the USSR Academy of Sciences, Novosibirsk, 1963.
184. H.W.Morse, J.Phys.Chem., **34**, 1554 (1930).
185. F.M.Shemyakin and V.V.Kulebakina, Izv.Vys.Ucheb. Zaved., Khim.i Khim.Tekhnol., **6**, 35 (1963).
186. F.M.Shemyakin, V.V.Kulebakina, and N.K.Medvedeva, "Ionoobmennaya Tekhnologiya" (Ion-Exchange Technology), Izd.Nauka, Moscow, 1965, p.256.
187. F.M.Shemyakin, A.I.Berdnikov, and N.K.Medvedeva, "Primenenie Khromatograficheskogo Metoda pri Kontrole Kachestva Materialov" (Application of the Chromatographic Method in the Quality Control of Materials), Izd.Moskov. Doma NTP, 1964, No.1, p.98.
188. F.M.Shemyakin, A.I.Berdnikov, A.G.Zaitsev, V.V.Kulebakina, and N.K.Medvedeva, "Ionnyi Obmen i Khromatografiya" (Ion Exchange and Chromatography), Izd.Voronezh Gos.Univ., Voronezh, 1965, p.136.
189. N.L.Olenovich, A.A.Morozov, and E.G.Siritsova, Ukrain. Khim.Zhur., **25**, 509 (1959).
190. M.Watanabe, The Earth (Japan), 8, 407 (1927); Chem. Abs., **24**, 1267 (1930).
191. M.Milone and G.Cetini, Ann.Chim.(Italy), **43**, 648 (1953).
192. M.Milone, G.Cetini, and F.Ricca, Ann.Chim.(Italy), **43**, 659 (1953).
193. M.Milone, G.Cetini, and F.Ricca, Ann.Chim.(Italy), **45**, 1018 (1955).
194. G.Cetini and F.Ricca, J.Chim.phys., **55**, 315 (1958).
195. J.D.Spain, Analyt.Chem., **32**, 1622 (1960).
196. J.D.Spain, F.L.Ludeman, and A.K.Snelgrove, Econ.Geol., **57**, 248 (1962).
197. A.C.Chatterji and H.Bhagwan, J.Colloid.Sci., **13**, 232 (1958).
198. K.Krishnamurti and B.V.Dhareshwar, Nature, **181**, 766 (1958).
199. W.Ostwald, Kolloid Z., **40**, 144 (1926).
200. J.Salvinien and J.J.Moreau, Compt.rend., **235**, 46 (1952).
201. J.Salvinien, J.J.Moreau, and R.Gaufrès, J.Chim.phys., **50**, 1 (1953).
202. F.R.Meeks and H.Kosenkranius, J.Colloid Sci., **17**, 1 (1962).
203. V.V.Rachinskii and A.A.Lur'e, Dokl.Akad.Nauk SSSR, **152**, 1365 (1963).
204. L.K.Lepin', Uspekhi Khim., **9**, 533 (1940).
205. A.A.Lur'e, Candidate's Thesis, Timiryazev Agricultural Academy, Moscow, 1965.
206. A.A.Lur'e, Kolloid.Zhur., **28**, 871 (1966).
207. F.Helfferich, "Ionenaustauscher" (Translated into Russian), Inostr.Lit., Moscow, 1962.
208. F.Helfferich, J.Phys.Chem., **69**, 1178 (1965).
209. O.N.Grigorov and A.I.Tarshis, Kolloid.Zhur., **11**, 1390 (1949).
210. A.G.Koblyanskii, Zhur.Obshch.Khim., **24**, 18 (1954).
211. E.Brochmann-Hanssen, J.Amer.Pharmaceut.Assoc.(Sci. Edn.), **43**, 307 (1954).
212. E.N.Boichinova and V.B.Aleskovskii, Trudy Leningrad. Tekhnol.Inst.im.Lensoveta, **48**, 133 (1958).
213. T.I.Kalinina and V.B.Aleskovskii, Trudy Leningrad.Tekhnol.Inst.im.Lensoveta, **48**, 124 (1958).

214. A.I.Vulikh, Zhur.Prikl.Khim., **36**, 2321 (1963).
215. G.H.Osborn, "Synthetic Ion Exchangers: Developments in Theory and Application" (Translated into Russian), Izd.Mir, Moscow, 1964.
216. A.G.Koblyanskii and M.Kh.Kameneva, Trudy Krasnodar. Inst.Pishch.Prom., **11**, 73 (1955).
217. A.A.Lur'e and V.V.Rachinskii, Izv.Timiryazev.Sel'-skokhoz.Akad., 4, 179 (1966).
218. E.N.Gapon and G.M.Shuvaeva, Dokl.Akad.Nauk SSSR, **70**, 1007 (1950).
219. E.N.Gapon and G.M.Shuvaeva, "Issledovaniya v Oblasti Khromatografii" (Studies in Chromatography), Izv.Akad. Nauk SSSR, Moscow, 1952, p.41.
220. E.Hayek and F.Lorenz, Monatsh., **84**, 647 (1953).
221. W.Noddack and E.Bankmann, Z.Electrochem., **58**, 725 (1954).
222. R.Fricke, W.Neugebauer, and H.Schäfer, Z.anorg.Chem., **273**, 215 (1953).
223. W.Neugebauer and H.Schäfer, Z.anorg.Chem., **273**, 227 (1953).
224. E.V.Alekseevskii, Zhur.Russ.Fiz.-Khim.Obshch., Chast' Khim., **62**, 817 (1930).
225. H.Specker and H.Hartkamp, Naturwiss., **40**, 271 (1953).
226. E.J.Miller, J.Amer.Chem.Soc., **47**, 1270 (1925).
227. N.Schilow, H.Schatunowskaja, and K.Tschmutow, Z.phys. Chem., **148**, 233 (1930).
228. M.M.Dubinin, Uspekhi Khim., **24**, 513 (1955).
229. G.Venturello and N.Agliardi, Ann.Chim.appl., **30**, 224 (1940); Chem.Abs., **36**, 5439 (1942).
230. M.Shibata, Science (Japan), **19**, 570 (1949); Chem.Abs., **45**, 7845 (1951).
231. N.A.Shilov and L.K.Lepin', Vestnik Lomonosov.Fiz.-Khim.Obshch., **1**, 1 (1919).
232. A.A.Lur'e, "Spravochnik po Analiticheskoi Khimii" (Handbook of Analytical Chemistry), Izd.Khimiya Moscow, 1965.
233. A.P.Dushina and V.B.Aleskovskii, Zhur.Neorg.Khim., 8, 2194 (1963) [Russ.J.Inorg.Chem., 1147 (1963)].
234. M.Milone and G.Cetini, Atti R.Accad.Sci.Torino, Classe Sci.fis.mat.nat., **90**, la, 3 (1955–1956).
235. V.V.Rachinskii and A.A.Lur'e, Izv.Timiryazev.Sel'-skokhoz.Akad., 4, 198 (1964).
236. A.A.Lur'e, Zhur.Anal.Khim., **21**, 929 (1966).
237. E.N.Gapon and T.B.Gapon, "Khromatograficheskii Metod Razdeleniya Ionov" (The Chromatographic Method for the Separation of Ions), Inostr.Lit., Moscow, 1949, p.9.
238 G.Cetini and F.Ricca, Gazzetta, **85**, 434 (1955).
239. S.A.Ivanov, Zhur.Anal.Khim., **14**, 729 (1959).
240. V.V.Rachinskii and A.A.Lur'e, Dokl.Akad.Nauk SSSR, **162**, 1326 (1965).
241. A.A.Lur'e, Zhur.Fiz.Khim., **41**, 25 (1967) [Russ.J.Phys. Chem., 12 (1967)].
242. V.D.Kopylova and K.M.Ol'shanova, "Khromatografiya, Ee Teoriya i Primenenie" (The Theory and Applications of Chromatography), Izv.Akad.Nauk SSSR, Moscow, 1960, p.389.
243. E.N.Gapon and T.B.Gapon, Zhur.Obshch.Khim., **19**, 1627 (1949).
244. Y.Oka and A.Murata, Sci.Reports Res.Inst., Tôhoku Univ., Ser.A, **3**, 82 (1951).
245. Y.Oka and A.Murata, Sci.Reports Res.Inst., Tôhoku Univ., Ser.A, **3**, 707 (1951).
246. Y.Oka and A.Murata, Sci.Reports Res.Inst., Tôhoku Univ., Ser.A, 3, 711 (1951).
247. Y.Oka and A.Murata, Sci.Reports Res.Inst., Tôhoku Univ., Ser.A, **5**, 343 (1953).
248. Y.Oka and A.Murata, Nippon Kagaku Zasshi, **72**, 657 (1951); Chem.Abs., **46**, 6030 (1952).
249. Y.Oka and A.Murata, Nippon Kagaku Zasshi, **73**, 494 (1952); Chem.Abs., **47**, 2631 (1953).
250. Y.Oka and A.Murata, Nippon Kagaku Zasshi, **73**, 496 (1952); Chem.Abs., **47**, 2631 (1953).
251. M.B.Celap and T.J.Janjic, Bull.Soc.chim.Belgrade, **25–26**, 125 (1960–1961).
252. T.J.Janjic and M.B.Celap, Bull.Soc.chim.Belgrade, **25–26**, 133 (1960–1961).
253. M.B.Celap, T.J.Janjic, and Z.M.Spanovic, Bull.Soc. chim.Belgrade, **25–26**, 527 (1960–1961).
254. T.J.Janjic and M.B.Celap, Bull.Soc.chim.Belgrade, **25–26**, 531 (1960–1961).
255. M.B.Celap, T.J.Janjic, and D.Stojkovich, Bull.Soc.chim. Belgrade, **27**, 279 (1962).
256. M.B.Celap, T.A.Janjic, and D.Radanovic, Bull.Soc.chim. Belgrade, **28**, 19 (1963).
257. A.Lewandowski and W.Kiełczewski, Roczniki Chem., **28**, 285 (1954).
258. A.Lewandowski, W.Kiełczewski, and H.Hoffmann, Poznan. Towarz.Przyjaciol Nauk, Wydzial Mat.Przyrod.Prace Komisji Mat.Przyrod., [A], **7**, 129 (1956).
259. W.Kiełczewski, Roczniki Chem., **30**, 953 (1956).
260. W.Kiełczewski, Chem.Analit., **2**, 336 (1957).
261. W.Kiełczewski, Chem.Analit., **4**, 151 (1959).
262. A.Lewandowski and M.Owoc, Zeszyty Nauk.Uniw. im. A.Mickiewicza, Mat., fiz.chem.. **28/3**, 9 (1960).
263. W.Kiełczewski and J.Tomkowiak, Chem.Analit., **5**, 889 (1960).
264. W.Kiełczewski and J.Gera, Chem.Analit., **7**, 579 (1962).
265. W.Kiełczewski and J.Tomkowiak, Chem.Analit., **7**, 925 (1962).
266. W.Kiełczewski and J.Supiński, Chem.Analit., **8**, 59 (1963).
267. W.Kiełczewski and J.Miloczewska-Podolak, Chem.Analit., **8**, 95 (1963).
268. W.Kiełczewski and A.Beszterda, Chem.Analit., **9**, 545 (1964).
269. W.Kiełczewski and M.Schneider, Chem.Analit., **9**, 693 (1964).
270. W.Kiełczewski and J.Supiński, Chem.Analit., **10**, 677 (1965).
271. W.Kiełczewski and W.Uchman, Chem.Analit., **10**, 915 (1965).
272. A.J.Hłyńczak, J.S.Knypl, and R.Antoszewski, Chem. Analit., **5**, 407 (1960).
273. I.Schneider, Chem.Analit., **10**, 653 (1965).
274. N.Ganchev and K.Koev, Compt.rend.Acad.bulg.Sci., **14**, 247 (1961).
275. N.Ganchev and K.Koev, Mikrochim.Ichnoanalyt.Acta, 1, 87 (1964).
276. N.Ganchev and K.Koev, Mikrochim.Ichnoanalyt.Acta, 1, 92 (1964).
277. N.Ganchev and K.Koev, Mikrochim.Ichnoanalyt.Acta, 1, 97 (1964).
278. H.Nagai, Nippon Kagaku Zasshi, **76**, 1246 (1955); Chem. Abs., **51**, 12735 (1957).
279. H.Nagai, Kumamoto J.Sci., Ser., **A2**, 304 (1955).
280. K.M.Ol'shanova and V.D.Kopylova, Trudy Moskov.Tekhnol.Inst.Myasn. i Mol.Prom., **5**, 54 (1955).
281. K.M.Ol'shanova and V.D.Kopylova, Trudy Moskov Tekhnol. Inst.Myasn. i Mol.Prom., **6**, 184 (1956).
282. K.M.Ol'shanova and N.M.Morozova, Izv.Vys.Ucheb. Zaved., Khim. i Khim.Tekhnol., **2**, 63 (1958).
283. K.M.Ol'shanova, Izv.Vys.Ucheb.Zaved., Khim. i Khim. Tekhnol., **4**, 734 (1961).
284. K.F.Nedobora, Sbornik Stud.Rabot.Moskov.Tekhnol.Inst. Myasn. i Mol.Prom., **3**, 100 (1955).
285. A.V.Divak, Sbornik Stud.Rabot.Moskov.Tekhnol.Inst. Myasn. i Mol.Prom., **7**, 35 (1962).
286. F.S.Stefkin, Uch.Zap.Mordov.Univ., **27**, 3 (1963).
287. K.M.Ol'shanova and N.M.Morozova, Mol.Prom., 7, 30 (1958).
288. N.M.Morozova and K.M.Ol'shanova, Mol.Prom., 12, 26 (1959).

289. N.M.Morozova and K.M.Ol'shanova, "Problema Intensifikatsii Tekhnologicheskikh Protsessov v Myasnoi i Molochnoi Promyshlennonti" (The Problem of the Acceleration of Technological Processes in the Meat and Milk Industries), Moscow, 1959, p.97.
290. K.M.Ol'shanova, N.M.Morozova, and G.Muromtseva, Myasn.Ind.SSR, 2, 47 (1961).
291. K.M.Ol'shanova, N.M.Morozova, and V.D.Kopylova, Zavod.Lab., **29**, 24 (1963).
292. K.M.Ol'shanova, M.A.Potapova, V.D.Kopylova, and N.M.Morozova, "Rukovodstvo po Ionoobmennoi, Raspredelitel'noi i Osadochnoi Khromatografii" (Manual of Ion-Exchange, Partition, and Precipitation Chromatography), Izd.Khimiya, Moscow, 1965.
293. V.D.Kopylova, Candidate's Thesis, Moscow Technological Institute of the Meat and Milk Industry, 1957.
294. V.D.Kopylova and K.M.Ol'shanova, Kolloid.Zhur., **20**, 456 (1958).
295. V.D.Kopylova and K.M.Ol'shanova, "Issledovaniya v Oblasti Ionoobmennoi, Raspredelitel'noi i Osadochnoi Khromatografii" (Studies in Ion-Exchange, Partition, and Precipitation Chromatography), Izd.Akad.Nauk SSSR, Moscow, 1959, p.113.
296. P.I.Kaushanskaya, "Ionoobmennaya Tekhnologiya" (Ion-Exchange Technology), Izd.Nauka, Moscow, 1965, p.265.
297. G.L.Pospelov and P.I.Kaunshanskaya, Kolloid.Zhur., **25**, 215 (1963).
298. P.B.Afanas'ev, R.B.Zel'dovich, and O.M.Todes, Zhur. Fiz.Khim., **23**, 156 (1949).
299. I.N.Grigorenko, N.L.Olenovich, and A.A.Morozov, Zhur. Anal.Khim., **15**, 115 (1960).
300. A.A.Lur'e, Zhur.Anal.Khim., **22**, 689 (1967).
301. R.Barrer, "Diffusion in Solids" (Translated into Russian), Inostr.Lit., Moscow, 1948.
302. H.S.Carslaw and J.C.Jaeger "Conduction of Heat in Solids" (Translated into Russian), Izd.Nauk, Moscow, 1964.
303. W.Morse and G.W.Pierce, Z.phys.Chem.(Frankfurt), **45**, 589 (1903).
304. J.Hausmann, Z.anorg.Chem., **40**, 110 (1904).
305. M.Watanabe, Kolloid Z., **32**, 320 (1923).
306. V.Morávek, Kolloid Z., **49**, 39 (1929).
307. J.Traube and M.Shikata, Kolloid Z., **32**, 313 (1923).
308. P.B.Mathur, Bull.Chem.Soc.Japan, **34**, 440 (1961).
309. F.M.Shemyakin and P.F.Mikhalev, "Fiziko-Khimicheskie Periodicheskie Protsessy" (Periodic Physicochemical Processes), Izd.Akad.Nauk SSSR, Moscow–Leningrad, 1938.
310. K.H.Stern, Chem.Rev., **54**, 79 (1954).
311. P.B.Mathur, Bull.Chem.Soc.Japan, **34**, 437 (1961).
312. A.A.Lur'e, Kolloid.Zhur., **28**, 534 (1966).
313. K.M.Ol'shanova, Trudy Kom.Anal.Khim.Akad.Nauk SSSR, **6(9)**, 277 (1955).
314. K.M.Ol'shanova and Z.A.Koloskova, Trudy Moskov. Tekhnol.Inst.Myasn. i Mol.Prom., **8**, 109 (1958).
315. K.M.Ol'shanova and M.A.Potapova, Trudy Moskov.Tekhnol.Inst.Myasn. i Mol.Prom., **8**, 113 (1958).
316. V.Vukčević-Kovačević, Acta Pharm.Jugoslav., **3**, 27 (1953); Chem.Abs., **48**, 9785 (1954).
317. E.Tiede and W.Schikore, Ber., **B75**, 586 (1942).
318. E.Tiede, "Handbuch der Präparativen anorganischen Chemie", Stuttgart, 1954, p.1311.
319. A.N.Gurvich and T.B.Gapon, "Khromatografiya, Ee Teoriya i Primenenie" (The Theory and Applications of Chromatography), Izd.Akad.Nauk SSSR, Moscow. 1960, p.355.
320. R.E.Liesegang, "Geologische Diffusionen", Dresden, 1913.
321. R.E.Liesegang, "Die Achate", Dresden 1915.
322. R.J.Hartmann, E.W.Kannig, and F.G.Klee, J.Chem. Educ., **11**, 346 (1934).
323. G.L.Pospelov, P.I.Kaushanskaya, and S.S.Lapin, Geol. Rudn.Mestorozh., **2**, 45 (1961).
324. G.L.Pospelov and P.I.Kaushanskaya, Geol. i Geofiz., 9, 41 (1962).
325. P.I.Kaushanskaya, Geol. i Geofiz, 6, 96 (1963).
326. G.L.Pospelov and P.I.Kaunshanskaya, "Ionoobmennaya Tekhnologiya" (Ion-Exchange Technology), Izd.Nauka, Moscow, 1965, p.261.
327. M.Shibata and T.Uemura, Nippon Kagaku Zasshi, **72**, 541 (1951); Chem.Abs., **46**, 3458 (1952).
328. G.M.Shuvaeva, Trudy Vses.Sel'skokhoz.Inst.Zaochn. Obucheniya, **5**, 77 (1961).
329. V.D.Kopylova and K.M.Ol'shanova, Izv.Vys.Ucheb.Zaved., Khim. i Khim.Tekhnol., 3, 46 (1958).
330. H.Nagai, Rev.Univ.Ind.Santander, **5**, 325 (1963); Chem. Abs., **59**, 5774 (1963).
331. T.B.Gapon, A.M.Gurvich, and K.V.Chmutov, Vestnik Akad.Nauk SSSR, (10), 58 (1960).
332. H.Nagai and T.Deguchi, Bunseki Kagaku, **12**, 552 (1963); Chem.Abs., **59**, 13330 (1963).
333. H.Nagai, Nippon Kagaku Zasshi, **76**, 1246 (1955).
334. H.Nagai, Nippon Kagaku Zasshi, **77**, 1267 (1956).
335. H.Nagai, Nippon Kagaku Zasshi, **77**, 1794 (1956).
336. H.Nagai, Nippon Kagaku Zasshi, **78**, 285 (1957).
337. H.Nagai, Nippon Kagaku Zasshi, **78**, 840 (1957).
338. H.Nagai and T.Kikuchi, Nippon Kagaku Zasshi, **81**, 1271 (1960).
339. H.Nagai and T.Nishigama, Nippon Kagaku Zasshi, **82**, 349 (1961).
340. H.Nagai and M.Muto, Nippon Kagaku Zasshi, **82**, A 43, 694 (1961).
341. H.Nagai, Kumamota J.Sci.Ser., **A2**, 304 (1955); Chem. Abs., **51**, 7221 (1957).
342. H.Nagai, Kumamota J.Sci.Ser., **A3**, 81 (1957); Ref.Zhur., Khim., 70493 (1958).
343. H.Nagai, Kumamota J.Sci.Ser., **A3**, 167 (1957); Chem. Abs., **53**, 17750 (1959).
344. H.Nagai, Kumamota J.Sci.Ser., **A3**, 171 (1957); Chem. Abs., **53**, 17750 (1959).
345. H.Nagai, Kumamota J.Sci.Ser., **A3**, 176 (1957); Chem. Abs., **53**, 17750 (1959).
346. H.Nagai, Kumamota J.Sci.Ser., **A5**, 99 (1960); Chem. Abs., **56**, 4071 (1962).
347. Kh.Yu.Kokk and V.T.Aleskovskii, Izv.Vys.Ucheb.Zaved., Khim. i Khim., Tekhnol., **7**, 564 (1964).
348. V.L.Zolotavin and V.K.Kuznetsova, "Metody Analiza Chernykh i Tsvetnykh Metallov" (Methods for the Analysis of Ferrous and Non-Ferrous Metals), Sverdlovsk–Moscow, 1953, p.23.
349. A.J.Velculescu and J.Cornea, Z.analyt.Chem., **94**, 255 (1933).
350. A.G.Kniga and V.I.Ustinskaya, Trudy Leningrad.Tekhnol. Inst.Pishchevoi Prom., **12**, 253 (1955).
351. C.Tiege, Véstník Králov.Ceské Společnosti Nauk, Třida Mat.-Přírod., 5, 1 (1949); Chem.Abs., **48**, 5022 (1954).
352. Y.Kobayashi and H.Takeno, Bunseki Kagaku, **13**, 1208 (1964).
353. F.R.Haba and C.L.Wilson, Mikrochim.Acta, No.1, 196 (1963).
354. E.N.Gapon, D.D.Ivanenko, and V.V.Rachinskii, Dokl. Akad.Nauk SSSR, **45**, 567 (1954).
355. V.V.Rachinskii, Izv.Timiryazev.Sel'skokhoz.Akad., **2 (6)**, 219 (1954).
356. E.N.Vinogradova and K.Iobst, Zavod.Lab., **26**, 796 (1960).
357. A.S.Konishcheva, Candidate's Thesis, Moscow Technological Institute of the Meat and Milk Industry, Moscow, 1967.

358. Y. Kobayashi and H. Takeno, Korë ëcyu, **78**, 60 (1965); Ref. Zhur. Khim., 16G181 (1966).
259. A. Lewandowski and S. Idzikowski, Chem. Analit., **10**, 919 (1965).
360. A. Lewandowski and S. Idzikowski, Chem. Analit., **11**, 611 (1966).
361. V. St. Lesichkov, Scripta Sci. Medica (Varna), **4**, 35 (1965).
362. H. H. Stamm and H. W. Kohlschütter, J. Inorg. Nuclear Chem., **27**, 2103 (1965).
363. R. Thomas, Chem.-Ztg., **88**, 75 (1964).
364. S. E. Kashlinskaya, N. P. Strel'nikova, and Z. Ya. Prelovskaya, Symposium, "Analiz Blagorodnykh Metallov" (Analysis of Noble Metals), Moscow, 1965, p. 16.
365. G. V. Muromtseva, Candidate's Thesis, Moscow Technological Institute of the Meat and Milk Industry, 1966.
366. Ts. S. Nachkebiya, Candidate's Thesis, Lenin State Pedagogic Institute (GPI), Tbilisi, 1966.
367. A. I. Ryabinin, Yu. A. Afanas'ev, and I. A. Aksenov, Zhur. Anal. Khim., **21**, 1258 (1966).
368. A. I. Ryabinin, P. I. Artykhin, and V. L. Bogatyrev, Radiokhimiya, **9**, 335 (1967).
369. H. L. Finston and J. Miskel, Ann. Rev. Nuclear Sci., **5**, 269 (1955).
370. R. W. Perkins, Analyt. Chem., **29**, 152 (1957).
371. M. Ziegler and W. Rittner, Z. analyt. Chem., **211**, 170 (1965).
372. G. Ackermann and K. Gressmann, Mikrochim. Acta, 4 (1966).
373. N. Ganchev and A. Gancheva, Compt. rend. Acad. bulg. Sci., **18**, 441 (1965).
374. N. Ganchev and K. Koev, Trudy Vys. Inst. Narodno Stopanstvo, Varna, **37**, 25 (1965).
375. N. Ganchev and K. Koev, Trudy Vys. Inst. Narodno Stopanstvo, Varna, **37**, 31 (1965).
376. N. Ganchev and Ya. Todorova, Trudy Vys. Inst. Narodno Stopanstvo, Varna, **37**, 35 (1965).
377. W. Kiełczewski and J. Thiel, Chem. Analit., **10**, 271 (1965).
378. W. Kiełczewski and M. Schneider, Chem. Analit., **11**, 111 (1966).
379. W. Kiełczewski, M. Schneider, and J. Tomkowiak, Chem. Analit., **11**, 343 (1966).
380. K. Koev, Mikrochim. Acta, 1028 (1965).
381. K. Koev, T. Mihova, and A. Nedelcheva, 1033 (1965).
382. A. Lewandowski and A. Dorożalska, Chem. Analit., **10**, 1261 (1965).
383. H. Nagai, Nippon Kagaku Zasshi, **78**, 1334 (1957); Chem. Abs., **52**, 13 527 (1958).
384. H. Nagai, Kumamoto J. Sci. Ser., **A3**, 181 (1957); Chem. Abs., **53**, 17 750 (1959).
385. H. Nagai and T. Deguchi, Nippon Kagaku Zasshi, **86**, 516 (1965); Ref. Zhur. Khim., 14G44 (1966).
386. H. Nagai, Bunseki Kagaku, **15**, 50 (1966); Ref. Zhur. Khim., 16G51 (1966).
387. H. O. Phillips, and K. A. Kraus, J. Amer. Chem. Soc., **85**, 486 (1963).
388. J. G. Sabo, Chem. Analyst, **54**, 110 (1965).
389. Ts. Todorova and T. Zhecheva, Zavod. Lab., **32**, 417 (1966).
390. Ya. Todorova, Izv. Vys. Inst. Narodno Stopanstvo, Varna, 117 (1966).
391. H. Ven Horst, M. F. Rogers, and H. T. Singh, Analyt. Chem., **37**, 1279 (1965).

Timiryazev Moscow Agricultural Academy

U. D. C. 541.182.1

Structure Formation in Disperse Systems in an Electric Field

L.G.Gindin and A.E.Vol'pyan

The application of an electric field to disperse systems usually results in the aggregation of the particles of the dispersed phase and their organisation into characteristic structures oriented along the lines of force. Processes of this kind are observed both in finely dispersed colloidal systems and in coarsely dispersed systems–emulsions, suspensions, powders. Despite the extremely varied phenomenological picture of the structure-formation processes, which in many respects is due to the nature of disperse systems, the mechanisms and dynamics of their development also have much in common. Analysis of the fundamental mechanism and the kinetics of these processes constitute the theoretical aspect of the problem of structure formation in disperse systems in an electric field.

Apart from the purely theoretical interest, the problem does not lack practical importance. It is sufficient to say that structure-formation processes underlie phenomena such as, for example, the breakdown of liquid dielectrics and the dehydration of petroleum in an electric field.

In this review an attempt is made to give a brief outline of the historical development of the problem, to characterise its present state, and to suggest the possible ways in which it may develop further. As far as we are aware, the structure-forming effect of an electric field on disperse systems was first described by Rafinesque[1] and Hohlfeld[2], who observed the formation on the surface of a charged object of thread-like structures made up of smoke particles.

The investigations of Munk af Rosenschöld[3,4], who must be regarded as the original discoverer of the coherer and who anticipated Branly by half a century, were carried out in the 1830's. In his experiments a tube filled with wood charcoal powder in an electric circuit completed the circuit under the influence of electric discharges occurring in its vicinity; when the tube was shaken, the circuit was reopened. In the 1880's studies on the electrical conductivity of metallic powders were renewed and led to the discovery of coherers or fritter-detectors of electromagnetic