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Advances in the Thin-layer Chromatography of Inorganic Ions

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The review deals with studies published during 1960-1967 and partly in 1968 on the applications of thin-layer chromatography. Much attention has been devoted to the description of specific procedures which improve the efficiency of the method. Possible applications of the method in inorganic and analytical chemistry have been noted. The bibliography comprises 228 references.

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I. INTRODUCTION

Thin-layer chromatography (TLC) on plates, which has been fairly widely used in organic chemistry, has found increasing application in inorganic chemistry starting in the 1960's. This is demonstrated by the increase in the number of publications. Thus one paper dealing with the application of thin-layer chromatography in inorganic chemistry was published in 1960, four papers were published in 1962, about twenty papers in 1965, thirty papers in 1966, and more than sixty papers in 1967.

The scope of thin-layer chromatography and in many cases some of its advantages over other methods for the separation and concentration of microamounts of substances are responsible for its vigorous development together with other effective methods such as extraction, column chromatography, etc. The method may be used to separate and identify from several tens of microgrammes to tenths and sometimes hundredths of a microgramme of complex mixtures.

The universality and simplicity of the method and the clear-cut separation after a short period of analysis make thin-layer chromatography (in combination with sensitive analytical methods) suitable for the solution of many problems involving the determination of microgramme amounts of elements.

Although in the last three years many publications on inorganic thin-layer chromatography have appeared, adequate reviews are not available. The wide scatter of the publications is a considerable inconvenience to readers. A number of monographs[1-7], apart from describing the principle of the method and the experimental technique, discuss mainly the applications of thin-layer chromatography in organic analysis. These publications deal very briefly and by no means exhaustively with data on inorganic thin-layer chromatography and the specific thin-layer chromatographic procedures for inorganic ions are not indicated. There are a number of reviews on inorganic thin-layer chromatography[8-16] but they are not sufficiently comprehensive.

We hope that our attempt to give as far as possible a complete review of studies on inorganic thin-layer chromatography between 1960 and 1967 inclusive (partly in 1968) and to deal with the principal trends, possibilities, and applications of the method for the analysis of inorganic ions will prove useful to readers, particularly now when the interest in this method by chemists increases steadily, as shown by the widening of the range of its applications and the increase in the number of relevant publications from year to year.

In the present review we shall only describe briefly the principle of the method and the experimental technique, because these problems have been thoroughly dealt with in the books and reviews mentioned above. In each section we shall note the characteristic procedures which enhance the effectiveness of inorganic thin-layer chromatography.

The experimental technique is as follows. Small amounts of the test solutions (of the order of 1–5 μl) are placed at the starting point on a thin layer of sorbent covering a plate. The plate is dried and the edge below the starting line is immersed in a mobile solvent contained in a hermetically sealed chamber. As the solvent moves along the layer of sorbent, the ions of the elements are separated in accordance with the partition coefficients under the given conditions. The position of the solvent front line is noted and after the plate has been dried the zones containing the elements are detected by spraying with solutions of appropriate reagents which give rise to colour or luminescent reactions with the elements to be detected. When radioactive elements are separated, radiometry and radioautography are employed.

The quantitative characteristic of the position of the substance in a chromatogram is its R_f value (the ratio of the distance between the starting line and the centre of the spot to the distance between the starting line and the solvent front line). The R_f value is characteristic of a given compound on a given sorbent in a given system, and depends on a number of conditions: experimental method, purity and moisture content of the sorbent, thickness of the layer, purity of the solvent, amount of substance deposited, duration of separation, etc, (see Ref. 6, p. 7). Therefore in order to obtain reproducible R_f values, it is necessary to perform experiments under rigorously standardised conditions. The standard conditions recommended by Stahl for thin-layer chromatography[17] are quoted below: (1) plate dimensions 200 × 200 mm and 200 × 100 mm; (2) thickness of dry layer 0.1–0.3 mm; (3) plates stored in a closed vessel over silica gel; (4) distance from the starting line to the lower edge of the plate 15 mm and to the side edge 10 mm; (5) distance traversed by the solvent (distance between the starting line and the solvent front line) 100 mm; (6) chamber saturated with solvent vapour (chamber closed by a ground lid and walls lined with strips of filter paper wetted with the mobile phase; (7) plate immersed in the solvent to a

depth of 0.5 cm; (8) elution temperature 18–25°C; relative humidity of air 40–65%; (9) standard sorbents; (10) careful purification of the solvents; (11) size of sample of 0.1–1% solution 1–5 μl.

Since not all these conditions are observed in practice, the R_f values quoted in the literature may differ and the R_f values quoted in the Tables below must be regarded only as a comparative characteristic of the separation of ions of the elements.

II. QUALITATIVE INORGANIC THIN-LAYER CHROMATOGRAPHY

1. SEPARATION OF CATIONS

Alkali and Alkaline Earth Elements

A number of studies have been made on the separation of these elements[18–28]. Solutions of the acetates[5,18], sulphates[18], nitrates, chlorides[20–22,24–26], and polyiodides[27] of alkali and alkaline earth elements are deposited on the sorbent layer. The time taken by the solvent front to rise to a height of 10 cm varies from 10 to 120 min, depending on the composition of the mobile phase. Initially various investigators employed silica gel without added gypsum. Mixtures of methanol, ethanol, and propanol with acetic acid and also with addition of acetylacetone and other complex-forming substances have been used as a mobile phase[18–21]. However, under these conditions a clear separation was not achieved.

Best results are obtained on cellulose[22,23] and corn starch[26]. The R_f values for cations in the chromatography of individual specimens and their mixtures are usually the same. These methods make it possible to separate and detect 1×10^{-6}–5×10^{-9} equiv. of each of the test cations, i.e. smaller amounts than in paper chromatography. On cellulose, it is possible to separate any alkaline earth element from mixtures with others when its relative content in the mixture is as low as 1 : 500. Magnesium may be separated[23] not only from large amounts of beryllium, calcium, strontium, and barium but also from iron, titanium, cobalt, nickel, zinc, zirconium, cadmium, antimony, and bismuth.

It has been noted that the method involving the use of heteropolyacids as sorbents[20] is unsuitable for the rapid separation of alkali metals. However, on oxinegermanododecamolybdate, using 0.01 M NH_4NO_3, it proves possible to separate caesium from other alkali metals and also from yttrium, ruthenium, zirconium, niobium, and strontium.

A mixture of cellulose with zinc hexacyanoferrate(II), which is selective in relation to alkali metal ions[24], has been used for the rapid (16 min) separation of sodium, potassium, rubidium, and caesium. Rapid separation of these elements is achieved when 0.2 M ammonium nitrate is used as a mobile solvent.

Alkali metals are also satisfactorily separated on other inorganic ion exchangers, for example, on thin layers of crystalline zirconium and titanium phosphates. The latter is the best sorbent for the separation of alkali metals, particularly sodium and potassium[25].

In the separation of elements of this group considerable difficulties arise in connection with the detection of the alkali metals on the chromatogram. It is very difficult to choose a sensitive reagent giving a colour or luminescent reaction under these conditions. Sometimes solutions of violuric acid are employed[18,21] but this does not always yield good results. Therefore alkali metals are frequently identified radioautographically[20,24,25]. Alkaline earth metals are detected by illumination with ultraviolet light after spraying the plate with a solution of 8-hydroxyquinoline[22,26].

Transition Elements

The majority of studies[19,26,28–56], on inorganic thin-layer chromatography have dealt with the separation of mixtures of transition elements in different combinations. The sorbents most frequently employed are silica gel[19,29–33,36–40,42,43,48,49,52,53] and cellulose[34,46,50,54], and also alumina[37,45,51], starch[26,35,41], etc. Mixtures of compounds of the elements separated are deposited on the plate in the form of solutions of the chlorides or nitrates[31,33–37,40,41,43,52,54], sulphates[38], and sometimes various complexes[29,30,37,46,49,53]. The mobile phases employed to separate transition elements are extremely varied. In many cases acetone[19,26,35,39,41,42,46,48,51,52], various alcohols (ethanol, methanol, butanol, and others)[30,34,36,39,42,44,45,53], inorganic acids[31,32,36,50,54], organic acids[28,30], etc., are used as one of the components. The duration of chromatography ranges from 10–30 to 120–180 min. The choice of the reagent for detection is determined by the composition of the mixture to be separated. Rubeanic acid is used to identify copper, cobalt, nickel, and platinum[30,38,51], 8-hydroxyquinoline is used to determine zinc, cadmium, iron, mercury, chromium, and aluminium[33,34,35,39,40], ammonium sulphide is used for cadmium, iron, bismuth, copper, lead, mercury, and silver[26,36,41], dithizon is used for lead, silver, and mercury[40], and stannous chloride is used for rhenium, noble metals[45,51,52], and others. Elements separated in the form of chelate complexes are detected on the chromatogram by their intrinsic colour[29,37,41,49]. The separation of various combinations of transition elements has been described: iron, nickel, cobalt, copper, manganese, chromium, silver, zinc, cadmium, aluminium, and mercury[19,26,27–42]; titanium, zirconium, thorium, scandium, UO_2^{2+}, and niobium[43]; vanadium, molybdenum, tungsten, and rhenium[44,45,54]; niobium and tantalum[47]; noble metals[48–53].

Certain characteristic features and procedures in the thin-layer chromatographic method used to separate this group of elements may be indicated. For example, in order to improve the separation of 1-nitroso-2-naphthoxides of iron, nickel, cobalt, and copper, repeated chromatography has been employed with the aid of two solvent systems[29]; iron(III) and cobalt are separated in a solvent containing pentyl alcohol and, when the plate is placed in a system containing dioxan, copper, iron(II), and nickel are separated.

Two-dimensional chromatography has been used successfully[35] to separate iron, aluminium, and chromium and zinc, cobalt, manganese, and nickel.

The method of circular chromatography on a thin layer of sorbent usually gives a clearer separation than on paper. The zones of different elements consist of sharply outlined concentric rings. Thus noble metals are very readily separated on a layer of alumina[51]. Hashmi and Adil[51] succeeded in obtaining by this method about fifteen chromatograms on a 10 × 20 cm plate, the formation of each taking about 2 min. Mercury, copper, cadmium, nickel, and zinc have been separated by circular chromatography on a thin layer of silica gel impregnated with dithizon[42]. The solutions analysed are deposited at

the centre of the plate and the mobile solvent (mixture of acetic acid and acetone) is supplied from a dropping funnel at the point of deposition. The dithizonates of these cations form coloured rings in the chromatograms.

A number of transition metals have been separated by thin-layer chromatography of their complexes with dithizon (silver, gold, palladium, and yttrium)[49], 1-nitroso-2-naphthol (cobalt, nickel, manganese, and iron)[37], thiocyanate complexes (zinc, copper, cadmium, cobalt, and nickel)[30], and others.

An interesting procedure involving precipitation thin-layer chromatography has been used[33] to separate copper, iron, and cobalt on a layer of silica gel 0.2 mm thick containing 14% of 8-hydroxyquinoline as the reagent precipitating the metals. The zones of the different elements consist of discrete bands, the content of a particular element being estimated approximately from the width of the band.

Recently thin-layer chromatography on ion exchangers has been increasingly employed, liquid anion exchangers (high-molecular-weight amines and salts of quaternary ammonium bases)[31,54], with which silica gel or cellulose are impregnated, being used particularly extensively. It is best when the carrier is inert with respect to the impregnating phase. Aqueous acid solutions are usually employed as eluents. It has been shown that, by varying the concentration of the acid in the eluent and the type of ion exchanger, it is possible to achieve satisfactory separation of a wide variety of mixtures of inorganic ions. Apart from liquid anion exchangers, anion exchangers such as Amberlite CG-400[28], Dowex-1, and DEAE-cellulose[46,55] and the cation exchangers Amberlite CG-120[28] and Dowex-50[55,56] are used in thin-layer chromatography.

In thin-layer chromatography with phase reversal, which is employed fairly frequently—in particular also for the separation of transition metals, the carrier is usually silica gel. The stationary phase is most often tributyl phosphate (TBP) (solutions in ethyl ether[32], benzene[43], and carbon tetrachloride[50]). Nickel–copper–silver–zinc–iron, cobalt–copper–silver–zinc–iron (mobile phases—aqueous acid solutions)[32], niobium–tantalum (mobile phase—solution of ammonium thiocyanate in a mixture of oxalic and 6 *N* hydrochloric acids)[47], rhodium–ruthenium–palladium–gold (mobile phase—2 *N* hydrochloric acid)[47], etc. mixtures have been separated on such sorbent layers. Solutions of di-(2-ethylhexyl)phosphoric acid (D2EHPA) and tri-iso-octylamine (TIOA)[33] are also employed as stationary phases, which in this case function also as cation- and anion-exchangers respectively. Erbium–holmium–terbium–gadolinium, europium–lanthanum, yttrium–strontium (D2EHPA), and zinc–cobalt–manganese (TIOA) mixtures have been separated on resins impregnated with these reagents.

Non-transition Elements

Certain non-transition elements (bismuth, antimony, cadmium, arsenic, tin, selenium, tellurium, and thallium) have been separated from one another and from transition elements in a number of investigations[28,34,36,57-63], where sometimes the same procedures were employed as in the separation of transition elements, for example separation of the complexes[58], thin-layer chromatography on the ion-exchange resins Amberlite CG-400 and CG-120[28], etc.

The sorbents used to prepare the thin layers were of a wide variety of types: silica gel[59,61,63], kieselguhr[57], cellulose[34-58], starch[60], and ion-exchangers[28]. The mobile solvents in partition thin-layer chromatography frequently include alcohols (ethanol, propanol, and butanol) or ketones [acetone, hexone (4-methyl-2-pentanone—Ed. of Translation), ethyl methyl ketone, and others] and various acids (hydrochloric, nitric, acetic, and tartaric). Selenium and tellurium are separated with a solution of TBP in benzene. Solutions of ammonium fluoride (for arsenic, iron, and bismuth)[28] or sodium chloride (for arsenic, cadmium, and barium)[28] are used as eluents in ion-exchange processes on resins. The duration of the chromatographic process is as usual 10–180 min.

Colour reactions of the elements with dithizon[57,60] and ammonium sulphide[36,57] are used for identification. Arsenic, antimony, and tin separated in the form of dithizonates are identified by their intrinsic colour[58].

The groups of elements for which methods of separation have been developed are listed below: bismuth, antimony, cadmium, arsenic, lead, mercury, and thallium[57]; arsenic, antimony, and tin[34,58-60]; arsenic, iron, and bismuth[28]; arsenic, cadmium, and barium[28]; selenium and tellurium[61-63]; bismuth from lead, cadmium, copper, and nickel and lead from cadmium, nickel, and copper[66].

Lanthanides

The separation of lanthanides which have similar properties is one of the most complex problems in analytical chemistry. Difficulties increase when it is necessary to separate ultrasmall amounts of the elements. In this case it is helpful to employ together with paper chromatography also thin-layer chromatography, which permits the separation and identification of submicrogramme amounts of lanthanide mixtures. A number of papers have been published on the methods for the separation of lanthanides[64-69]. Various two- and multi-component mixtures of lanthanides can be separated by thin-layer chromatography. The chromatographic separation process terminates after 10–180 min. The zones containing the separated elements can be successfully located with Arsenazo III[69] and 8-hydroxyquinoline[64,66] and also radiometrically[64,65,68].

Di-(2-ethylhexyl)phosphoric acid (D2EHPA) is widely used for the separation of lanthanides. The high separation factor for lanthanides achieved when they are extracted by D2EHPA led to studies on partition chromatography involving the application of this acid either as a mobile solvent or as the stationary phase on various carriers: silica gel D for thin-layer chromatography[66], a copolymer of poly(vinyl chloride) and poly(vinyl acetate)[64], and others. In experiments by the phase reversal method the sorbent layer is impregnated with D2EHPA dissolved in a mixture of carbon tetrachloride and ethyl ether[64] or in butanol[65]. It cannot be dissolved in toluene, since the sorbent layer impregnated with such a solution cracks.

The technique of horizontal thin-layer chromatography can also be employed at 60–80°C.[64] The mobile phase in the phase reversal method is usually hydrochloric or nitric acid solution at different concentrations. Elements with a high atomic number migrate more slowly than those with a low atomic number at any constant acidity. With increasing acidity of the eluent, the rate of migration of the lanthanides down the plate increases also. The ion-exchange mechanism of the interaction between lanthanides and the sorbent has been noted[67].

Elution with nitric acid leads to better results in some cases, more clearly outlined spots being obtained, which

is probably due to rapid equilibration in the system nitric acid–D2EHPA. It is suggested that the introduction of complex-forming substances into the mobile phase should also improve the separation of difficult mixtures.

To improve the separation of lanthanides, the repeated elution procedure employed; it improves, in particular, the separation of cerium and praseodymium [66]. The separation of lanthanides is best carried out on as thin a sorbent layer as possible, with a high content of D2EHPA [67]. Three-component and four-component mixtures of elements can be separated by this method (for example: lanthanum–praseodymium–samarium; terbium–gadolinium–erbium [64]; lanthanum–cerium–praseodymium–samarium; lanthanum–cerium–neodymium–samarium; praseodymium–samarium–gadolinium; neodymium–samarium–gadolinium; samarium–europium–gadolinium; gadolinium–terbium–dysprosium; terbium–dysprosium–holmium–erbium; terbium–dysprosium–holmium–yttrium; holmium–erbium–ytterbium; holmium–yttrium–ytterbium [66]; and others).

The separation of mixtures of a large number of lanthanides may be achieved by increasing the sorbent layer capacity, by altering the thickness of the sorbent layer, and by using two-dimensional chromatography (in two mutually perpendicular directions). Thus by one-dimensional chromatography with a thickened sorbent layer (500 μm against 250 μm usually employed) with 12 ml of D2EHPA + 34 ml of n-butyl alcohol applied to 30 g of silica gel, it is possible to separate up to 5 elements of the cerium and yttrium groups: lanthanum–cerium–praseodymium–samarium–europium (mobile solvent—0.5 *N* hydrochloric acid); terbium–dysprosium–holmium–erbium–ytterbium (4 *N* nitric acid) [66]. In two-dimensional chromatography with the same eluents and with deposition of mixtures of substances at two points on the left-hand and right-hand edges of the plate, it is also possible to separate five elements of the yttrium group (7 μg of an ytterbium–erbium–holmium–dysprosium–terbium mixture at each spot) and four elements of the cerium group (35 μg of a lanthanum–cerium–neodymium–samarium mixture at each spot [67]).

D2EHPA can also be used as a mobile phase [65,68]. One then uses silica gel, without the addition of gypsum, impregnated with buffer solutions or acids (perchloric acid gives more reproducible results than hydrochloric acid). The mobile phase, a solution of D2EHPA in carbon tetrachloride, is first equilibrated with the stationary phase. Since D2EHPA is itself very strongly adsorbed on silica gel, two solvent fronts are formed, the first being due to the migration of carbon tetrachloride along the plate. When dilute solutions of D2EHPA are employed, the second front lags appreciably behind the first. Therefore 1 M D2EHPA solutions are employed in order to avoid this phenomenon.

It was found that, when the mixtures of substances to be analysed by the phase reversal method are deposited on the plate in the form of aqueous solutions, the pH of the stationary phase alters and 5–10% of the lanthanide (detected with the aid of radioactive isotopes) remains at the site of deposition in the chromatographic experiments. Therefore it is best to employ solutions of mixtures in organic solvents. This procedure yields spots which are usually symmetrical. "Tails" and jagged spots are rarely encountered. The spots which migrate with the solvent front are very narrow which permits the separation of up to five components (cerium–samarium–europium–gadolinium–terbium and promethium–samarium–europium–gadolinium–terbium) when, for example, 0.15 M perchloric acid is used as the stationary phase and 1 M D2EHPA in carbon tetrachloride as the mobile phase. Lanthanum and cerium are separated with 0.01 M perchloric acid as the stationary phase and heavy lanthanides (lutetium–ytterbium–thulium) are separated using 1.75 M perchloric acid and 0.5 M D2EHPA [68]. In the separation of lanthanides and in the removal of impurity elements from them solutions of DBP in benzene (1 : 1 and 1 : 10) [69] have been employed as the mobile phase in addition to D2EHPA; under certain conditions, it proved possible to separate with their aid cerium(IV)–thorium–UO_2^{2+}, neodymium–UO_2^{2+}, neodymium–praseodymium, cerium(III)–cerium(IV), europium(II)–europium(III), and other mixtures which are normally difficult to separate.

Non-lanthanide impurities (iron, copper, nickel, calcium, mercury, and zinc) in amounts between 10^{-1} and 10^{-2}% have been detected in mixtures of lanthanides [69] using acetone as the mobile solvent.

Actinides

It is of particularly great interest to employ the fast and highly sensitive thin-layer chromatographic method for the analysis of tracer amounts of radioactive elements, particularly short-lived isotopes. However, the number of studies in this field is still very limited [43,70–74].

The combination of thin-layer chromatography for the separation of elements with subsequent radioautographic recording of the spots on photographic (or X-ray) film has proved very successful in the detection of submicroamounts of radioactive elements. At the same time it is possible to employ colour or luminescent reagents [71–74]. The rapidity and simplicity of analysis by this method, the clear-cut separation, and the clarity of the results are the advantages of this procedure compared with other micromethods. Silica gel is usually employed as a carrier for the stationary phases.

In experiments with uranium ores and in the treatment of irradiated nuclear fuel selective separation of uranium from as large a number of other ions as possible is of great importance. It is therefore not fortuitous that several thin-layer chromatographic studies concerning this problem have been made [43,70–72], since the method is very rapid and economical. It has proved possible [72] to separate uranium on a sorbent layer consisting of silica gel and cellulose and fixed with starch from 55 cations (including the most important cations—uranium decomposition products). The mobile solvent was a mixture of hexone [4-methyl-2-pentanone (Ed. of Translation)], and TBP saturated with 4.7 *N* nitric acid. Separation from thallium proved to be impossible under these conditions.

Selective separation of uranium(VI) from a mixture with iron, nickel, cobalt, and zinc in sulphuric acid solution has been achieved using tri-iso-octylamine. This liquid amine has been particularly effective in experiments by the phase reversal method designed to separate uranium from molybdenum, cobalt, nickel, zirconium, thorium, and other elements [71]. In connection with the development of studies on the synthesis of new transplutonium elements, the problem of the separation of microamounts of the transplutonium elements from the main bulk of uranium or plutonium and also from the fission products is of undoubted interest. The possibility of the separation of microgramme amounts of uranium and plutonium from tracer amounts of americium and curium by thin-layer chromatography on silica gel using a mixture of TBP and benzene as the mobile solvent has been demonstrated [73].

The extraction of plutonium and its separation from uranium and other elements present at the same time by the thin-layer chromatographic method proposed by Volynets and Milyukova[74] can be usefully carried out in studies on solutions of complex composition with high β- and γ-activity when it is desirable to work with minimal volumes for reasons of safety. In the system 3 M nitric acid–23% solution of TBP in Synthin it is possible to separate quantitatively by this method plutonium(IV) and plutonium(VI) from plutonium(III). By combining the partition of plutonium(IV) in the systems 3 M nitric acid–23% TBP solution in Synthin and 1 M perchloric acid–23% TBP solution in Synthin with a single pass of the mobile phase, it is possible to separate quantitatively plutonium from uranium, lanthanides, zirconium, nickel, lead, copper, chromium, and iron and to determine radiochemically its amount in the spot with an error of ±10–15%. The duration of analysis of 0.03 ml of the initial solution is 60–90 min.

Heterovalent Forms

One of the interesting fields of application of the thin-layer chromatographic method is the separation of elements in various valence states. Studies have been made on the separation by this method of the heterovalent forms of mercury, arsenic, antimony, chromium, selenium, tellurium, iron, plutonium, cerium, and europium (Table 1). Usually the separation is very clear-cut. Silica gel fixed to the plate with starch or gypsum is most often employed as a sorbent.

Complete and Systematic Analysis of Cations

Some of the studies on inorganic thin-layer chromatography deal with the behaviour of large groups of cations and anions under particular conditions[78–86]. The chromatographic behaviour of many ions has been studies on thin cellulose or silica gel layers impregnated with both neutral organophosphorus compounds (TBP, tri-n-octylphosphine oxide, and others[81,83]) and liquid ion exchangers (amines, alginic acid, etc.), using solutions of hydrochloric, nitric, sulphuric, hydrobromic, hydriodic, thiocyanic, perchloric, and other acids[71,80,82,84,85].

The separation of a number of cations and anions having similar properties by thin-layer chromatography on organic and inorganic ion exchangers (Dowex-1 × 10, Dowex-50, Chelex 100, zirconium hydroxide, and others) has been described[87]. The effects of the composition of the eluents on the chromatographic behaviour of a large group of cations on cellulose have been investigated[86,88].

Methods for the separation of a wide variety of numerous combinations of elements have been suggested on the basis of such systematic studies and the determination of the differences in the behaviour of ions.

For qualitative semimicroanalysis, it has been suggested that 40 cations and 19 anions be detected by circular thin-layer chromatography with a duration of analysis, including the time required for the preparation of the solution to be analysed, of 2–3 h (duration of chromatographic process 2 min).

The principles governing the choice of sorbents and solvents for optimum chromatographic separation have been

Table 1. Heterovalent forms

Elements separated	Initial solution	Sorbent	Mobile solvent	Method of detection	R_f	Duration of separation, min	Refs.
Hg^{II} and Hg^{I} As^{V} and As^{III} Sb^{V} and Sb^{III}		silica gel + starch	butanol + benzene + 1 *N* HNO_3 + 1 *N* HCl (50:46:2.6:1.4)				19
Cr^{IV} and Cr^{III}	$^{51}CrCl_3$ $Na_2{}^{51}CrO_4$	Al_2O_3 + gypsum	Na_2SO_4 and Na_2CO_3 solution	radiometry	Cr^{III} (0.0); Cr^{VI} (0.60)	120	75
Te^{VI} and Te^{IV} Se^{VI} and Se^{IV} Cr^{VI} and Cr^{III}		silica gel	isobutyl methyl ketone, ethyl acetate; n-butyl acetate				63
As^{V} and As^{III}	solutions of As_2O_3 in NaOH and of $Na_2HAsO_4.7H_2O$ in water	silica gel + gypsum	acetone + 15 M H_3PO_4 (50:1)	$SnCl_2$ solution followed by 5% solution of $Na_2S_2O_3$	As^{III} (0.0); As^{V} (1.0)	20	76
Fe^{II} and Fe^{III}		ditto	acetone + 5 (or 10)% 1 *N* $HClO_4$	0.1% methanol solution of pyridyl-azonaphthol	Fe^{II}(~0.65 or ~0.75); Fe^{III}(~0.1 or ~0.3)		77
ditto	1-nitroso-2-naphthoxides in chloroform	silica gel D + Al_2O_3 D (1:1)	benzene	intrinsic colour	Fe^{II} (0.0); Fe^{III} (0.50)		37
Pu^{III} and Pu^{IV}; Pu^{VI}	solutions in 3 *N* HNO_3	silica gel + starch impregnated with 3 *N* HNO_3	TBP + synthin (23:77)	radioautography; radiometry; 0.1% solution of Arsenazo III	Pu^{III} (0.0) Pu^{IV} and Pu^{VI}—with solvent front	60–90	74
(1) Ce^{III} and Ce^{IV} solution of NH_4Cl added at point of deposition) (2) Eu^{II} and Eu^{III} ($MgSO_4$ solution added at point of deposition)	nitric acid solutions	silica gel + starch	(1) TBP + benzene (1:10) (2) water	0.1% aqueous solution of Arsenazo III; $NH_4OH + H_2O_2$ (4:1)		30–90	69

Table 2. Anions

Elements separated	Initial solution	Sorbent	Mobile solvent	Method of detection	R_f	Duration of separation, min	Refs
F^-, Cl^-, Br^-, I^-	1 M solutions of NaF, NaCl, KBr, and KI	silica gel + gypsum	acetone + butanol + conc. NH_4OH + H_2O (65:20:10:5	1% ethanol solution of Bromocresol Red; 1% ammonium-alkali soln. of $AgNO_3$; 0.1% soln. of zirconium-alizarin lake in HCl	$Fe^->Cl^->Br^->I^-$	30—40	93
F^-, Cl^-, Br^-, I^-, CN^-, SCN^-, N_3^-, $Fe(CN)_6^{3-}$ $Fe(CN)_6^{4-}$	solutions of potassium and sodium salts of the anions	silica gel	(1) 1-butanol + 1-propanol + di-n-butyl amine (45:45:10); (2) 1-butanol + benzylamine (90:10); (3) 1-propanol + $CHCl_3$ + benzylamine (60:30:10)	with suitable reagents in visible and ultraviolet parts of spectrum	$I^->SCN^->Br^->Cl^->$ $>N_3^->Fe(CN)_6^{3-}>$ $>Fe(CH)_6^{4-}>CN^->$ $>F^-$	55—95	94
F^-, Cl^-, Br^-, I^-	0.5% aqueous salt solutions	MN-300 cellulose	acetone + water (4:1)	0.1% ethanol solution of dichlorofluorescene and $AgNO_3$; ultraviolet light	R_f values increase with atomic weight of anions and are almost independant of cations		95
ClO_4^-, ClO_3^-, ClO_2^-, BrO_3^-, IO_3^-	0.1 M solutions of sodium salts	Al_2O_3G + Kieselguhr G (1:1)	butanol + acetone + conc. NH_4OH + water (8:10:2:1)	solution of anilinium phthalate in butanol	$ClO_4^->ClO_3^->BrO_3^->$ $>ClO_2^->BrO_3^->IO_3^-$	40—50	96
F^-, Cl^-, Br^-, I^-, IO_3^-, BrO_3^-, ClO_3^-		silica gel + gypsum	acetone + ethyl methyl ketone + 14% NH_4OH (30:20:5)		$I^->Br^->Cl^->F^-$; $ClO_3^->BrO_3^->IO_3^-$		97
(1) I^-, Br^-, Cl^-,		(1) MN-300 cellulose + Dowex 1 × 10 in OH-form	(1) 1 M $NaNO_3$				87
(2) PO_4^{3-}, $P_3O_7^{4-}$;		(2) cellulose + Biorex-5 in Cl-form;	(2) 1 M $NaNO_3$				
(3) AsO_3^-, AsO_4^{3-};		(3) ditto	(3) 2 M NaCl				
(4) $HCOO^-$, CH_3COO^-, ClO_3^-, BrO_3^-, IO_3^-; CN^-, SCN^-, $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$		(4) " zirconium hydroxide	(4) 2 M NaCl and 3 M NaCl				
F^-, Cl^-, Br^-, I^-; ClO_4^-, ClO_3^-, BrO_3^-, IO_3^-	0.1 M solutions of alkali metal salts of anions	corn starch	acetone + 3 *N* NH_4OH (7:3)	2% solution of $AgNO_3$ (Cl^-, Br^-, I^-) and 1% solution of KI in 0.1 M HCl (ClO_3^-, BrO_3^-, IO_3^-) 1% ethanol solution of Bromocresol Red (F^-); 0.05% solution of Methylene Blue (ClO_4^-)	I^- (0.78); Br^- (0.60); Cl^- (0.40); F^- (0.04); ClO_4^- (0.82); ClO_4^- (0.97); ClO_4^- (0.82); BrO_3^- (0.53); IO_3^- (0.06)	90	98
PO_4^{3-}, $P_2O_7^{4-}$, PO_3^-, PO_2^{3-}	0.1 M solutions of sodium salts	silica gel + starch	methanol + conc. NH_4OH + 10% trichloroacetic acid + water (50:15:5:30)	1% solution of $(NH_4)_2MoO_4$ and 1% solution of $SnCl_2$ in 10% HCl	$PO_2^{3-}>PO_3^{3-}>PO_4^{3-}>$ $>P_2O_7^{4-}$	50—60	99
Phosphates	1-2% solutions of phosphates	cellulose + collodion	solutions based on dioxan	solution of Na_2MoO_4 followed by reducing solution		75	100
ditto	1-2% solutions of sodium triphosphates	cellulose + collodion	methanol + dioxan	solutions of $(NH_4)_2MoO_4$ and others		75	101
Polyphosphates	0.1 M solutions of Na_3PO_4, $Na_4P_2O_7$, and $Na_5P_3O_{10}$	silica gel	methanol + NH_4OH + CCl_3COOH + H_2O (15:15:5:65)	1% solution of $(NH_4)_2MoO_4$, 1% solution of $SnCl_2$ in 10% HCl			102
ditto		cellulose	methanol (isopropyl alcohol) or dioxan + 10% aqueous solution of CCl_3COOH + 98% CH_3COOH or 25% NH_3 solution and water				103
Sulphates and polythionates	1% solutions of potassium and sodium salts of corresponding acids	silica gel + starch	methanol + 1-propanol + conc. NH_4OH + water (50:50:5:10); methanol + dioxan + conc. NH_4OH + water (30:60:10:10)	0.1 M ammoniacal solution of $AgNO_3$ and 0.1 % solution of Bromocresol Green in dil. ammonia	$S_5O_6^{2-}>S_4O_6^{2-}>S_3O_6^{2-}>$ $>S_2O_6^{2-}>S_2O_3^{2-}$; $S_2O_8^{2-}>SO_3^{2-}>$ $>S_2O_3^{2-}>SO_4^{2-}$	45	104
NO_3^-, $S_2O_3^{2-}$, CrO_4^{2-}, N_3^-, CN^-, SCN^-, BO_3^{3-}, S^{2-}, AsO_2^-, AsO_4^{3-}, NO_2^-, SO_4^{2-}, PO_4^{3-}	1 M solutions of sodium and potassium salts of anions; boric acid	corn starch	acetone + 3 M NH_4OH (1:4)	1% solution of KJ in 0.1 *N* HCl (NO_2^-, $S_2O_3^{2-}$, CrO_4^{2-}); $FeCl_3$ solution (N_3^-, CN^-, SCN^-) 0.1% solution of Congo Red (BO_3^{3-}); 0.2 *N* solution of $AgNO_3$ (S^{2-}, CrO_4^{2-}, AsO_3^{3-}, AsO_4^{3-}), etc.	$SCN^->NO_3^->NO_2^->$ $>N_3^->S_2O_3^{2-}>S^{2-}>$ $>SO_4^{2-}$; $CrO_4^{2-}>BO_3^{3-}>$ $>AsO_4^{3-}>PO_4^{3-}>$ $>AsO_2^->CN^-$	90	105

described[89]. The most compact and in practice most convenient graphical presentation of the results has been adopted, for example, in Refs. 82, 83, and 90.

The present author believes that the value of such systematic studies consists in the fact that, on the basis of known R_f data, it is possible to choose rapidly the conditions for the separation of many mixtures of elements in the solution of specific problems. Thus Brinkmann et al.[82] demonstrated in a series of qualitative separations the suitability of the recorded R_f values for analysis by thin-layer chromatography in hydrochloric acid solutions on liquid anion exchangers (nickel–cobalt–manganese–zinc, nickel–cobalt–copper–manganese–iron, aluminium–indium–gallium, aluminium–titanium–uranium–iron, aluminium–uranium–iron–zirconium, copper–cadmium–lead–bismuth–mercury, lead–bismuth–tin–cadmium, zinc–cadmium–lead, arsenic–antimony–tin, arsenic–antimony–bismuth, and many two-component mixtures have been separated). Naturally, the separation should be carried out under standard conditions.

2. SEPARATION OF ANIONS

After the thin-layer chromatographic layer had been successfully applied in inorganic analysis for the separation of cations, studies began on its employment for the separation of anions. The thin-layer chromatography of a number of inorganic anions has been investigated[91,92]. Halides and pseudohalides, halogen oxy-acids, phosphates, sulphates, polythionates, and others have been separated by this method (Table 2).

Cellulose, starch, and silica gel are usually employed as sorbents. Ion-exchange resins have also been used to separate chlorine-36, bromine-82, and iodine-131.[55]

In the separation of anions the mobile solvents should be more polar than in the separation of cations because anions are less solvated and have a lower capacity for the formation of solvate systems with solvents other than water[93,94]. Usually systems containing methanol, acetone, water, and ammonium hydroxide are employed in the separation. Only iodides show a tendency to migrate also in non-polar solvents.

Among special procedures used to separate anions, mention should be made of precipitation chromatography for the separation of I^-, Br^-, Cl^-, and PO_4^{3-} on silica gel powder impregnated with silver nitrate as the precipitant[107] and two-dimensional chromatography of mono-, di-, and tri-phosphoric acids on a thin layer of cellulose[108]. The following mixtures of radioactive anions have been successfully separated: Cl^-, SO_4^{2-}, and PO_4^{3-};[109] Cl^-, ClO_2^-, ClO_3^-, and ClO_4^-;[106] I^-, IO_3^-, and TeO_3^{2-}.[110]

In the study of halides it was established that the R_f values increase with the atomic weight of the anion and are almost independent of the cation. The separation of halides from cations on cellulose is due to a cation-exchange process. In thin-layer chromatography on cellulose (in contrast to paper chromatography) there is a possibility of complete separation of cations from anions due to the larger area of contact and the larger number of exchange steps per unit length.

Phosphates cannot be separated on a sorbent layer fixed with gypsum since insoluble calcium phosphate is formed. Usually in such cases the sorbent is fixed with starch. Whereas on paper the separation of condensed phosphates with $n = 1-8$ and $n > 8$ is possible over a period of 16 h, thin-layer chromatography takes 1 h.

The possibility of separating and detecting microamounts of twenty inorganic anions has been investigated[92].

3. THIN-LAYER CHROMATOGRAPHY OF COMPLEX COMPOUNDS

As already mentioned earlier, certain elements have been separated in the form of complexes[111]. Thus, when suitable mobile solvent systems were selected, it proved possible to separate the dithizonates of arsenic, antimony, and tin[58], cadmium, copper, cobalt, mercury, manganese, nickel, zinc, lead, and bismuth[112,113], silver, gold, palladium, and platinum[49], 1-nitroso-2-naphthoxides of cobalt, nickel, manganese, and iron[29,37], diethyldithiocarbamates of chromium, manganese, iron, cobalt, copper, zinc, silver, cadmium, mercury, lead, calcium, magnesium, bismuth, tin, and antimony[114,115], cyanide complexes of iron[116,117], certain Complexonates, in particular those of cobalt, rhodium, and platinum[53], cobalt(II) and cobalt(III), manganese(II) and manganese(III)[116,117], acetylacetonates of iron, cobalt, and chromium[116,117], and other complexes. The square planar complexes of platinum(II) and palladium(II) have been separated by thin-layer chromatography[118].

The use of the thin-layer chromatographic method for the fine separation of geometrically isomeric complexes, namely the *cis- trans*-isomeric complexes of cobalt[119,120] and platinum[121], is of great interest. The purity of the preparations may be determined and the hydration and hydrolysis of these complexes may be investigated by thin-layer chromatography. The stoichiometric composition of palladium(II) complexes with certain phosphorus-containing organic compounds has been studied[122]. The composition of the palladium(II) phosphorodithioate complex has been determined as 1 : 1 by thin-layer chromatographic versions of the isomolar series and molar ratio methods.

The examples quoted above evidently do not exhaust the possibilities of thin-layer chromatography in studies on complexes, but the rate of development of studies in this field is still inadequate.

4. THIN-LAYER CHROMATOGRAPHY AND RADIOCHEMICAL METHODS

Since thin-layer chromatography permits the separation and identification of small amounts of substances, this micromethod constitutes a good auxiliary procedure in radiochemistry. With its aid, it is possible to separate also inactive substances labelled with radioactive isotopes. The recording in some way (radiometry, radioautography) of the emission by the components separated on the chromatogram constitutes an excellent, highly sensitive method for their detection.

The possibility of a rapid chromatographic process and of recording particle tracks in thick-layer emulsions makes the method attractive for the separation and detection of short-lived isotopes. The principle of the separation of inactive and active substances is the same. The studies on thin-layer chromatographic radiochemical analysis have been reviewed[123].

Thin-layer chromatography and the radiochemical method may be combined in two versions[124]: (1) radioactive substances are separated on a plate and then determined; (2) inactive substances separated on a plate are converted into active substances and then determined. In the latter case one may use in principle either the so

called method of radiochemical reagents or irradiation with neutrons. Both these methods are still relatively little employed because of technical difficulties. When the chromatogram is irradiated with neutrons, the impurities contained in the sorbent are also activated and interfere. The method of radiochemical reagents also imposes certain requirements: the sorbent must be inert and the excess reagent must be readily removed. Because of these requirements, the radiochemical reagent method has limited applicability. Mercury, copper, and cadmium separated on a plate have been determined by treatment with $H_2{}^{35}S$ prepared in a special apparatus from $ZN^{35}S$ and 2 *N* sulphuric acid[124].

The methods for the separation of radioactive substances are more numerous. They are all largely associated with the separation of mixtures of elements produced by radioactive breakdown. For example, thorium-234 (decomposition product) has been separated by thin-layer chromatography on silica gel in 25 minutes from small amounts of uranyl nitrate with the aid of a mixture of solvents consisting of ether, water, and TBP[109]. Chlorine-38, sulphur-35, and phosphorus-32, produced by irradiation of ammonium chloride with neutrons[109], can be successfully separated. The elements are detected in the chromatogram radiometrically and are identified by their half-lives.

In studies by thin-layer chromatographic and radiometric methods of the chemical behaviour of sodium pyrophosphate and sodium salts of chlorine acids (solid specimens and solutions) during neutron activation[106], higher phosphates were not detected among the reaction products and only $P_2O_7^{4-}$, PO_4^{3-}, and PO_3^{3-} were separated and identified. The presence of cations (copper, zinc, and magnesium) had a catalytic effect on the cleavage of pyrophosphate on irradiation and influenced the quantitative ratios of various forms. After irradiation of the solid salts and solutions of NaCl, $NaClO_2$, $NaClO_3$, and $NaClO_4$, the radioactivity of Cl^- ions was found to be maximum in all cases. The addition of Cu^{2+} ions increased the extent of formation of chloride.

Examples of the separation of microamounts of two- and multi-component mixtures of radioactive substances without a carrier, which are of interest for radiochemists (^{140}Ba–^{140}La, ^{133}Ba–^{133}Cs, ^{47}Ca–^{47}Sc, Sr–Y, ^{72}Zn–^{72}Ga, ^{95}Nb–^{182}Ta, ^{95}Zr–^{95}Nb, I^-–IO_3^-–TeO_3^{2-}, SO_4^{2-}–PO_4^{3-}, etc.) have been quoted[110]. The positions of the zones containing various elements were established automatically with the aid of a counter and a pen recorder.

In order to follow the separation of the test elements, radioactive isotopes may be introduced into the solution and their emission can be used to investigate by radiometric and radioautographic methods the distribution of the mixture components on chromatograms, as was done, for example in Refs. 69, 125, 126, and others.

For radioautographic detection of spots, use is usually made of an X-ray film, which remains in contact for a specified time with the chromatographic plate and is then developed in the usual way. A semiquantitative visual analysis and photometric quantitative measurements may be made on the basis of the intensity of the blackening of the spots under the influence of the radioactive emission.

5. ELECTROPHORESIS OF INORGANIC IONS

One of the promising trends in the development of the thin-layer chromatographic method is thin-layer electrophoresis. A description of the equipment for and technique of electrophoresis in a thin layer of carrier may be found, for example, in Refs. 127–131. Electrophoresis in a thin layer of carrier (both low- and high-voltage) differs little in experimental technique and apparatus employed from paper electrophoresis but does have a number of characteristic features: the layer of carrier on the plate may be impregnated with a larger amount of electrolyte than paper and because of this the electric field may be applied for longer periods (without risk of rapid drying of the layer), which in turn increases the effectiveness of the separation. The absence of a fibrous structure in the carrier eliminates diffusion-dependent spreading of the spots, so that the zones of the elements separated are more compact than in paper electrophoresis and the separation is more clear-cut. Owing to the greater capacity of the carrier layer compared with paper much greater amounts of the substances may, if necessary, be deposited for separation without the formation of diffuse spots. This is very important in the analysis of highly pure specimens where it is necessary to separate very small amounts of impurities. As a result, it is possible to achieve a much greater analytical sensitivity than in paper electrophoresis.

The possibility of varying the carrier is another advantage of inorganic thin-layer electrophoresis. Acetylcellulose[132] and cellulose[131], quartz sand[129], starch[133], heteropolyacid salts[134], kieselguhr[131], silica gel with starch[135,136] or with gypsum[137], a mixture of Teflon and cellulose[138], and photographic gelatine[139] have been used as carriers in this method.

Various mixtures of cations and anions can be satisfactorily separated by thin-layer electrophoresis (Table 3).

The separation of elements by electrophoresis is based on the difference in the stabilities of the complexes formed by the ions of the elements with a complex-forming agent (electrolyte) and in the case of alkali metals on the different degrees of association of the ions with the electrolyte anions[140].

The association constants of alkali[141] and alkaline earth[142] metal ions have been determined by the electromigration method from the mobilities.

Combination of thin-layer electrophoresis with thin-layer chromatography in two-dimensional separation has not been described in inorganic analysis but may prove to be useful.

III. QUANTITATIVE INORGANIC THIN-LAYER CHROMATOGRAPHY

The thin-layer chromatographic method for the separation and concentration of ultramicroamounts of substances is particularly important when combined in a rational manner with quantitative methods for the determination of the separated components. While inorganic thin-layer chromatography is widely used for a qualitative characterisation of chemical mixtures, the quantitative applications of this method have been described in a comparatively small number of publications and mainly in recent years. The method of quantitative microanalysis with the aid of thin-layer chromatography is employed in two versions: analysis after removal from the sorbent of the separated components and direct determination on the plate[143–145].

1. DETERMINATION OF SUBSTANCES AFTER ELUTION FROM THE ADSORBENT

In this case the substance to be determined is first removed from the adsorbent by elution with a suitable solvent from the zone on the plate where it was localised.

Table 3. Thin-layer electrophoresis

Elements separated	Carrier	Electrolyte	Potential gradient, V cm^{-1}	Duration, min	Method of detection	References
Rb and Cs	quartz sand	3.5 x 10^{-3} M solution (w.r.t.W) of ammonium paratungstate	19	18	radiometry	129
Ditto	ditto	0.34 M $K_4Fe(CN)_6$ + 0.052 M KNO_3	8.5	30	ditto	140
Li, Na, K, Rb, Cs	silica gel G	NH_4Cl + HCl buffer solution (pH 2.18) in 1:2 propylene glycol–water mixture	circular electric field with a potential of 400–500 V and a current of 40–45 mA		spraying with colour and luminescent reagents	137
Na, K, Rb, Cs	heteropoly acid salts	0.001–0.1 M NH_4NO_3	50	20	radioautography	134
Lanthanides	acetylcellulose (cellogel)	0.2–0.8 M solution of α-hydroxy-isobutyric acid	40–70	~30	radiometry, radioauto-graphy	132
	cellulose	1.1 M solution of α-hydroxy-isobutyric acid, pH 2.4	60 (cooling to −10°)	120	ditto	138
32 cations	ditto	0.1 M solution of α-hydroxy-isobutyric acid	50	20	spraying with 1% ethanol solution of 8-hydroxy-quinoline, NH_3 vapour, u.v.light	131
20 cations	silica gel + starch	0.15 M citric acid solution	1200 V/30 cm	20	spraying with suitable reagent	135
33 cations and 13 anions	kieselguhr	0.05 M solution of lactic acid (cations); 0.1 *N* NaOH (anions)	13–45	from 2 to 5	radiometry	130
IO_3^- and IO_4^-	Alabaster (Ignited gypsum)	0.05 M $(NH_4)_2CO_3$	300–400 V/30 cm	90–120	radiometry	128
20 anions	silica gel S-HR and starch	0.05 M Na_2CO_3	1000 V/30 cm	20	colour reactions	136

Usually the sorbent is scraped off along the outline of the spot and then transferred to the elution vessel. In the resulting solution the substance is determined by one of the sensitive (usually instrumental) methods, for example spectrophotometrically, polarographically, etc. Precautions must be taken to prevent losses in the transfer of the sorbent on the one hand and to ensure complete extraction on the other. The effect of impurities which are also eluted from the sorbent is screened off by using selective and specific methods for the determination of the relevant element.

This method is more time consuming than direct determination on the chromatogram, is more complex, and may involve certain losses of the substance but at the same time it allows determination of the isolated components by highly sensitive and accurate micromethods. To reduce the errors in this version of quantitative thin-layer chromatography, special devices are employed to elute the substances from the chromatographic zones[146–148].

Two methods have been described for the isolation of the components from the layer of adsorbent by additional elution[149]. In the first method after elution of the mixture in a vertical direction the adsorbent layer is dried, part of the adsorbent around the spots (visible in ultraviolet light) is removed, and a pentagon cut out from ashless filter paper is placed on the adsorbent near the spot. The plate with the adsorbent and the paper is covered by glass and with the aid of a paper bridge horizontal elution with a fast-acting eluent, which displaces the components from the adsorbent to the upper part of the paper pentagon, is carried out. The part of the paper containing the substance is cut off and the substance is extracted with a suitable solvent. In the second method the additional elution from the adsorbent layer containing the spots is carried out in an open chamber with a fast-acting eluent. The substance is concentrated in a small part of the layer which is then scraped off the plate. The substance is extracted from this part of the adsorbent by the usual methods.

The substances eluted from the adsorbent in one way or another are determined by different procedures. In some investigations[150–153] microgramme amounts of nickel, uranium, cobalt, and bismuth were determined spectrophotometrically with morpholine-N-dithiocarbonate after their separation from other elements of the $(NH_4)_2S$ or H_2S groups on cellulose powder. Condensed phosphates have been determined as phosphomolybdenum blue[101] after elution from a layer of cellulose powder.

In the analysis of the components of semiconductor alloys, gold was determined[154] (after separation of other elements) by oscillographic inversion polarography.

After removal from the plate of the section of sorbent containing the substance to be determined, the latter can be determined with fairly high accuracy without elution. For this purpose, thin-layer chromatography is combined with reflection spectroscopy. The separation is usually carried out on cellulose or silica gel layers. After the detection of the element with the aid of a suitable reagent, the layer with the spot is taken off the plate, ground carefully in an agate mortar to a homogenous mixture, and placed in the reflection cell of a spectrophotometer. Usually between 0.05 and 6–10 μg of the test substance is determined with a relative error of ±2–6%. For example, the following substances have been determined by this method: aluminium, bismuth, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, nickel, silver, tin, and zinc[155]; chromium[156]; iron, nickel and cobalt[157]; copper, nickel, and zinc[158].

Very high sensitivity was achieved in the determination of uranium in minerals using activation analysis[159]. Uranium separated quantitatively from impurities on a thin layer of silica gel was carefully transferred from the plate together with the sorbent into a polyethylene bag and was irradiated in a reactor with a neutron stream (1.7×10^{12} neutron $cm^{-2}s^{-1}$) for 30 min. The amount of uranium in the sample was determined from the activity of the neptunium-239 formed from the uranium. A calibration curve relating the area of the neptunium-239 peak at 106 keV to the amount of uranium in the sample was first obtained. The activity was measured 4 h after irradiation.

The sensitivity of the method is 0.02%.

Mass spectrometry is used for the analysis of small amounts of a substance sorbed on a thin layer[160]. The specimen in a thin glass capillary with a sealed end is put in the chamber of the mass spectrometer so that after the evacuation and heating (150–200°C) of the source the sorbed substance is evaporated and enters the electron beam of the source. In this way it is possible to analyse all substances stable at a given temperature and having a vapour pressure $> 10^{-7}$ mmHg.

2. DIRECT DETERMINATION ON THE PLATE

Since sharply outlined small spots of the separated substances are usually obtained in thin-layer chromatography, the components can be successfully determined directly on the chromatogram. This procedure is very rapid. The plotting of calibration curves under rigorously identical conditions lowers the error resulting from the possible non-uniform distribution of the substance in the thickness of the layer. At any rate, we believe that the error in such determination should not exceed the error due to the losses of the substance in the elution process.

Direct determinations on the plate can be carried out by various procedures: (1) by a semiquantitative method involving the visual comparison of the size and colour intensity of the spots with the dimensions and colour of a spot formed in the chromatography of known amounts of the substance; (2) quantitatively from the accurately measured area of the spot; (3) by photometric investigation of the spot (in some cases in ultraviolet light); (4) by measuring the emission of radioactive substances, etc.

In a direct quantitative determination it is particularly necessary to standardise carefully the conditions of the chromatographic processes (uniformity of the thickness of the sorbent layer and its grain size, its purity, and its moisture content, identical times taken by the solvent to traverse the plate, deposition of exact volumes of the solvent, saturation of the chamber with solvent vapour, controlled amounts of the reagent required for development, temperature, etc.).

Some of these procedures will now be considered.

Determinations from the Area of the Spot

The technique of this method is simplest, no special apparatus is required, and the determination is fairly rapid. The content of the substance in the spot is calculated on the basis of the fact that the logarithm of the weight of the substance is a linear function of the square root of the spot area[143].

In this case it is possible to make determinations using a calibration plot (which is best constructed on the basis of data obtained on the chromatographic plate used in the analysis of the test specimen) or by the method of additions (calculation by a formula). An advantage of the second procedure is that it does not require the plotting of a calibration graph and is more accurate.

The spot areas are determined with a planimeter or by superimposing a sheet of transparent paper on the layer outlining the spots, and measuring the areas of the resulting figures by placing the outlines against millimeter paper.

For example, chromic acid has been determined by the method described (from the area of the spot)[161]. The linear relation between the amount of chromic acid and the area of the coloured spot was found to hold in the range 50–300 μg of CrO_3. The error of the determination was ±6%.

The method has been used to analyse mixtures of potassium and magnesium acetates[143] and also for the determination of 1–7 mg of PO_4^{3-} per litre in the presence of chloride ions and 1–5 mg ml^{-1} each of I^-, Br^-, and Cl^-, when these were present simultaneously, after separation of the anions by thin-layer precipitation chromatography[107].

Densitometric Method

After the development of the spots on the chromatograms with colour reagents, the substances are determined from calibration plots with the aid of special devices (densitometers) using a linear relation between the dimensions and colour intensity of the spot on the one hand and the amount of the element contained in it on the other[162].

Nickel, cobalt, copper, lead, manganese, chromium, mercury, zinc, bismuth, iron, barium, and strontium have been determined in this way[163]. In the determination of 0.1–3.2 μg of the element the possible error is in the range between 0.2 and 2.1%. Densitometric measurements on a chromatogram with the aid of a chromoscan [chromoscope? (Ed. of Translation)] have been made after separation of microgramme amounts of iron, nickel, and cobalt[164].

A special device described by Pataki and Kunz[165] may be used for a direct quantitative determination on thin-layer chromatograms of spots containing fluorescent substances.

The Radiochemical Method

Spots containing radioactive substances are scanned directly on the chromatograms with the aid of special apparatus whereby the content of the given element may be found from the distribution of radioactivity on the plate. An example of the application of this method[166] is the determination of $^{125}I^-$.

3. ANALYSIS OF NATURAL AND TECHNICAL MATERIALS BY THIN-LAYER CHROMATOGRAPHY

Very few studies have so far been made in this field. In many cases when the weight of the test objects is very small, the chromatographic micromethod for the separation of elements in combination with highly sensitive methods for the subsequent quantitative determination proves to be very promising. The simplicity and rapidity of the method make it suitable for large scale analysis.

Analysis of Natural Objects

The thin-layer chromatographic method combined with densitometric determination of the elements directly on the chromatogram may be used to analyse the magnetic fraction of cosmic dust (the iron–nickel–cobalt system)[164]. The weight of the specimen analysed (cosmic spheres found in the region where the Tunguska meteorite fell) was 3–10 μg. The separation was carried out on a thin layer of KSK silica gel fixed with starch. The mobile solvent was a 99 : 1 mixture of acetone and 3 *N* hydrochloric acid. The duration of the chromatographic process was 15–20 min. The elements were detected by spraying with solutions of rubeanic acid and 8-hydroxyquinoline. The average relative error of the determination at the 0.95 confidence limit was ±22% for iron, ±15% for nickel, and ±9% for cobalt.

Thin-layer chromatography has been used for the qualitative analysis of sulphide ores and minerals [167], as well as for the quantitative determination of tellurium in minerals containing mercury (cinnebar) [126], using TBP-benzene mixture (3 : 7) to separate tellurium from Hg, Au, Sb, As, and Bi. Microgramme amounts of tellurium were determined spectrophotometrically with bismuth II after elution from the sorbent; for a 100 mg sample the accuracy was within ±10%.

The possibility of semiquantitative analysis of water (including natural water) under field conditions using microcrystalline cellulose as a sorbent has been investigated [168]. The mobile solvent for the separation of the cations was a solution of Complexon(III) [sodium salt of EDTA (Ed. of Translation)] in dilute nitric acid to which was added dioxan and antipyrine or a solution of *sym*-collidine in nitric acid. A mixture of ethanol, pyridine, water, and concentrated ammonia was used to separate the anions. After spraying with a suitable reagent, calcium (10 mg ml^{-1}), magnesium and iron (1 μg), aluminium (0.02 μg), manganese (0.3 μg), Cl^- (5 μg), SO_4^{2-} (20 μg), PO_4^{3-} (25 μg), F^- (5 μg), NO_3^- (10 μg), and SO_3^{2-} (100 μg) were determined visually.

Analysis of Technical Materials

Thin-layer chromatography has been used [154] to separate microgramme amounts of components of semiconductor alloys based on lead, tin, and indium. The following mixtures have been separated on a thin layer of silica gel fixed with starch using various eluents: lead–gallium; lead–antimony; lead–tin; tin–zinc; tin–gallium; tin–indium; tin–gold; tin–arsenic; indium–aluminium. The possibility of a quantitative determination of the elements (after elution from silica gel) by oscillographic inversion polarography has been demonstrated for gold. In this determination the standard deviation was 2.8%.

In the analysis of technical preparations of lanthanides (neodymium and yttrium oxides) by thin-layer chromatography, non-lanthanide impurities (iron, copper, mercury, zinc, and calcium) were detected when their content in the lanthanide mixture was 10^{-2}–10^{-1}%. [69]

Thin-layer chromatography can be conveniently employed in the analysis of highly pure materials at the stage of separation where the main bulk of the interfering elements has already been separated by some other procedure. This was done, for example, in the determination of 10^{-3}–10^{-5}% of lanthanides in highly purified uranyl nitrate [125]. The initial salt sample taken for analysis weighed 0.05–5 g. The main bulk of uranium (90–95%) was separated by preliminary extraction and the final separation of milligramme amounts of uranium and microgramme amounts of lanthanide impurities was achieved by repeated ascending thin-layer chromatography on silica gel with a mobile solvent consisting of a 5 : 95 TBP–benzene mixture. The sum of lanthanides remaining at the starting point after elution from silica gel was determined spectrophotometrically with Arsenazo III or Arsenazo M. The standard deviation was about 5–8%.

IV. POSSIBLE APPLICATIONS OF THIN-LAYER CHROMATOGRAPHY IN ANALYTICAL AND INORGANIC CHEMISTRY

On the basis of our own experience and the literature, we believe that the rapid and simple thin-layer chromatographic method will be used in future in combination with sensitive quantitative analytical methods (luminescence analysis, spectrophotometry, polarography, radiography, mass-spectrometry, etc.) and in different versions (partition, ion-exchange, precipitation, multi-dimensional, and gradient chromatography, thin-layer electrophoresis, etc.) for the following purposes: (1) as a method for the separation and concentration of substances and the analysis of various natural and industrial micro-objects using samples down to 10^{-5}–10^{-6} g (minerals, inclusions, articles produced in semiconductor engineering and electronics, etc.); (2) for the rapid separation and identification of short-lived radioactive elements (for example transplutonium elements) with radioautographic detection of the elements on a thick layer of emulsion; (3) as a rapid control method for the determination of the purity of preparations at different stages of the purification of substances (probably largely with a sensitivity of 10^{-2}–10^{-3}%); (4) in a preparative version for the separation of milligramme amounts of elements free from specified impurities (for example in the preparation of standards); (5) for the investigation of the chromatographic behaviour of compounds of metal ions in different valence states (in particular in the study of the disproportionation of elements); (6) for the investigation of problems of complex formation, the mechanism and kinetics of sorption, many other theoretical questions, etc.

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During the preparation of this review for the press, a number of studies were published, the most interesting of which are listed below.

Transition elements: iron–copper, cobalt–copper, iron–cobalt, and cobalt–lead mixtures have been separated by thin-layer chromatography [169]; the glycinate complexes of cadmium, cobalt, copper, nickel, platinum, and zinc have been separated on cellulose layers [170]; chromium, iron, zinc, and nickel have been separated on carboxymethyl- and DEAE-cellulose [171]; manganese and mercury [172], the noble metals [173–179], and rhenium, molybdenum, tungsten, and vanadium [180–182] have been separated; zirconium has been isolated and separated from scandium, yttrium, thorium, uranium, and the lanthanides [183]; cations of analytical groups III and IV have been separated by thin-layer ion-exchange and precipitation chromatography [184].

Non-transition elements: microgramme amounts of indium have been separated from iron, aluminium, gallium, and titanium on cellulose layers [185]; arsenic, antimony, and tin have been separated in the form of pyrrolidinedithiocarbamates [186]; arsenic, antimony, and bismuth [187] and selenium and tellurium [188,189] have been separated.

Lanthanides and actinides: scandium, yttrium, the lanthanides, thorium, and uranium have been separated [190,191].

Heterovalent states: tellurium(IV) and tellurium(VI) [192] and arsenic(III) and arsenic(V) [193] have been separated; the separation of iodine in various states of oxidation has been achieved [194].

Systematic thin-layer chromatography: a number of studies have been made on the systematic thin-layer chromatography of many cations [195–201].

Anions: the sorption behaviour of twenty seven inorganic anions has been investigated[202]; the behaviour of halides[203] and phosphates[204] has been studied.

Radiochemistry: a number of papers have been published on the combination of thin-layer chromatography and radiochemistry[208-210].

Thin-layer chromatography of complexes: the separation of various cations in the form of complexes has been described—as glycinates[170], pyrrolidinedithiocarbamates[186], diethyl dithiocarbamates[211], complexes with salicylaldoxime[212], diketonates[213,214], pyridylazonaphthoxides[215,216], EDTA complexes[217], and others[218-220].

Quantitative thin-layer chromatography: spectrophotometric determination of iron[221,222]; densitometric determination of zinc[223,224]; determination of aluminium, beryllium, and chromium[225]; determination of metal ions in water[226]; analysis of minerals[227].

Thin-layer electrophoresis: this has been used to separate iodine in different states of oxidation[194] and the mixtures[228] $^{90}Sr-^{90}Y$ and $^{212}Rb-^{212}Bi$.

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