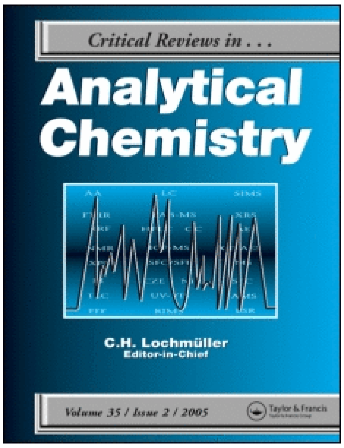

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Application of Thin-Layer Chromatography in Quantitative Inorganic Analysis and in Radiochemical Studies

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ABSTRACT: Thin-layer chromatography (TLC) or chromatography on planar beds finds many applications in the synthesis and determination of organic molecules. This review is devoted to an area of application at least as important but perhaps not as widely known — analysis of inorganic and radioactive substances. Information about the historical development, recent advances in both methodological and instrumental aspects and a scientometric analysis of the use of TLC for inorganic determinations in various fields is provided. Considerable space is devoted to description of the instrumental methods known to be successful in the determination of and quantitative estimation of inorganic TLC zones *directly on the plate* (densitometry, fluorimetry, radiometry, planimetry, visual methods, etc.) and after elution of the material from the developed zones. Methods applicable to most of the elements of the Periodic Table are summarized as are those for various natural and industrial samples including minerals, ores, rocks, waters, metals, salts, biological samples, botanical materials, foodstuffs, drugs and cosmetics.

KEY WORDS: thin-layer chromatography, quantitative inorganic analysis, radiochemical methods.

I. INTRODUCTION

The determination of inorganic ions and inorganic complexes has many areas of important application. The range is from minerals to medicine and from plating solutions to nuclear surety materials. Food, drugs, cosmetics, water, and more are all examined for their major, minor, trace, and ultra-trace content of inorganic materials. The inorganic analyst has a virtual arsenal of tools to choose from for the final measurement step once the inorganic materials are isolated from the sample matrix. Each manipulation step introduces errors from material loss and random error in the process. The separate determination of inorganic materials with very similar chemical properties is especially challenging. As with all areas of analysis, the critical step is a successful separation of the analytes one from each other and the matrix in which they occur. This paper presents a broad review of the development and application of a method which often permits *both* the separation and final determination *in situ* of the inorganic components of a sample. It is a method which permits the use of very small amounts of total sample and is applicable below the ppb range with proper provisions for detection of the separated components. The technique is a very common one — thin layer chromatography — but applied here to inorganic systems.

Many advanced physical and physicochemical methods of analysis are used for quantitative determination of organic and inorganic substances in various samples and liquid chromatography, including high-speed

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chromatography using thin layers of sorbents (thin-layer chromatography, TLC), occupies a worthy place among these. This is very evident from the large number of the monographs, and reviews published in recent years.[1-23] Quite a number of theoretical papers are in print which are directed specifically to improving the performance of TLC.[24-44] The general symmetry of the mobile phase (MP) movement and effect of MP composition on the distribution of eluted substances are discussed in several works.[28,35,36,38] The factors affecting the shape and size of the chromatographic zones and conditions of the optimization of the process of ion separation by TLC have also been considered.[26,27,29,32] The possibilities of using the computational methods for the optimization of substance separation have been considered but for the column, not the TLC, variation of chromatography.[24,25,39-41] Theoretical investigations in the field of optical (and other) methods of substance detection of the chromatograms are well represented in several papers.[42-44]

The use of TLC for inorganic analysis became one of directions for the development of this method in the last two to three decades.[4,5,45-59] The objective of the prior reviews[12,51-59] was to summarize studies on the quantitative estimation of the thin-layer chromatograms of inorganic ions. Among these, and of particular importance are the publications which contain information about the use of TLC for the qualitative and quantitative analysis of inorganic ions in the periods from 1960 to 1972,[46] 1972 to 1980,[45] and 1990 to 1994.[58] The ways to estimate quantitatively thin-layer chromatograms by various highly sensitive physical and physicochemical methods are the focus of this review. Both direct methods and those involving the removal of the actual sorbent from the plates are discussed. Sources of error in the quantitative TLC, the accuracy and precision of the measurements, and the calibration procedures are likewise examined. The use of instrumental techniques in the quantitative TLC, the detailed estimation of various physicochemical methods of detection, the fundamentals of the measurement procedures, and instrumentation were described in another monograph.[9] In this review, specific applications of the various variations of TLC in the actual phases of quantitative inorganic analysis and in radiochemistry will receive more attention.

II. GENERAL CHARACTERISTIC OF THE TLC AND ITS IMPORTANCE FOR INORGANIC ANALYSIS AND FOR RADIOCHEMICAL STUDIES

Special Features of Use of TLC in the Inorganic Analysis and in the Radiochemical Studies. The TLC methods introduced in 1938 by the Soviet scientists Izmailov and Shraiber[60] have been used quite successfully in organic analyses.[61-62] There were, however, practically no examples of the use of this method for the analysis of samples of an inorganic nature in the first period of its development. The first paper on inorganic TLC analysis was published in 1949[63] and the next one appeared in 1960.[64] A period of intense development and a dramatic increase in the number of publications on this subject took place in subsequent years. This effort and its successes made the method one of most promising in analytical chemistry. There were approximately 20 publications in 1965, but more than 60 to 70 papers were published each year beginning in 1967. At present, there are more than 1000 works in print in this application area. The method is widely used today in analytical chemistry and in radiochemical studies. Work on TLC of inorganic ions published before 1965 are summarized in the paper[65] where the potentials of the method were estimated in this field of analytical chemistry. The conclusion reached is that it is expedient to employ this method for the determination of trace amounts of inorganic elements in combination with other micromethods of separation and concentration. It was pointed out in previous studies[49] that the TLC makes it possible to work with nanogram and microgram quantities of substances and provides absolute limits of detection at levels of 10^{-8} to 10^{-7} μg. This sensitivity makes TLC comparable with such physical methods as atomic adsorption, mass spectrometry, X-ray fluorescence, etc. In addition, TLC is advantageous in comparison with these methods because of its simplicity, ease of use, and availability of the equipment needed.

An application of new sorbents, variation in performing the chromatographic process (ascending, descending, circular, anticircular, etc.), as well as some special procedures and techniques of work (two-dimensional development of chromatograms, gradient elution, repeat elution, application of electrical field, etc.) opened a wide range of possibilities of TLC in inorganic and radiochemical studies.

The classical TLC method possesses a number of considerable advantages over some other versions of liquid chromatography (e.g., microcolumn chromatography, high performance TLC), among these are ease of operation and relatively low cost. Although while classical TLC is somewhat inferior to the above methods in limit of detection and in determination accuracy, TLC is more rapid (ca. tenfold) in comparison with paper chromatography and provides 10 to 100 times lower determination limits. These analytical advantages of TLC make clear that it is both reasonable and expedient to employ it in inorganic analysis. Thin-layer chromatography can be used quite successfully for separation of practically any mixture of cations and anions. The majority of publications is devoted to the separation and identification of cations including mostly all groups of the Periodic Table. This method is used also for solving such important problems of analytical chemistry as separation of numerous anions and complexes, separation of some elements in different oxidation states, separation of groups of hardly separated elements including those of rare, rare-earth, actinide, and precious metals.[5] Thin-layer chromatography is not limited to practical problem-solving. An interesting field of the use of TLC is in solving some of the theoretical problems in analytical and inorganic chemistry. The importance and perspective on the use of TLC for solving such problems is supported by the substantial number of publications devoted to the studies of formation and stability of complexes, hydrolysis and polymerization of ions, as well as sorption mechanism and kinetics. The theoretical work has its impact on the practical since information obtained in such studies creates a basis for the development of reliable and reproducible methods for analysis of inorganic compounds.[49]

Recently, TLC has been employed for solving various problems of radiochemistry, for example for determination of the oxidation states of actinides, etc. A combination of TLC with radiometric or radioactivation methods of detection enlarges the scope and promise of TLC and increases the sensitivity of the determination and performance estimation due to a fortunate, mutual augmentation of the advantages of both techniques.

Rational Fields of TLC Application. The main trends in the development of TLC in the recent years are the areas of improvement of the instrumentation and automation, changing to the quantitative analysis, theoretical substantiation of the ways for more effective TLC performance, and also the expansion of the domain of its practical employment.

Taking into consideration the analytical potential of the method, the most promising areas for TLC application must be said to be in the analysis of inorganic materials and substances[49] and, specifically, in the quantitative analysis of small samples (in combination with the highly sensitive instrumental methods of determination), and in rapid semiquantitative testing. Inorganic TLC has been employed to date to solve:

- analyses of microsamples and small quantities of substances (minerals, inclusions, alloys of precious metals, toxic and radioactive substances)
- estimation of the purity of various preparations (salts, reagents, etc.) with the impurity content 10^{-4} to $10^{-3}\%$
- analytical control of technological processes (analyses of solutions, alloys, etc. in industry)
- semiquantitative waste water analysis
- obtaining reference samples of various substances (as a preparative version)
- investigation of the behavior of elements in different valence states and in different ionic forms
- rapid preliminary choice of the conditions for mixture separations in a column mode of chromatography

Method Development. An analysis of the scientific and technical papers published over a considerable period demonstrates the progress in instrumentation and methodical development of the TLC method. It can be seen[23,66] that some 2800 patents were registered, and more than 200 papers published in Germany, the U.S., Japan, and the USSR from 1973 to 1987. These were all devoted to the development of sorbents, equipment, accessories for detection and quantitative determination of elements in chromatographic zones, methods and procedures of TLC experiments. The most promising recent developments are

- in the field of sorbents: obtaining of finely divided sorbents with particle size of 5 to 10 mm including the modified ones possessing special properties and having narrow particle size dispersion;
- in the field of equipment: employment of automated apparatus for sample application and for detection of substances on the chromatograms;
- in the field of methodical versions: fulfillment of the TLC-process under pressure with the continuous flow of eluate, anticircular version of TLC, etc.

The information about the state-of-the art for TLC and about trends in its development, elaboration of new sorbents and new processes for preparation of separating layers, new equipment for TLC, and procedures, systems for detection, and quantitative determination of elements in the chromatographic zones were collected in the review[66] and new equipment for quantitative TLC itself as described.[67-73]

Automation of the TLC Method. The number of publications discussing problems of automation and computerization of chromatographic methods including TLC has increased rapidly in recent years.[74-77] The principal directions of these studies are

- automation of the chromatographic process itself
- automation of the obtained data treatment
- database formation

Each of the separate stages of the chromatographic method have been automated. Sampling and development is often the first direction (application of samples on a chromatographic plate including the use of laboratory robot systems,[78] multiple,[79-81] or two-dimensional chromatography[82-84]). The computer-controlled radiometric scanning of β- and γ-radiation emitters after their separation on a thin layer is described.[85-90] The greatest number of the publications is devoted to the automation of the process of densitometric and fluorimetric measurements of the developed chromatogram.[88-95]

Placing and removing of thin-layer plates, sampling and application of samples, multidimensional separation, and repetitive elution are discussed in literature. Also, consideration is being given to the problems of automation of obtaining derivatives of spectra, high-speed microdensitometric scanning, spectral detection, and recording of radioactive compounds.[97] Nevertheless, there are many unsolved problems in the basic challenge of TLC automation.

When the first paper on constructing a database for TLC of inorganic ions was published,[96] it was pointed out that there was no need to use expensive computers for the "cheap" TLC. To the contrary, the use of computers permits improvement in the separation process and the avoidance of systematic errors. Employment of computers for calculation of concentrations of the components separated on thin-layer chromatograms decrease the RSD value of the results ca. twofold in compared to the graphical method routinely used. The analysis time can be reduced by ~30% as well. Considerable recent attention has been focused on the use of computers for TLC optimization.[98] The software is produced for computer calculations to optimize a mobile phase composition with the use of mathematical methods.

Scientometric Analysis. The trends in scientific papers and patents published during a 10-year period ending in 1987 were analyzed earlier in the review. Conclusions were drawn about the tendencies in the TLC development, about leading countries and institutions, patenting of the inventions in the field, frequency of the use of various techniques for quantitative estimation of thin-layer chromatograms, etc.[23] It was pointed out that the greatest number of scientific papers on TLC were published in Germany, Australia, India (ca. 20% in each), Russia, Japan, U.S., Great Britain, and Canada (ca. 5 to 10% each). Moreover, TLC is widely employed in Sweden, Finland, Poland, Hungary, Netherlands, Spain, Israel, and other countries and is used most frequently in pharmacy, biology, and medicine. The analysis of foodstuff components is also carried out with the aid of TLC.

In general, such trends in the development and use of TLC are still present in more recent years. The following list of leading institutions dealing with the development and application of TLC based on published information are

- universities and institutions of higher education in Canada, Japan, Austria, India, Great Britain, Germany, U.S., Switzerland, Yugoslavia, Russia, Poland, etc. (70% of publications)
- research centers in Pakistan, U.S., Great Britain, Switzerland, Netherlands, Germany, etc. (15% of publications)
- research institutes of the Academies of Sciences of Russia, Switzerland, Hungary, Germany, Spain, Finland, etc. (10% of publications)
- companies in Switzerland (Camag), Germany (Merck), U.S. (Coca-Cola), etc. (5% of publications).

Many of the developments are the subject of active patents especially in the area of equipment. It is possible to point out the following groups of countries according to the number of the granted patents. First group: Germany, U.S., and Great Britain; second group: Japan, Switzerland, Russia, France; third group: Rumania and Poland. The distribution of the patents over the patented subjects is following. The majority of patents concern the instrumentation (U.S., Germany, Great Britain, etc.). Following, are patents on the sorbents (Germany, Russia, U.S., Japan, Great Britain, etc.). Finally, Germany, U.S., and Great Britain are active in the patenting of new procedures and techniques.

We can estimate approximately the frequency of use of various versions of TLC for quantitation by carrying out the analysis of the information published over the period from 1960 to 1990 on the quantitative TLC of the inorganic substances.[4] The data on the percentage of publications concerning the combining of TLC with various techniques for the determination of inorganic ions in the chromatographic zones is presented below.

Method of determination	%
Densitometry, spectrophotometry, reflectance spectrophotometry	50
Fluorimetry	11
Radiometry (including neutron-activation analysis)	10
Visual techniques	5.5
Planimetry	5
X-ray fluorescence	3.5
Mass spectrometry	3.5
Ring-oven techniques	3
IR spectrometry	2
Electrochemistry	2
Atomic emission	1
Atomic absorption	1
Other (photoacoustic, ESR, Raman spectroscopy etc.)	2–3

Densitometry, fluorimetry, and radiometry are the prevailing techniques for the chromatogram quantitation. It is evident that the densitometry has become the most widely used technique in recent times. The frequency of its employment is approximately constant beginning from 1970. Other spectroscopic techniques except densitometry and fluorimetry came into use only after 1973. Mass spectrometry and X-ray fluorescence are the most prevailing among those other methods.

The data presented in Sections III and IV which follow make it clear that the range of the techniques for the quantitation of thin-layer chromatograms is sufficiently broad to provide a solution to a wide variety of problems in inorganic analysis and radiochemical investigations.

III. BASIC FIELDS OF APPLICATION OF TLC IN RADIOCHEMICAL STUDIES

It is common knowledge that measurement characteristics of TLC depend to a large extent on the techniques used for the detection of the separated substances. In this connection, it is worthwhile to note that the employment of radiochemical methods is especially promising especially because these methods are characterized by low detection limits and excellent resolution. There are two ways of combining TLC with radiochemical methods:

1. Separation of radioactive substances and direct determination of them on the plate.
2. Separation of the investigated inactive substances and subsequent neutron-activation determination of them in chromatographic zones.

The quantitative measurement of the zone radioactivity can be carried out either after elution of the substances from the sorbent, or by scanning of zones and bands on the chromatograms using special instruments, and autoradiography, fluorography, and other techniques can be employed as well. Some examples of the use of TLC in radiochemical studies are described in literature. There are examples of the use of TLC for investigations of the purity of the radioactive preparations, for separation of fission products, for separation and isolation of trace and ultratrace amounts of radionuclides including separations in the analysis of natural and industrial objects (see Table 2). TLC has been actively used in recent years for study-ing the chemistry of actinides including the determination of their oxidation states. The fields listed are discussed below in more details.

Investigation of Radionuclides in Different Oxidation States. TLC was successfully used for the study of disproportionation of Pu(IV) in solutions of nitric and sulfuric acids.[99] This was possible because different valence forms of plutonium were distributed differently on the chromatograms with the mobile phase system 1*M* $HClO_4$ – Synthine solution of TBP (23%). The behavior of the plutonium forms of different valence states was at first investigated using TLC. The plutonium compounds were adsorbed on thin layers of silica gel from solutions in nitric, hydrochloric, perchloric, and sulfuric acids in the concentration range from 0.1 to 5.0 *M*.[99] Optimum conditions for the separation of Pu(IV) and PU(VI) from PU(III) were chosen as follows: a silica gel layer on the plate is saturated with 3 *M* nitric acid; the mobile phase is the solution of TBP in Synthine (23%). Pu(IV) and Pu(VI) are quantitatively concentrated in these conditions near the solvent front line. The same conditions were used to separate plutonium from uranium and other related elements.

The chromatographic behavior of americium in different oxidation states was also investigated.[100] Silufol and Merck chromatographic plates were used and the mobile phases were solutions of PMBP in isobutanol. The results obtained were used for the identification of americium in different oxidation states in acetate solution containing potassium tungstophosphate as complex-forming reagent. These results made possible the separation of ^{243}Am from daughter ^{239}Np in nitric acid solutions. Solutions of di-2-ethylhexyl phosphoric acid were also used as mobile phases.[101] The use of Sorbfil plates (Krasnodar, Russia) with thin layers of silica gel was described for the identification of oxidation states of americium which were present in indicator concentrations in solutions of nitric acid of various concentrations.[102] Conditions for the separation of americium from iron were found.

TLC was also employed for the separation of elements with very similar chemical properties in different oxidation states. Thus, in the work[103] Pr(III) and Pr(IV) as well as Tb(III) and Tb(IV) were separated and detected with the aid of radioactive indicators ^{143}Pr and ^{160}Tb. The separation of Ce(III) from Ce(IV) and Eu(II) from Eu(III) was achieved.[104,105] The separation efficiency was estimated using radioactive isotopes ^{144}Ce and $^{152\text{-}154}$Eu. Low concentrations of intermediate oxidized forms of sulfur (SO_4^{2-}, $S_2O_3^{2-}$, $S_3O_6^{2-}$, and $S_4O_6^{2-}$) were investigated with the aid of TLC. Such intermediates labeled with radioactive isotopes were formed in the reactions of elemental sulfur with metal sulfides in aqueous medium. The zones were detected by autoradiography.[106] Hexahalogeno-complexes of trivalent and tetravalent iridium labeled with ^{92}Ir were separated by TLC after neutron irradiation of aqueous solutions.[107]

Estimation of Radiochemical Purity of Preparations. TLC is a convenient technique for detecting trace impurities in radioactive pharmaceuticals. This method was used to estimate the radiochemical purity of ^{99m}Tc preparations.[108-110] Berthold BF-5300 γ-counters[108] and a scanning instrument[111] were used for recording γ-radiation on TLC plates. The traces of ^{90}Mo in a commercially available pertechnetate were determined by TLC on MN-300 cellulose with butanol-1 saturated with 1 *M* HCl as mobile phase.[110] A very good separation of molybdenum from technetium was achieved (R_f values were 0.0 to 0.2 and 0.7 to 1.0, respectively). In order to achieve rapid response to the need to control the radiochemical purity of the labeled xenon trioxide using TLC, the concentrations of iodine compounds were quantitatively estimated employing a one hundred-channel amplitude pulse analyzer AI-100-1. The determinations of $^{133}XeO_3$ and $^{131}IO_4$ in zones after separation were carried out by the measurements of γ-spectra on the corresponding parts of chromatograms. A high-speed scanner, that simplifies considerably the measurement procedure, was described for the determination of ^{125}I on thin-layer plates when various amino acids were analyzed.[113] The determination of ^{131}I by scanning and autoradiography was described for organic substances used in medical diagnostics and therapy.[114]

Separation and Concentration of Radionuclides in the Analysis of Various Samples. Separation of radionuclides by TLC has some advantages in comparison with column and paper chromatography. The technique is simple and permits to control the choice of most suitable eluants for separation of complex mixtures of radionuclides. It is most expedient to use TLC for the resolution the short-lived radionuclides.

In recent years, TLC was actively used for isolation of actinides from solutions of complex composition characterized by high γ- and β-activities, when it was desirable to work with minimum volumes of solution for safety, convenience, and rapidity.[115-117] For example, the technique makes it possible to isolate rapidly (in 25 min) and efficiently ^{234}Th (decay product) from small amounts of uranyl nitrate using a mixture of solvents consisting of diethyl ether, water, and TBP.[116] A separation of ^{38}Cl, ^{35}S, and ^{35}P formed after neutron irradiation of NH_4Cl is described. These radionuclides were identified by their half-life periods, and their amounts on the chromatograms were determined radiometrically.[116] Some examples of TLC separation of two- and multicomponent mixtures of radioactive substances without carriers are presented.[115-117] The separation of the following radionuclides are of considerable current use in radiochemical studies: ^{140}Ba - ^{140}La, ^{133}Ba - ^{133}Cs, ^{47}Ca - ^{47}Sc, ^{90}Sr - ^{90}Y, ^{72}Zn - ^{72}Ga, ^{95}Nb - ^{182}Ta, ^{95}Zr - ^{95}Nb, etc. The detection of the individual elements was carried out radiometrically in an automatic mode. TLC was used for the separation of Sn^{2+}, Sb^{3+}, and TeO_4^{2-} in the investigation of the decay chain ^{125}Sn ⇒ ^{125}Sb ⇒ ^{125}Te. The radioactivity of the separated substances was determined by a Geiger-Muller counter, and the radiochemical purity of the isolated elements was estimated γ-spectrometrically.[118] The isotope ^{125}Tc was isolated without carrier.

The use of TLC on Kieselgel MNS-HR for the separation of the daughter ^{113m}In from the parent radionuclide ^{113}Sn is known.[119]

Partition TLC has been applied successfully for inorganic ions. Plutonium can be isolated from the complex mixtures consisting of U, rare earths, Cu, Cr, Ni, Pb, Fe, and Zn.[99] This separation is performed using 3 *M* HNO_3 - Synthine solution of TBP (23%) using a single chromatographic run on thin layer of silica gel impregnated in part with 3 *M* HNO_3 and also with 1 *M* $HClO_4$. Thus, separated plutonium was further determined on the plate radiometrically with RSD = 10 to 15%. The analysis time is 60 to 90 min, and the volume of the analyzed solution was 0.03 mL. Conditions were found for the separation of Am(III) from Pb, Ni, Fe, and partly from U and La using the system nitrate solution — silica gel with tri-*n*-octylamine.[120] The maximum concentration of Am(III) in the upper chromatogram zones can be achieved when the layer is saturated with 4 *M* solution of $LiNO_3$ (the initial solution contained 7.2 *M* of $LiNO_3$). The mobile phase was 0.1 to 0.2 *M* cyclohexane solution of TOA equilibrated with 7.2 *M* $LiNO_3$. The americium determination in the concentrated zones was carried out radiometrically with RSD = 5 to 7%.

Selective separation of uranium from a possibly large number of other ions is very important in the work with uranium ores or irradiated nuclear fuel. It is not surprising, therefore, that several publications on TLC are devoted to such separations.[121-125] The efficient separation of uranium from 55 cations (including the most important decay products) is achieved with layers of silica gel or cellulose in the analysis of uranium-containing minerals.[123] The mobile solution was a mixture of hexane and TBP saturated with 4.7 *M* HNO_3. The isolated uranium was determined on the sorbent by neutron activation analysis. The ^{239}Np content that was measured by γ-spectrometry. Triisooctylamine was successfully employed as mobile phase for the separation of uranium from Mo, Co, Ni, Zr, Th, and other elements.[124] The separation of uranium from Th, Zr, and rare earths is also described.[126]

Ascending TLC on silica gel with the use of the mixture TBP — benzene (1:1) as mobile phase was employed for the separation of U from Pu(IV) and transplutonium elements at the concentration ratios U:Pu = 500:1 and U:Am = 20 000:1.[121] The volume of initial 1 *M* solution of these elements in $HClO_4$ was 0.02 mL. The possibility of the separation of plutonium from transplutonium elements with 1 *M* HNO_3 was demonstrated in the same work. The mixture TBP — benzene (1:10) was used as mobile phase. The conditions for the separation of Ac, Ra, Th, Pu(IV), Am, UO_2^{2+}, Pb, and Bi are reported.[127] The separation of U, Np, Pu, and Am is described.[128,129]

Recently the use of TLC became popular for the analyses of environmental samples. A method for strontium determination in soils is proposed that includes the selective extraction with dicyclohexano-18-crown-6 in chloroform, application of the extract on a thin-layer plate and separation of the radioisotopes of strontium and yttrium using circular TLC.[130] This method makes it possible to determine separately ^{89}Sr and ^{90}Sr. The chemical yield of strontium exceeds 90%. The detection limit is about 0.5 Bk/g, with an RSD of about 2 to 5%. The proposed method is rapid enough (the whole procedure takes 3 to 4 h) and easy to carry out compared to other methods. The reproducibility of the results is adequate for the requirement. A method is known of the separation of the ^{90}Sr from the daughter yttrium on silica gel or cellulose treated with calcium oxalate. The determination of ^{90}Sr in water and milk can be carried out by measurements of the radioactivity of the separated elements with the aid of a computerized multichannel analyzer.[131]

Radioactive isotopes are used to observe the development of TLC separation of nonradioactive elements. The distribution of mixture components on chromatograms can be studied by use of radioactive isotopes whose radiation is measured by radiometry and autoradiography. Such investigations were carried out in the works.[104,132-136]

Neutron activation with subsequent γ-spectrometry is employed for the determination of some nonradioactive elements after isolation by TLC. For example, a simple method was developed for preconcentration of rare earths by TLC on Fixion 50 × 8 plates using ammonia solutions of oxalic acid and ammonia chloride as eluants. Subsequent γ-spectrometric analysis of the irradiated concentrates was carried out.[137] Using this method, it is possible to determine 8 to 9 rare earths elements in samples of rocks with masses up to 30 mg. The limits of detection are from 0.05 to 0.4 μg for Eu, Sm, Tb, Yb, and La or from 1 to 10 μg for Tu, Ce, and Nd. The RSD values are equal to 5 to 20% for 5- to 10-fold higher concentrations than the limits of detection.

The more detailed information on the quantitative determination of individual elements in chromatographic zones using nuclear-physical methods is presented in Section IV.A.2 (see Table 2).

IV. TLC IN QUANTITATIVE ANALYSIS OF INORGANIC MATERIALS

A. Combination of TLC with Various Methods of Determination

1. Optical Methods

Spectroscopic methods of ion determination in the chromatographic zones are widely used in the analysis of inorganic substances. Densitometry and fluorimetry are most widely applied spectroscopic methods *in situ* determination of elements. Fluorimetry is comparable with for densitometry in the time of analysis (2 min) but surpasses it in the detection limit by 10^3 to 10^4 times (10^4 to 10^{-1} and 10^{-1} to 10 µg, respectively). The reproducibility of optical scanning in fluorescence measurements is 1.5 to 2 times better than the reproducibility of measurements of the radiation absorption. X-ray fluorescence and photothermal spectrometry are also employed for *in situ* analysis. It is possible as well to determine elements reliably and quantitatively, after removal from a plate, the portion of sorbent containing the substance to be determined (but without its elution) using reflectance spectroscopy, atomic absorption and emission spectrometry, infrared and mass spectrometry, X-ray fluorescence analysis.

Spectrophotometric (colorimetric) determination of elements in the zones requires eluting the substance to be determined from the sorbent. The ring-oven method (with visual detection) can also be placed in this group of methods. Physical and physicochemical methods of determination such as infrared and mass spectrometry, radiometry, polarography, etc., can also be employed after elution. The domain of the use of the elution technique is rather large. It includes the determination of various elements (including alkali, alkaline-earths, heavy, noble, and rare ones) using different detection methods. Various vacuuming devices are recommended[138,139] for the removal of sorbent from the plate and its transfer into the vessel for elution. It is possible to remove the sorbent from TLC systems with the use of the automated devices which are most often used for the analysis of radioactive substances.[140,141] The method for the extraction of the substances under determination with the use of solvents is discussed.[9] The analyzed substances can be transferred onto solid supports before determination, e.g., in the method of ring-oven colorimetry [142] and in the methods described[143,144] in which the substance is transferred from the sorbent layer onto a intermediate porous carrier (filter paper, potassium bromide). The devices for substance elution from chromatograms are described.[145]

Densitometry and Reflectance Spectroscopy. The theory of quantitative densitometric determination of substances on thin-layer chromatograms and some peculiarities of using different densitometers are discussed.[146] It is shown[147] that the processes of light transmission through thin dispersing and absorbing layers of sorbent can be best of all described by the discrete step model. A review on the methods for quantitative photometry of thin-layer chromatograms for research purposes and routine analyses was published.[147a] Methods for direct determination of micro- and nanogram quantities of substances on chromatograms by reflectance spectrometry are discussed in the review.[147b] The works[148,149] are devoted to the problems of sensitivity enhancement in densitometric determinations. Instrumentation and systems for optical scanning of chromatograms are described in previously published papers.[150-166] A device was described for the correction of the results of densitometric measurements of light absorption by colored spots on chromatograms. The light scattering effect was employed for such corrections.[167] The modern densitometric technique for the determination of substances in chromatographic zones is comparable in its capabilities with radiochemical methods. However, the former is less time consuming and more safe and is why this technique is widely used.[168-170] Direct densitometry possesses some advantages over other techniques employing elution or zone removal (for example, before quantification by reflectance spectroscopy) because the use of these techniques may lead to losses or contaminations of separated substances. The results of *in situ* measurements depend on a number of factors which are not taken into account in the photometry of solutions: nature of the layer, its thickness, and humidity, presence of contaminants, composition of the solvent system used, mobile phase flow rate, accuracy of sampling, dimensions of the start zone, direction of scanning, etc. One of the problems of this method is the necessity to provide starting zones uniform in their shape and dimensions. The results of quantitative estimation of thin-layer chromatograms by densitometry and planimetry can be affected by the type of sorbent, its specific surface and microporosity, uniformity and thickness of the layer, particle size and pore size, etc.[172-176]

Spectrometric scanning of zones on chromatographic plates is usually carried out in one direction with the use of special instruments. It provides a reproducibility of about 2%. Spot scanning in both forward and reverse directions provides better compensation of background fluctuations. Careful and proper selection of the necessary wavelength for scanning, which depends on the R_f value, it is possible to provide faster and more reproducible measurements.[177] More precise estimation of thin-layer chromatograms can be achieved with the use of scanning by the zigzag technique at two wavelengths.[178,179] This scanning technique with the computer control of zone position, including the use of the devices for automatic sample application in the shape of a band, is discussed.[59a] A method of optical scanning with subsequent mathematical data treatment was successfully used in a microvariant of TLC.[191]

Several factors (instrumental drift, integrator linearity, scanning speed, etc.) were investigated which affect the reliability of element determination by direct densitometric measurements,[180,181] for example, in the zinc determination on layers of cellulose MN 300 HR. The error of the determination results depends also on the linearity of the calibration plots.[182] It was noted[183] that the calibration plots for measurement of spot color on thin-layer chromatograms using the light-transmission technique can be described by linear equations providing that there is no supersaturation of spots with the substance. A linear form of the Kubelka-Munk equation was derived for the quantitative photometric determination of substances on thin-layer chromatograms.[184] It was possible to obtain a calibration plot which was linear and independent of the solvent nature in a wide concentration range when an automated function transformer was used for simultaneous measurements of light transmission and reflectance.[185] A linear detecting system was designed, and the advantage of the two-dimensional technique of integration over the unidimensional one, was demonstrated.[186] A comparative study was carried out of the most widely used methods of mathematical treatment of densitometric measurements to estimate the linearity of Bouguer-Lambert-Beer law, Kubelka-Munk function, Trailer equation, etc.[187,188] A technique is proposed for selecting and optimizing the working parameters of a Shimadzu C-900 scanning densitometer operating in the transition mode for recording chromatograms obtained by high performance TLC.[189] It was shown[190] that the application of a new approach to the quantitative densitometric estimation of thin-layer chromatograms made the analysis easier and faster. This new approach includes recording of the first and second derivatives. In addition to the instrument, an electronic set-up for the determination of the fourth derivatives enlarged the potentialities of the method, especially in the determination of unresolved components.

The densitometric technique was applied to determine the following elements on the chromatograms: alkali and alkaline earths,[21a,192] noble,[193-195] rare,[196] heavy elements,[21a,170,171,192,197-210] various elements,[211-213] and anions.[214-216] The more detailed information on the conditions for the determinations of various elements can be found.[4] The following materials were analyzed by means of a combination of TLC with a densitometric technique: waste waters,[24] magnetic fraction of interplanetary dust particles,[206] monazite,[217] molasses,[216] etc.

Reflectance spectroscopy is applicable to the determination of substances both directly on the chromatogram and after zone removal from the plate. When a thin-layer chromatogram is estimated *in situ* by reflectance spectrophotometry, the total error depends on the following factors:

- inaccuracy of sample application onto the plate
- inaccuracy of plate position in relation to the light beam center
- inaccuracy of the measurement itself
- the real peak height on the chromatogram

That is why all the procedures of the chromatographic process and measurement should be standardized to obtain as reproducible results as possible. When such conditions are satisfied, it is possible to achieve the RSD value 1 to 5% or 4 to 6% for parallel determinations of substances on the same chromatogram or on different chromatograms, respectively. When reflectance spectrometry is used after the removal of a spot from the plate and placing the sorbent into the spectrometer cap the separation of elements is usually carried out on thin layers of cellulose or silica gel. After detecting the element with suitable visualizing reagent, the layer containing the spot is scrapped from the plate, pulverized thoroughly in a agate mortar till a uniform mass is obtained, and placed into the reflectance cell of the spectrophotometer. It is possible to determine in such a way the amounts of substances from few hundredth to 10 μg with the RSD 2 to 6%.[218-222] In our opinion, reflectance spectrometry offers no special advantages in comparison with direct densitometry. Moreover, particular care has to be taken to avoid losses when the sorbent is taken off the plate and pulverized. Reflectance spectrometry was used for the determination of Ni, Cu, Zn, Co, Al, Be, Cd, Cr, Fe, Pb, Mn, Hg, Ag, Sn (see Reference 4, p. 49–54), and other elements.[223] The advantages and drawbacks of optical measurements in transmitted and reflected light are discussed, and a conclusion was drawn that the reflectance technique is less sensitive to the optical noises than the transmission one.[224,225]

Fluorimetry. Fluorimetric methods for the quantitative estimation of thin-layer chromatograms are based on the measurements of the fluorescence intensity or the degree of its quenching which depend on the quantity of the substance in the chromatographic zone. The radiation with a wavelength of the initial exciting one is measured displaying a principal difference of fluorescence methods from densitometric ones. The fluorescence of separated substances is usually excited with electromagnetic radiation at a corresponding wavelength. The technique based on measuring the intensity of fluorescence is most extensively employed. The reason is that the quenching technique cannot meet many requirements of quantitative detection. Photometric measurements of fluorescence are performed both in a transmission mode (the measurements on the opposite side from the radiation source) and in a reflectance mode. It is shown theoretically and confirmed experimentally that the fluorescence measurements are more preferably performed on the side of irradiation. The reason is that on the opposite side the radiation is considerably less intensive.[226] The intensity of excited fluorescence is proportional to the substance concentration taking into account its fluorescence coefficient. A two-point calibration technique is described[227] for fluorescence scanning densitometry in high-performance TLC.

The results of the quantitative detection of substances by the fluorescence techniques and their comparison with the densitometric methods was discussed.[9] Nonuniform distribution of the substances to be determined along the thickness of the sorbent layer and the influence of the size of the chromatographic zones on the sensitivity of the fluorimetric methods were taken into consideration. The limits of detection are mainly dependent on the background noise. A low level of noise is the basic advantage of the fluorimetric techniques. It was demonstrated[228] that the optical scanning on the basis of fluorescence measurement was usually characterized by the reproducibility 1 to 2%, a necessary amount of the substance of about 10^{-4} to 10^{-1} μg, and a time of analysis of about 2 min. A decrease of the limit of detection of substances can be achieved as a result of an enhancement of an fluorescence increase due to the increase of the initial radiation intensity, particularly, due to the employment of lasers as sources of radiation.[229-231] In this case, there is no danger of the photolysis of the determined compounds. The instrumentation for the fluorometric detection of the separated substances is described.[9,232]

Some theoretical studies on the selection of the conditions for fluorimetric measurements and their mathematical description were made.[149,233,234] These papers contain also the comparison of the fluorimetric and densitometric techniques and the description of the corresponding instrumentation.[235-241] Fluorimetric methods were applied to the determination alkali and alkaline earth elements,[192,242] lead,[243,244] aluminium,[245,246] iron, tungsten, titanium, germanium, arsenic, antimony,[247] lead, bismuth, uranium, thorium, copper, cobalt, nickel, cadmium,[248,249] noble metals,[250] rare earth elements,[251] and other elements[252] in chromatographic zones.

X-Ray Fluorescence. A new technique for the detection and identification of substances in chromatographic zones has been proposed, namely *in situ* X-ray fluorescence microanalysis (XRFMA).[253-255] This technique requires no pretreatment. The plate is irradiated with a collimated beam of primary X-ray radiation with an energy 40 to 60 kV. The resulting characteristic spectrum of X-ray fluorescence is recorded to obtain qualitative and quantitative information about the chemical composition of the individual chromatographic zones.

The proposed technique was used for the investigation of the sorption behavior of Ni, Co, Mo, Rb, and Y in solution with in their $n \times 10^{-4}$ - 2 M solutions on thin layers of silica gel or an ion exchanger (Fixion 50 × 8). The standard error of the intensity measurements was mainly determined by the statistical error of the pulse counting. That is why the RSD value was not more than 3% for the chosen time interval (40 to 100 s) providing a set of not less than 1000 counts per point. The repetitive scanning of the concentration curves makes it possible to decrease the RSD value by 1.5 to 2 times since in XRMFA the samples are not destroyed . The scanning was performed using X-ray fluorescence microanalyzer.[256] The main field of application of this new method is the determination of inorganic and organoelement compounds. In principle, all the elements of the Periodic Table beginning from lithium ($Z = 3$) can be determined. The described technique is characterized by a high selectivity since every element can be determined on the chromatogram independently of the presence of any other elements. The limit of detection is 10^{-9} to 10^{-10} μg of a substance. The local resolution of this technique is characterized by the least possible diameter of the analyzed zone (0.1 to 1.0 mm). It makes possible to determine nanogram and microgram amounts of substances in the zones of small diameter (with the area up to 1 mm^2). The combination of TLC and XRFMA expands the capabilities of *in situ* analysis as compared with other similar techniques. It makes possible:

- an increase in the number of analyzed samples and the number of determined elements
- permits quantitative estimation of the ratio of the various forms of the same element (differing in their oxidation states or in other qualities) after their separation (when the transformation kinetics is slow)

- makes possible a determination of the completeness of the chromatographic separation of elements
- permits to investigate the patterns of element distribution not only along the whole chromatogram but in each individual zone as well

Thus, the new "hyphenated" technique proposed can be used to solve analytical problems which cannot be solved separately either by chromatography (e.g., in case of incomplete separation of two or more compounds every of which differs qualitatively from the others by the presence of at least one element) or by XRFMA (e.g., when it is necessary to determine different ionic forms of the same element). The technique of combining TLC and XRFMA is an almost universal one. It can be used, in particular, for the investigation of planar chromatograms on any support (glass, polymeric film, aluminum foil). The support does not affect the results of analysis since the background due to the sorption layer and to the support is taken into account in the determination of element concentration from the X-ray lines.

The technique of X-ray local fluorescence scanning of thin-layer chromatograms could find widespread application in the analysis of natural and industrial microsamples and small amounts of substances (e.g., minerals, microocclusions, materials for radioelectronics and semiconductor industry, precious and toxic elements, etc.). It may be of interest to apply this technique to the investigation of complex formation, behavior of elements of different oxidation states and different composition. Maximum local resolutions were achieved in the physicochemical investigations of the systems sorbent (ion-exchange resin) and solution (rubidium chlorides and nitrates, hydrochloric acid). The aim of this study was to calculate various parameters of a chromatographic system from the experimental data on the distribution of substance in the chromatographic zone. In particular, the porosity of sorbent and the exchange constants for rubidium and hydrogen ions were calculated.[255]

The procedure of pressing a part of sorbent containing the determined substance into disks of about 30 mm in diameter with subsequent direct measurement is recommended for the quantitative determination of *total* amount of the component in the chromatographic zone. Such a procedure permits usually to obtain the RSD 10 to 20%.[257]

The analysis of zones containing microgram amounts of different phosphates after their separation by TLC was carried out by X-ray emission spectroscopy[258] and heavy metals (In, TL, Sn, Pb, Bi, Os, Ir, Ru) were detected on thin-layer chromatogram in the form of 8-mercaptochinoline or 1-hydroxy-2-pyridinethione complexes.[259] An X-ray fluorescence scanner for thin-layer chromatograms has been described.[260] The instrument was used for the determination of phosphorus, sulfur, chlorine and iodine with the limit of detection about 2 µg. The microanalysis of thin layers of Ti and PbSnTe on a silicon base from X-ray radiation arising after sample irradiation by electrons was carried out.[261]

Atomic Absorption Spectrometry. Atomic absorption spectrometry (AAS) was proposed as a technique for the detection and identification of the chromatographic zones.[262] However, so far AAS was relatively seldom employed in combination with TLC. The technique was mainly used for the determination of noble metals,[263-265] rare,[266] and heavy elements.[267]

Atomic Emission Spectroscopy. Atomic emission spectroscopy (AES) is easily combined with TLC. A powdered sorbent containing the component under determination can be directly introduced into the arc ionization source after removal from the corresponding part of chromatogram. Cellulose is most often used as sorbent since it burns without sputtering. The examples of the application of TLC-AES combinations are not numerous.

AES was used for the determination in the chromatographic zones of platinum group metals,[268] rare-earth elements, tantalum,[270] alkaline-earth elements.[271] In the last case, preliminary elution of the elements from the sorbent before introducing the sample into the spectrometer was used. The limits of detection are usually $n \times 10^{-3}$ to 10^{-5}%.

Infrared Spectrometry. There are two ways of IR-spectrometric measurements for the identification of substances separated by TLC. The first of them includes the elution of the determined substance from the sorbent and subsequent investigation of eluate or potassium bromide disks onto which the substance is transferred.[272-274] The second technique includes direct IR measurements on thin-layer plate.[275-276] The direct determination, although being rather fast, possesses a number of serious drawbacks. The most important of them is a strong absorption of the IR radiation by the material of support and by the stationary phase causing spectral superpositions. The interferences can be caused by the absorption bands of the functional groups of solvents used as mobile phases and partly retained in the thin layer of sorbent due to the intermolecular interaction with the stationary phase. On the other hand, the recovery of the determined component from the sorbent before IR determination is a rather long and tedious operation that can lead to losses or contamination of the sample. It is preferably to deal with the samples of 100 to 200 μg. Preliminary elution is usually used when inorganic ions are determined by the IR spectrometry.[273,274]

An interesting procedure is proposed for this purpose.[277] A thin-layer plate after completing the development is treated with a strongly acting solvent in the second direction (as in two-dimensional chromatography). This solvent provides the complete transfer of the component to the powder transparent for IR radiation is chloride, diamond powder, etc.). The powder is placed on the support connected with thin-layer plate by a bunch of glass fibers. In so doing, it is possible to minimize all the problems connected with the transfer of substance. The solvent retained in the powder can be evaporated before measuring.

The results of the determination of glycidoxypropylate complexes of some metals by the FTIR spectrometry, densitometry, and fluorimetry were compared.[278]

Mass Spectrometry. Mass spectrometry is a convenient technique for the identification substances separated by TLC.[279-281] Unlike some other physical methods of analysis, the sample is completely used up during the analysis. As small samples as 1 to 2 μg are usually employed because mass spectrometry provides the detection limits 10^{-11} to 10^{-14} g.

Transfer of the analyte from TLC-plate to the mass spectrometer can be performed either directly (e.g., by withdrawal of a part of sorbent containing the determined substance from the support and transferring it into the mass spectrometer) or by use of preliminary elution of the substance from TLC-plate and introducing the eluate into the evaporating chamber of the mass spectrometer as is usually carried out for the identification of organic substances.[282-288] The first way seems to be the most promising one.

Ionization by the bombardment by fast atoms is the most convenient way for combining TLC and mass spectrometry. That is why such a technique does not require removing the test substance from the plate and permits to investigate nonvolatile and thermally unstable compounds.[284] A rapid and simple technique was developed[285] for transferring the sorbent with the substance after determining zone location on the plate (by a usual method, e.g., by uv-fluorescence). The end of the probe for introducing the sample into the mass spectrometer is pressed to the spot by a adhesive tape. Thereafter, 1 to 2 μL of a solvent (CH_2Cl_2, CH_3OH) and 2 to 5 μL of a liquid matrix (glycerin or thioglycerin) were added to the sorbent on the end of probe. Then, the probe is introduced into the ion source of the mass spectrometer. The analysis is carried out using a high-resolution instrument. A device for scanning 1 × 10 cm TLC-plates by use of a pulse CO_2 laser was developed.[286] So far mass spectrometry was not often used for the detection of inorganic substances on TLC-chromatograms. Preliminary elution of the determined substance from the sorbent before its introducing into the mass spectrometer is employed. Fe, Co, Mn, Ni, Zn, Cu, Rh, Pb, Cd, and Hg were identified by this technique in the form of their complexes with tetraphenyl porphyrin.[289, 290] The method proposed was employed for the analysis of biologic samples.

Spectrophotometry. Spectrophotometric measurements (in UV or visible regions) can be carried out by the estimation of the absorbance of the eluate containing the determined substance in the form of a colored complex. It is possible also to separate a colorless substance from the sorbent zone and to subject it to the reaction with a suitable reagent to form a colored product. In any case, the eluate is brought to a known volume and investigated on a spectrophotometer a colorimeter. The results can be calculated using the corresponding calibration plots or molar absorptivities. A linear relationship between the color intensity and the substance concentration should be obeyed. Successful application of the photometric techniques depends of the band shift to the range of longer wavelengths. In this case the results are less affected by interferences from the substances coextracted from the sorbent. Spectrophotometry provides limits of detection which are at least 10 times lower compared with the other optical techniques.[291] Spectrophotometric determinations after eluting analytes from the sorbent are quite often used in inorganic analysis. The following elements and compounds have been determined: alkaline earth elements,[292,293] aluminum,[294] cadmium and others,[295] cobalt,[296] bismuth,[297] iron,[298] nickel,[299] iron and mercury,[300] cobalt, nickel, bismuth and other,[301,302] mercury, cobalt, nickel,[303,304] precious metals,[305] uranium,[306] tellurium,[133] uranium, nickel, cobalt, and bismuth,[307] rhenium,[308] zirconium,[309-311] rare earth elements,[103,312-315] phosphates,[316-318] and polythionates.[319]

The "Ring-Oven" Method. This technique also called ring colorimetry or circular colorimetry is a special method for the analysis on filter paper disks placed into a ring oven usually heated to 100 to 110°C. The substances are detected not in a spot-like form but in the form of sharp concentrated rings. Such rings are formed as a result of solvent displacement from the center of the spots to its periphery during evaporation. The first publication on this technique appeared in 1954,[320] the first monograph — in 1961 and repeatedly in 1970.[321] The following aspects were discussed: instrumentation and its use for the analysis of cations, anions and organic substances; use of this technique in radiochemistry, toxicology, for air pollution estimation, etc. Particular emphasis has been placed on the combination of the ring-oven method with other techniques such as solvent extraction, paper and thin-layer chromatographies. This analytical technique is very simple, rapid, and highly sensitive.

When TLC is combined with the ring-oven technique, the procedure is as follows. A corresponding zone containing the test substance isolated by TLC is scrapped from the plate, the obtained sample is applied as a spot on a paper disk, and the latter is placed into a ring oven. The spot is eluted with an appropriate solvent feeding it into the center of the spot. Sharp rings are formed as a result of the process of adsorption chromatography. The color intensity of these rings can be measured visually by comparison with the corresponding scale. The works[321-322] are devoted to the problems of combining TLC with the ring-oven technique. The procedures and corresponding devices are described in detail.[322]

The employment of the ring-oven technique for the estimation of radioactive element concentrations in the zones of thin-layer chromatograms was mentioned in the work.[323] Of particular interest is use of this technique in radiochemistry because of its relative safety as it requires only quite a few microliters of solution for the analysis. The ring-oven technique was employed for semiquantitative determination of the following elements and ions after their TLC separation: iron. copper, nickel, cobalt,[324] platinum group metals,[325-327] nickel, cobalt, palladium, titanium, yttrium, zirconium,[328] lead, bismuth, uranium, thorium, nickel, copper, cobalt, cadmium,[248] vanadium(IV), vanadium(V), iron(II), iron(III),[329] titanium, zirconium, thorium, and rhenium, molybdenum, zirconium, thorium and rhenium, molybdenum, tungsten, etc.,[330] germanium, arsenic, antimony, etc.,[331] germanium, tin, lead, zinc, cadmium, mercury,[332] alkaline earth elements,[333] selenium tellurium, tin,[334] iron, mercury, thallium, antimony,[335] polythionates.[336]

Photothermal Spectrometry and Electron Spin Resonance. The fundamentals of photothermal spectrometry have been described.[337-342] Photoacoustic spectrometry was firstly employed for the determination of organic substances on chromatographic plates. Inorganic ions were determined by this technique on Silufol plates[340] and other substances, e.g., fluorescein were determined.[341] There is no limitation for the form and structure of samples which can be powders, paper, pastes, coatings, etc. with the weight down to a few milligrams.

The photothermal method makes it possible to achieve the relative limits of detection $n \times 10^{-5}\%$ wt. or the absolute limits of detection down to $n \times 10^{-11}$ μg for solid materials; the detection limits depend on the radiation source and on the technique for acoustic oscillation measurements. Therefore, this method is one of most sensitive spectrometric techniques in analytical chemistry. The most effective way to further increase the sensitivity of the optical-acoustic method is the use of lasers as sources of radiation.

The examples of the photothermal detection of inorganic ions are presented in Table 1. The complex of cobalt with 1-(2-pyridilazo)-2-naphtol was also determined by photoacoustic spectroscopy.[349]

A combination of TLC with electron spin resonance (ESR) is described as the technique for the determination of Cu(II) and VO^{2+} after scraping off the corresponding zones of sorbent from a thin-layer plate and placing the samples into a capillary tube (an ampoule for ESR measurements).[348] The elements were determined using calibration plots. Al(III), Cr(III), Mn(II), Co(II), Ni(II), Zn(II) do not interfere with the determination of Cu(II) and VO^{2+} while there is some interference from Fe(III). The RSD values were 1.8% for the determination of 10^{-4} *M* Cu(II) and 1.66% for the determination of 10^{-3} *M* VO^{2+}.

Radiochemical and Nuclear-Physical Methods. As mentioned above (Section III), nuclear-physical methods are among the most sensitive techniques for detection, identification and quantitative determination of elements in chromatographic zones. Some problems of quantitative estimation of thin-layer chromatograms are discussed.[9] The combinations of TLC and radiochemical techniques of the analysis of inorganic substances are described.[5]

Some instruments and devices for the qualitative and quantitative analysis of thin-layer radiochromatograms are described.[350-357] A method was reported for removing the layers of cellulose or mixtures of cellulose and silica gel from glass thin-layer plates and subsequent measurements of the radioactivity of substances contained in individual zones.[358] A convenient device was proposed for the detection of radioactive spots by autoradiography.[359] Radiometric scanning can be carried automatically,[360] and the results can be processed by computer.[361,362]

There are few ways of detection and measurement of zone radioactivity on the chromatograms. These are direct determination of elements on the plate (radiometric measurements of the spot, scanning of the chromatogram, autoradiography) and determination of the radioactive elements after isolation of a zone from the chromatogram (radiometric analysis of the sorbent powder, eluate or solvent after sorbent destruction, neutron activation method). The works given in Section III[99-136] and in Table 2 are devoted to the combinations of TLC with various nuclear-physical techniques for detection and determination of substances. The automatic scanning of the radiochromatograms was especially effective when nanogram quantities of ^{51}Cr, ^{54}Mn, ^{59}Fe, ^{60}Co, ^{65}Zn, ^{109}Cd were present in the form of triocyonate complexes. A 128-channel ND-110 spectrometer with NaJ(Tl) crystal was employed.[360] An original system for the estimation of spatial distribution of molecules labeled with the positron-radiating radionuclides was proposed.[357] Autoradiography was employed for the detection and determination of trausuranium and elements[121,363] rare-earth elements,[314,315] S and P,[364,370] ^{24}Na, ^{42}K, ^{86}Rb, ^{137}Cs[371] on thin-layer chromatograms. Zones of inorganic ions labeled with the radioisotopes ^{137}Cs, ^{139}Ba, ^{140}La, ^{90}Y, ^{90}Sr, ^{24}Na, ^{42}K, ^{86}Rb were detected autoradiographically on chromatograms after separation of mixtures of these elements on thin layers of silica gel mixed with ammonium dodecanomolybdophosphate or zinc cyanoferrate.[372]

The noble elements,[366-368] rare earth elements,[130] and uranium[369] were determined in chromatographic zones by a neutron-activation method after their separation from accompanying elements by TLC and isolation of the chromatographic zones from the plates. For example, microgram quantities of Ag, Au, Pt, Pd, Rh, Ir were isolated separately on a thin layer of the sorbent based on the copolymer of styrene and (3) 5-methylpyrazole (PVB-MP-8T).[366-367] Uranium was isolated on a thin layer of silica gel,[369] and rare-earth elements on Fixion-50 × 8.[130] The distribution of iridium on a thin-layer chromatogram was estimated by a radioactivation method after its isolation from sulfate solutions containing a mixture of other platinum-group metals.[368]

Electrochemical Methods. Electrochemical methods for the detection of inorganic ions on thin-layer chromatograms have not been widely employed enough. However, these methods make it possible to achieve in principle the results with the RSD values down 1%. Electrochemical methods can be used for the determination of inorganic ions both directly in the sorbent layer and after their elution from the sorbent. Conductometric and polarographic detectors are used for this purpose. The most reproducible results can be achieved when polarographic detectors are used. The limits of detection for inorganic substances determined by alternating current polarography were about 1×10^{-11} g/ml.[373] Coulometric[374] and potentiometric[375] methods can be used for the detection of substances in solutions after their elution from the sorbent layer. The latter technique makes it possible to determine sulfide ions in 10^{-17} *M* solution in the presence of fluoride, chloride, sulfate, and phosphates.

Polarography. When a polarographic method of detection is used it is most expedient to carry out direct determination of elements in zones on the plate, although special devices are necessary. For example, an original device is proposed for this purpose.[376] The method is laborious and rather time-consuming. Moreover, it requires good separation and sharp localization of the separated substance on the sorbent layer. Electrochemical

Table 1. Conditions of the elements determination in chromatographic zones by photoacoustic method

Elements	Dyeing reagent	Sorbent	Mobile phase	R_f	Limit of detection	Frequency, Hz	RSD, %	References
Cu, Ni, Zn, Fe	Diethyldithiocarbamate (Cu), Dimethylglyoxime (Ni), Dithizone Zn), 1,10-Phenanthroline (Fe)	Paper, silica gel	-	-	Cu $4x10^{-3}$ Cu 1.23 Ni 1.16 Zn 0.2 Fe 0.4 @[mu]g/mL	38 30 30 30 36	3-10	340
Co, Cu, Ni	1-(2-Pyridylazo)-2-naphthol	Silica gel	Dichloromethane, ethanol, acetic acid 100:5:0.1	Co 0.05 Cu 0.25 Ni 0.7	Co 0.1 Cu 0.4 Ni 5 ng	45	10-50	343
Co, Cu, Ni, Fe	1-(2-Pyridylazo)-2-naphthol	Silica gel (Merck)	Dichloromethane, ethanol, acetic acid 100:5:0.1	-	0.1 ng	45	5 (for 40-50 ng)	344
Hg	Diphenylcarbazone	Filter paper	-	-	20 ng	-	8 (for 40-100 ng)	345
Al, Cu	Quinalizarine (Al), thiooxyne (Cu)	Filter paper	-	-	Al 0.03-0.6 Cu 0.1-1.0 @[mu]g	-	-	346
Ni	Dimethylglyoxime	Filter paper	-	-	5 ng	-	-	347

Table 2. Conditions of the elements determination in chromatographic zones by nuclear-physical methods

Elements	Isotope, its quantity	Accompanying elements, ratio of components	Sorbent	Mobile phase	R_f	Method of detection	Limit of detection, @[mu]g	RSD, %	References
Am, Cm, Pu	^{241}Am, ^{242}Cm, ^{244}Cm, indicator quantity, ^{239}Pu, ^{233}U, ^{238}U 0.1-100@[mu]g	U:Pu=500:1 U:Am=20000:1	Silica gel KSK	TBF - benzene (1:1); (1:10)	Am 0.0 Cm 0.0 U 1.0 Pu 1.0	Radiometry on the plate, radioautography	Indicator quantities	-	121
Pu	^{241}Pu	U, Fe, Pb, Ni, Cu, Cr, La, Zr	Silica gel saturated with 3M HNO_3	TBF - Synthine, 23:17	Pu 1.0, other elements 0.0-0.3	Radiometry on the plate, radioautography	Pu 0.1	10-15	363
Am	^{241}Am	La, U, Ni, Pb, Fe	Silica gel (Silufol) saturated with 4M $LiNO_3$	0.1-0.2 M TOA in cyclohexane	Am 0.5-0.7; Ni Pb, Fe 0.0; La 0.7-0.8	Radiometry	Am 0.05	5-8	120
Na, K	^{24}Na, (1.6-6.4)x10^3mCi ^{42}K, (0.12-0.48)x10^3mCi	Mg	Kiselgel with starch	Ethanol - acetic acid (100:2)	-	Radiometry on the plate with the lead diafragm	-	<1	21a
XeO_3	^{153}Xe, ^{131}I	IO_3^-, IO_4^-	Al_2O_3, unfixed layer	Acetone - 57% $HClO_4$ 9:1	IO_3^-, IO_4^- 0.0 XeO_3 0.67	Scanning	-	-	112

Cr, Mn, Fe	^{51}Cr, ^{54}Mn, ^{59}Fe, ^{60}Co, ^{65}Zn, ^{109}Cd; 0.5-1@[mu]Ci	Co, Zn, Cd	Silica gel (horisontal TLC)	Methanol - diethyl ether 20:80 with NH_4CNS 0.4 mg/mL	-	Automatic scanning	-	8-10	360
I	^{125}I	Aminoacids	Kiselgel N with starch	Chloroform - methanol - NH_3,50:25:2.5	0.55	Scanning	-	113	
F, I	^{18}F, ^{123}I, ^{124}I, ^{130}I; 600 ± 100 pCi	Organic molecules	Silica gel (Merck)	-	-	Scanning	-	-	357
Rare earth elements	^{90}Y, ^{93}Y, ^{156}Eu, ^{153}Sm, ^{149}Pm, ^{151}Pm, ^{147}Nd, ^{143}Pr, ^{141}Ce, ^{143}Ce, ^{140}La	^{99}Tc, ^{99}Mo, ^{97}Zr, ^{238}U, ^{140}Ba, ^{91}Sr, ^{132}Te	Silica gel	Diethyl ether.-bis-(2-ethylhexyl) phosphate - HNO_3; 100:3:2	Te, Mo, Zr, U 1.0; Ba Sr, Te 0.0, rare earth elements-intermedial values	Autoradiography	-	-	313
Rare earth elements	-	U	Silica gel KSK with starch	Tributyl phosphate -	Rare earth elements	Autoradiography	Indicator amounts	-	314

TABLE 2 (Continued)

				benzene 5:95	0.0; U 1.0				
Ce, Eu	^{144}Ce, ^{151}Eu, ^{152}Eu	Forms of varios valence: Ce(III), Eu(II), Eu(III)	Silica gel KSK, starch	Tributyl phosphate-1:10; water	Ce(III) Eu(II), 0.0; Ce(IV) Eu(III) 1.0	Radiometry after zone removal from the plate	-	-	104, 105
Pr, Tb	^{143}Pr, ^{160}Tb	Forms of various valence: Pr(III) Pr(IV), Tb(III), Tb(IV)	Silica gel KSK, starch	Tributyl phosphate - benzene, 1:10; water	Pr(III) Tb(III) 0.0; Pr(IV) 0,5-0,7 Tb(IV) 0,6-0,7	Radiometry after zone removal from the plate	-	-	103
S, P	^{35}S, ^{32}P, 0.72 and 0.2 mCi	--	Indium oxides	Methanol - trichloroacetic acid - dimethylamine, 55:3:52 Water - ethyleneglycol 55 : 5	—	Autoradiography	^{32}P 10^{-16}g	-	364
P, Cl	^{32}P, ^{38}Cl	Forms of various valence; $P_2O_7^{4-}$ PO_4^{3-}, PO_3^{3-}	Kiselgel MN S-HR	Methanol - NH_3 - 10%trichloroacetic	$Cl^- < ClO_2^- < ClO_3^- < ClO_4^-$	Neutron irradiation and separation by TLC, for ^{32}P-	-	-	365

				acid - water, 50:15:5:30 for P; isopropanol - tetrahydrofurane - conc. NH_3, for Cl		@[beta]-activity measurements on the plate, for ^{38}Cl- @[beta]-activity measurements after removal from the plate			
Pt, Pd, Rh, Ir, Au, Ag	-	Cu, Fe, Co, Mg, Ca, Al	Microcrystalline cellulose and adsorbent PVB-MP-8T (1:1)	1M HCl	Noble metals 0.0; others 1.0	Radioactivity measurem. after re- the plate and neutron irradiation	-	-	366, 367
Ir	^{192}Ir, short-lived isotopes ^{104}Rh, ^{104m}Rh, ^{197}Pt, ^{109}Pd	Pt, Pd, Rh	Silica gel (Woelm)	0.5M H_2SO_4	Ir, Rh≈ 1.0; Pt, Pd 0.0	Radioactivation analysis on the sorbent	Ir 0.01 @[mu]g	12	368
Rare earth elements (in rocks)	^{90}Sr, ^{90}Y, ^{46}Sc, ^{140}La, ^{141}Ce, ^{147}Nd, ^{153}Gd, ^{152}Eu, ^{153}Sm, ^{169}Yb, ^{170}Tu, ^{160}Tb	Ba, Sr, Mg, Ca, Sc, Ti, Zr, Hf, Fe, Sn, V, U, Cr Al, Th, etc. Rock forming elements	Fixion 50x8 in Na-form, circular mode of TLC	0.1M Oxalic acid - 2M NH_4Cl (pH 8-9)	Rare earth elements 0.0-0.1	Radioactivation analysis on the sorbent	0.05-10 @[mu]g per 1g of rock	5-20	136
U (in mine-	^{238}U, ^{239}U, ^{239}Np	Various elements in	Kiselgel	Hexane - tri-	-	Radioactivation	U 0.02% in mine-	-	369

TABLE 2 (Continued)

rals)		minerals		butyl phosphate (100:1) saturated with 4.7M HNO_3		analysis on the sorbent	rals		

Table 3. Conditions of the element determination in chromatographic zones by visual methods.

Object analyzed	Elements determined	Sorbent	Mobile phase	R_f	Dyeing reagents	Limit of detection or range of determined concentration	RSD, %	References
Waste .waters..	Fe, Ni, Cu, Zn	Fixion 50x8 in Na-form	4M CH_3COONa, pH 7.3	Ni>Cu >Zn> Fe=0	0.1% Ethanol solutions of rubeanic acid for Cu, dimethylglioxime for Ni; 0.1% carbon tetrachloride solution of dithizone for Zn and 1% water solution of NH_4SCN or Na_2S for Fe	0.3-6.0 mg/mL	8-14	408
Techn logical and waste waters	Set of the heavy metals in the form of diethyldithio-	Silufol (trapezoidal plates)	Acetone, chloroform	-	Inherent colors of chelates	5-10 values of maximum permissible concentrations (MPC)	-	409

	carbaminates (Cu, Ni, Cd, Fe, Cr, Zn)							
Waste waters of halvanic workshop and technological solution	Ni, Cu, Cr	Chelating cellulose with azopyrocatechol groups	n-Butanol-acetone-glacial acetic acid-5% NH_3-water; 7:5:3:3:2	Ni 0.19 Cu 0.25 Cr 0.71	Inherent colors of chelates	0.05-2 @[mu]g in the zone	-	410
Sea and fresh water	Hg, Cu, Cd	Silica gel	0.1% NaCl	-	2-(4-Iodophenyl)-3-(4-nitrophenyl)-5-phenyltetrazolium chloride - enzime - 0.1% solution of N-methylphenazonium methasulfate buffer solution (pH 7.2); 10:10:2:4	Cu 100 ng Hg 50 ng Cd 1@[mu}g	-	411
Platinum-based alloys of noble metals	Au, Pt, Pd, Rh	DEAE - cellulose in Cl^--form	3M NaCl	Rh> Pd> Pt> Au	0.1% Solution of sulfochlorophenol azorhodanine in H_3PO_4 (1:1)	Few micrograms	-	377 412
Cassiterite	Sn (II), Sn (IV)	Fixion	1M H_2SO_4	Sn(IV) 0.0 - 0.08; Sn(II) 0.3 - 0.9	0.1% Solution of Pyrocatechol Violet	0.1@[mu]g	-	413
Rocks	Rare earth elements Eu	Silanized silica gel	Diisopropyl ether-tributyl phosphate-conc. H_2SO_4; 100:80:90	-	0.25% Solution of 1,10-phenanthroline, NH_3, UV-radiation for Eu; 0.015M solution of Neothorine, NH_3 for La, Ce, Pr, Nd,	Eu 0.01-0.02 @[mu]g	-	414

TABLE 3 (continued)

					Sm, Gd, Tb, Er, Y, Dy			
Vegetable juices (watermelon, potatous, tomates, cucumbers)	NO_3^-	Silica gel (Silufol)	Acetone-water, 10:1; Ethanol-water, 10:1; Acetone-ammonia, 1:1	0.98 - 1.0	0.5% Solution of diphenylamine in conc. H_2SO_4	10@[mu]g/g	30	415
Mixtures of noble metals from the natural objects	Au, Pt, Pd, Rh	DEAE-cellulose	3M LiCl in 1M HCl	Au 0.20 Pt 0.10 Pd 0.05 Rh 0.10	0.5% Ethanol solution of p-nitroazodimethylaniline in 0.05 M acetate buffer solution (pH 2.2)	Au o.40, Pt 0.35, Pd 0.50, Rh 0.90 @[mu}g	10 - 30	305
Palladium mixed with non-precious metals	Pd	Modified chelating cellulose with the groups of sulfonitrophenol M	0.5-1.5M H_2SO_4	Long peaks at the start	Inherent colors	0.1-0.3 @[mu]g	-	416
Mixtures of noble metals	Pd, Au, Pt, Rh (Ir)	Silica gel with starch saturated with NH_4Cl (pH 2)	10^{-5}-10^{-6}M solutions of EDTA (pH 2)	Pd 0.03 Au 0.43 Pt 0.63 Rh 0.95 Ir 0.99	0.1% Solution of pyridilazonaphthol in 95% ethanol for Pd; 1% solution of Bismuthol II (Pt, Pd, Au) etc.	-	-	417
Mixtures of rare earth elements	La, Ce, Pr, Nd, Sm, Eu, Gd, Y,	Silica gel KSK with NH_4NO_3	0.11M HSCN in methylethyl ketone	La 0.08 Ce 0.24 Pr 0.31 Nd 0.38	0.1 Ethanol solution of Arsenazo I was added to 35% water solution of urotropin	1-5 ng	10 - 30	418

	Er, Yb	and starch 1:0.1:0.01		Sm 0.52 Eu 0.56 Gd 0.60 Y 0.65 Er 0.68 Yb 0.72				
Mixtures of Mo(W), La(Y) as component of refractory alloys	Mo, W, Y, La	Silica gel with starch, microcrystalline cellulose LK, DEAE-cellulose	0.1-0.5M TOA and 0.2M TOA. HCL in toluene 0.1-8M LiCl	La 0.0 Y 0.0 Mo, W 1.0 La 1.0 Y 1.0 Mo,W 1.0 - 0.22	0.1% Water solution of Pyrocatechol Violet for Mo and W; 0.1% of Arsenazo III in buffer solution (with pH 2) for Y and La	-	-	419

detection of substances on the plate was preformed in the continuous flow variant of TLC using commercially available equipment.[377] The sorbent zones containing the substance to be determined were transferred into a polarographic cell.[378,379] Excess sorbent did not interfere with the quantitative determination. The RSD was 3% under these conditions.

The components of a semiconductor alloy Sn-Au were separated by TLC on silica gel fixed on the plate by starch. Then gold was eluted from the chromatographic zone and determined by stripping oscillographic polarography.[380] The RSD of gold determination was 3% when the gold concentration was 0.3 μg/mL. A voltammetic technique was used for the determination (after elution) of heavy metals separated on a thin layer of sorbent.[381]

Conductometry. This method is convenient in the use of continuous flow separations. A conductometric detector is described,[382] that is suitable for TLC and paper chromatography. The detector consists of two parallel narrow gold plates (electrodes) placed on the sorbent layer. The conductometric cell is connected to a Wheatstone bridge with a differential amplifier. The output of the amplifier is connected with a recorder. One end of the plate is immersed in the eluent. The signal of the bridge becomes constant after stabilization of the eluent flow rate. From 2 to 10 μL of the analyzed mixture are applied onto the plate. The chromatographic peak is recorded when the zone of component is passing between the electrodes. The described detector was used for the analysis of aqueous solutions of Fe and Zn (2 μg/mL each), Fe and Mn (2 μg/mL each), Fe and Co (0.75 and 1.70 μg/mL), Fe, Cr, Co (1.5, 2.0, and 2.0 μg/mL). The separations were performed on the plates with a thin layer of silica gel G in various systems of solvents. The detector signals are linear in a large range of concentrations of the determined substance.

Kinetic Methods. Highly sensitive kinetic methods with spectrophotometric indication were employed for quantitative determination of the small amounts of palladium, rhodium, and iridium in chromatographic zones after their isolation from chloride[306,383] or sulfate[383-386] solutions and separation by TLC. The kinetic method for the determination of rhodium and iridium is based on the use of catalytic oxidation of manganese with hypobromide in alkaline medium. The determination of palladium is based on the reaction of manganese (III) reduction catalyzed by palladium (II) chloride. Kinetic determinations are very sensitive (the limits of detection are about $\approx 10^{-4}$ μg/mL), and, simple and rapid. There is no need in sophisticated equipment and expensive reagents to carry out kinetic measurements.

It is necessary to first remove the sorbent for the kinetic determination of rhodium in a chromatographic zone, because the presence of sorbent in the reaction vessel results in a decrease of the rate of the catalytic reaction of this element.[384] A technique of rhodium elution from the sorbent was developed that met this requirement.

The distribution of rhodium and iridium trisulfates on the chromatograms were investigated by a kinetic method. Conditions were found for maximum concentration of rhodium and iridium in the upper chromatogram zone in the studies of TLC behavior of the formed complexes in water and in sulfuric acid solutions (up to 3 M H_2SO_4).[385] A similar technique was used for the investigation of the properties of the sulfate complexes of these elements in highly concentrated acid solutions (3 to 18 M H_2SO_4).[386]

Spot Size Measurements (Planimetric Techniques). The determination of a substance in a chromatographic zone from the area of the formed spots is the technically easiest method. It does not require special sophisticated and expensive instrumentation. The calculations of the amount of substance in the spot are based on simple relationship: the logarithm of the substance mass is a linear function of the square root of the spot area.[21a,387,388] Some other relationships have been established but usually only a linear part of the function is employed. Area measurements are certainly not very accurate for the quantitative estimation of thin-layer chromatograms. The RSD values are usually about 10%. This technique can be used as a simple semiquantitative method. To obtain the most reliable and reproducible results of the planimetric estimations of thin layer chromatograms, it is necessary to obey thoroughly certain experimental conditions. These are first of all homogeneity of the sorbent particle size and its constant activity, stability of the layer thickness, constant composition of the vapor phase in the separation chamber, precise application of analyzed sample, and uniform size of the starting spots.[21a] To determine a substance in a spot from its area, calibration plots or additional techniques are employed. It is more preferable to construct the calibration plots on the basis of the data obtained on the same chromatographic plate.

There are some difficulties in the determination of a relationship between the quantity of the determined substance and the spot area. These difficulties arise from the fact that the spot edges are often diffuse, and the distribution of the substance in the spot is not uniform. Such difficulties can be avoided using a special procedure, channel TLC.[389] Better accuracy and more rapid planimetry of spots can be achieved by projecting the spot of the developed chromatogram by means of an epidiascope with eightfold enlargement.[390] It makes possible to determine the areas of the spots up to 80 mm^2 with the RSD less than 1%. The area of precipitation zone in precipitation chromatography is proportional to the ion concentration in the sample solution. Iodide, bromide, chloride, and phosphate ions were quantitatively determined from such a dependence using silver nitrate for the treatment of the silica gel layer. The mobile phase was the mixture isobutanol-ammonium acetate (4:1).[391]

Planimetric methods were employed in quantitative TLC for the determination of the following elements and ions: alkali and alkaline earth elements,[21a,392,393] iron, cobalt, nickel,[206] iron, cadmium, thorium, aluminium, nickel,[394] lead, chromium, manganese, nickel, mercury, zinc, bismuth, iron,[393] technecium,[395] chromium,[396] silver, vanadium, iron, copper, zirconium, cobalt, thallium, aluminium, lead,[397] mercury,[398] rhenium,[308,399-401] selenium, tellurium,[402] ortho- and pyrophosphates.[403]

Visual Semiquantitative Techniques. The simplest and most widely used in TLC for detection, identification, and semiquantitative determination of substances is visual estimation of the size and intensity of color (or fluorescence) of spots. The human eye is a detector in this technique, and human mind is a calculator. An opinion is expressed that 90% of the whole information about TLC we obtain due to visual sensing.[6] Hundredths and sometimes thousandths parts of a microgram of substance can be detected visually.

Visual techniques are very convenient for the observation of chromatographic behavior of the different ionic forms of elements on a sorbent thin layer, when easily hydrolyzed or polymerized elements are investigated. For example, the hydrolysis and polymerization of sulfate, nitro, and nitronitrite complexes of platinum,[404,405] sulfate complexes of rutenium,[406] the behavior of molybdenum and rare earth elements in hydrochloric acid solutions[407] have been investigated. Some conclusions about chemical transformations of ionic forms of elements in solutions were made on the basis of the changes in the chromatographic mobilities of elements, diffusivity and multiplicity of zones in combination with the results of spectrophotometric investigations of the solution studied. Semiquantitative visual determination of a substances in the zones was carried out by comparison with a series of zones reference samples which were usually placed on the same plate. The errors of the determination of substances by visual methods by the comparison of the sizes and color intensities of spots formed by test and reference samples is usually equal to 10 to 30%. To obtain more accurate and reproducible results, the experimental conditions should be standardized (thickness and activity of layer, saturation of chamber, constant path of solvent, etc.). Moreover, some other conditions must be carefully obeyed. In particular, the size of primary zones should be uniform, the volumes of the applied samples have to be accurately measured, the spraying of the plate with the detecting reagent should be uniform, the color of the compound formed should be stable.

The number of works connected with the visual estimation of thin-layer chromatograms of inorganic ions is very large, and it is not expedient to mention all of them in the present review. It is worthy to cite only those of them which contain the results of the systematic investigations of a large number of elements in various chromatographic systems with visual zone detection. Particularly, the works[180,181] can be included into this category (see also Reference 5). The most complete information on the techniques based on visual detection of inorganic ions can be found.[45,46,50] The lists of reagents used for the detection of inorganic ions on the chromatograms after their separation by thin-layer or paper chromatography are presented.[50,51,61] The ring-oven technique (see Section IV.A.1.) and the circular (radial) TLC[407] can be also related to visual semiquantitative methods.

Original methods with the use of visual detection of elements in chromatographic zones are based on the application of modified chelating sorbents with functional groups reacting selectively with the determined ions to form colored compounds. It makes possible to employ such sorbents (in particular, various forms of modified cellulose) for simultaneous selective concentration and detection of ions on the sorbent layer without additional spraying of the chromatogram. The conditions for the concentration and detection of ions on the plate may be the same as in solutions containing the corresponding monomeric reagents. The cellulose sorbents are convenient because the front of the mobile phase ascends on the plate quickly and uniformly. The presence of the chelating groups, providing selective action of the cellulose and detection of zones on the chromatogram without spraying, makes TLC on modified cellulose fast and selective. Some examples of the application of such sorbents are given.[410,416]

Some papers in which the visual technique were applied for semiquantitative estimation of thin-layer chromatograms of various are presented in Table 3. More detailed information about these procedures is reported in Section IV.C.

As in the previous years, the visual methods of detection are currently rather widely used. For instance, 49 ions were visualized after the separation of their various mixtures on thin layers of p-aminobenzyl cellulose in sulfate or chloride media.[420,421] A visual fluorescence method was used for the detection of 20 inorganic cations on thin layer of porous glass.[422] The chromatographic behavior of 58 inorganic ions was investigated by TLC with visual detection on PEI-cellulose using the mobile phase HCl - NH_4SCN. The possibility to separate and identify various mixtures of inorganic ions was demonstrated.[423] The zones of elements were detected visually after the separation of Cd, W, Zr, Zn, and V from some transition metal ions in a solvent system containing DMSO.[424] After the separation of Zn from Cd and Cu (II), the elements were detected in the systems containing mixed organic solvents (5-butylamine, acetone, and formic acid).[425] The visual determination of organophosphorus compounds was carried out[426] with the use of polyethylene polyamines. New systems with impregnated layers of sorbents,[427-429] thin layers of chitin and chitozan,[430] ion exchange sorbents based on silica gel with carboxylic groups[431] are employed for the separation and visual detection of various ions.

A number of works are devoted to TLC separation and visual detection of anions[432-435] and metal complexes.[436-444]

B. Quantitative Determination of Individual Elements in the Chromatographic Zones

The data on the methods for the determination of elements in chromatographic zones are presented in Table 4.

C. Analysis of Natural and Industrial Samples

TLC is employed widely enough for the quantitative analysis of various natural and industrial materials including geological samples (minerals, rocks, ores, soils), various waters (natural and waste), technological materials (metals, alloys, pure substances, salts, reagents), organic materials (biological samples, pharmaceutical, cosmetic preparations, plants, foodstuff), etc. The basic information about some methods for the analysis of various samples are presented in Table 5.

Minerals, Ores, and Rocks. TLC was used for the separation of milligram amounts of Hg as well as Au, Sb, As, and Bi from microgram quantities of tellurium for the determination of the latter in cinnabar.[135] The RSD was about 10% when the tellurium content was $n \times 10^{-3}\%$. Uranium was separated from the accompanying ions by means of TLC on silica gel for the determination of this element in minerals.[369] The zones containing uranium were detected by spraying the chromatograms with 3% alcohol solution of hydroxyquinoline and subsequent exposure in NH_3 vapor.

To determine microgram amounts of silver in a sulfide chalcopyrite ore, TLC on modified chelating cellulose containing groups was used in combination with electrothermal atomic absorption.[263,264]

TLC was employed for the detection of trace rare earth elements in ores and rocks[414] A method is proposed for ion-exchange concentration of eight rare earth elements and yttrium by TLC (circular mode) with subsequent neutron-activation determination.[137] Solutions of oxalic acid and ammonium chloride were used as eluting mobile phases. It made possible to quantitatively elute the rare earths into a concentrate. The concentrates then requirements of neutron activation analysis, the most important of which was sufficient purity in relation to the accompanying elements.

Waters. The works on the employment of TLC for water analysis are reviewed.[467] A method of the quantitative fluorimetric determination of selenium in natural waters, potable water, and biological fluids was described.[453] Selenium was determined after its isolation by TLC. The zones of Al, Be, and Cr were also detected on the chromatogram, and these elements were quantitatively determined fluorimetrically.[245]

The visual detection of zones was often used in water analysis. Thus, the possibility was shown to determine four elements (Ni, Cu, Fe, Co) in the form of chelates of pyridine 2-aldehyde 2-quinoline hydrazone in the sea water and sea weeds and algae. Each determination took less than 30 min, the RSD was 5 to 12% when the ring-oven technique was used.[324] The limits of detection (ng) were 10 for Ni, 8 for Cu and Fe, and 5 for Co.

Many ions (Ca^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, Mn^{2+}, Cl^-, SO_4^{2-}, PO_4^{3-}, F^-, NO_3^-, SO_3^{2-}) were semiquantitatively determined in water for boilers using a visual technique after TLC separation on microcrystalline cellulose Avicel.[454]

Table 4. Methods of determination of the individual elements in chromatographic zones

Element	Determination technique	References
	<u>First group of the periodic system</u> (Li, Na, K, Rb, Cs, Cu, Ag, Au)	
Lithium	Fluorimetry	192
Sodium	Densitometry	21a
	Radiometry	21a
	Ring-oven technique	333
	Planimetry	21a
Potassium	Densitometry	21a
	Radiometry	21a
	Planimetry	21a, 35
	Ring-oven technique	333
Rubidium	X-Ray fluorescence	255
	Ring-oven technique	333
Cesium	Ring-oven technique	333
Copper	Densitometry	21a, 199, 202, 207, 211
	Reflectance spectroscopy	208, 218, 220-222, 445, 446
	Spectrophotometry	302, 304
	Photoacoustic spectrometry	341, 343, 344, 346
	IR-spectroscopy	268, 303
	Mass spectrometry	289, 290
	Electron spin resonance	348
	Ring-oven technique	248, 324, 325
	Planimetry	21b, 397
Silver	Densitometry	193
	Reflectance spectroscopy	222
	Atomic absorption spectroscopy	263, 264

	Ring-oven technique	326
	Planimetry	397
Gold	Densitometry	194
	Spectrophotometry	305
	Atomic emission spectroscopy	412
	Polarography	380
	Ring-oven technique	326
	Second group of the periodic system (Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg)	
Berillium	Fluorimetry	245
	Spectrophotometry	292
Magnesium	Densitometry	21a
	Spectrophotometry	292, 293
	Atomic emission spectroscopy	271
	Planimetry	21a, 392
Calcium	Spectrophotometry	293
	Atomic emission spectroscopy	271
Strontium	Densitometry	211
	Spectrophotometry	293
	Atomic emission spectroscopy	271
	Planimetry	393
Barium	Densitometry	211
	Spectrophotometry	292, 293
	Atomic emission spectroscopy	271
	Planimetry	393
Zinc	Densitometry	199, 211
	Reflectance spectroscopy	180, 181, 218, 222
	Colorimetry	295
	Spectrophotometry	295, 302
	Fluorimetry	249
	IR-spectroscopy	274
	Mass spectrometry	289, 290
	Photoacoustic spectrometry	341

TABLE 4 (continued)

	Conductometry	382
	Ring-oven technique	332
	Planimetry	393, 394
Cadmium	Densitometry	197, 198
	Reflectance spectroscopy	222
	Colorimetry	295
	Spectrophotometry	295
	Fluorimetry	249
	Mass spectrometry	289, 290
	IR-spectroscopy	274
	Ring-oven technique	248,332
	Planimetry	394
Mercury	Densitometry	192, 199, 200, 211
	Reflectance spectroscopy	222
	Colorymetry	295
	Spectrophotometry	295, 300-303
	Photoacoustic spectrometry	345
	IR-spectroscopy	274
	Mass spectrometry	289, 290
	Ring oven technique	332, 335
	Planimetry	393, 398
	<u>Third group of the periodic system</u> (Al, Ga, In, Tl, Y)	
Aluminium	Densitometry	213
	Reflectance spectroscopy	222
	Spectrophotometry	294
	Fluorimetry	245, 246
	Photoacoustic spectrometry	346
	Planimetry	394, 397
Gallium	Densitometry	213
Indium	X-Ray fluorescence	259
Thallium	X-Ray spectrometry	259

	Ring-oven technique	335
	Planimetry	397
Yttrium	Spectrophotometry	312
	X-Ray fluorescence	255
	Ring-oven technique	328
	<u>Fourth group of the periodic system</u>	
	(Ge, Sn, Pb, Ti, Zr, Hf)	
Germanium	Fluorimetry	247
	Ring-oven technique	247, 331, 332
Tin	Reflectance spectroscopy	222
	Fluorimetry	447
	X-Ray fluorescence	259
	IR-spectroscopy	274
	Ring-oven technique	332, 334
Lead	Densitometry	211
	Reflectance spectroscopy	222, 243, 244
	Spectrophotometry	302, 339
	X-Ray fluorescence	259
	IR-spectroscopy	274
	Mass spectrometry	289, 290
	Ring-oven technique	248, 332
	Planimetry	393, 397
Titanium	Fluorimetry	247
	Ring-oven technique	247, 328, 330 331
Zirconium	Spectrophotometry	196, 309, 311
	Ring-oven technique	328, 330
Hafnium	Spectrophotometry	196
	<u>Fifth group of the periodic system</u>	
	(P, As, Sb, Bi, V, Ta)	
Phosporus	Densitometry	214, 215
	Spectrophotometry	316-318
	X-Ray fluorescence	258

TABLE 4 (continued)

	Autoradiography	364
	Radiometry	365
	Planimetry	403
	X-Ray fluorescence	448
Arsenic	Fluorimetry	247, 331
	Ring-oven technique	247, 331
Antimony	Fluorimetry	247
	Ring-oven technique	247, 331, 335
Bismuth	Densitometry	199, 211
	Reflectace spectroscopy	222
	Spectrophotometry	297, 302
	X-Ray fluorescence	259
	IR-spectroscopy	274
	Ring-oven technique	248
	Planimetry	393
Vanadium	Fluorimetry	247
	Ring-oven technique	247, 330, 331
	Electron spin resonance	348
	Planimetry	394, 398
Tantalum	Atomic emission spectroscopy	270
	<u>Sixth group of the periodic system</u>	
	(S, Se, Te, Cr, Mo, W)	
Sulfur	Densitometry	212
	Planimetry	212
	Spectrophotometry	319
	X-Ray fluorescence	448
	Autoradiography	364
	Ring-oven technique	336
Selenium	Ring-oven technique	334
	Planimetry	402
Tellurium	Spectrophotometry	135, 307
	Atomic absorption spectroscopy	266
	Ring-oven technique	334
	Planimetry	402

Chromium	Densitometry	211
	Reflectance spectroscopy	222, 245
	Spectrophotometry	203
	Radiometry	360
	Conductometry	382
	Planimetry	393, 396
Molybdenum	X-Ray fluorescence	255
	Spectrophotometry	301
	Ring-oven technique	330
Tungsten	Spectrophotometry	311
	Ring-oven technique	330
	<u>Seventh group of the periodic system</u> (F, Cl, I, Mn, Re)	
Fluorine	Radiometry	357
Chlorine	X-Ray fluorescence	448
	Radiometry	365
Iodine	X-Ray fluorescence	448
	Radiometry	113, 357
Manganese	Densitometry	204, 211
	Reflectance spectroscopy	222
	IR-spectroscopy	274
	Mass spectrometry	289, 290
	Radiometry	360
	Conductometry	382
	Planimetry	393
Rhenium	Spectrophotometry	308
	Ring-oven technique	330
	Planimetry	308, 399-401
	<u>Eighth group of the periodic system</u> (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt)	
Iron	Densitometry	205,206, 211
	Reflectance spectroscopy	222
	Fluorimetry	249

TABLE 4 (Continued)

	Ring-oven technique	247
	Spectrophotometry	298, 300
	IR-spectroscopy	274
	Mass spectrometry	289, 290
	Photoacoustic spectrometry	341
	Radiometry	360
	Conductometry	382
	Ring-oven technique	324, 330, 331, 335
	Planimetry	206, 393, 394, 397
Cobalt	Densitometry	199, 202, 206, 208, 211, 225
	Reflectance spectroscopy	220-222, 445
	Colorimetry	295
	Spectrophotometry	295, 296, 302-304
	X-Ray fluorescence	225
	Fluorescence	250
	Atomic absorption spectroscopy	267
	IR-spectroscopy	268, 274
	Mass spectrometry	289, 290
	Photoacoustic spectrometry	341, 343, 344
	Conductometry	382
	Ring-oven technique	248, 324, 325, 328
	Planimetry	21a, 206, 397
Nickel	Densitometry	199, 202, 211
	Reflectance spectroscopy	196, 206, 208, 218,220-222, 445, 446
	Spectrophotometry	295, 299, 301 304
	Colorimetry	295
	Fluorescence	250

	X-Ray fluorescence	255
	Atomic absorption spectroscopy	267
	IR-spectroscopy	274
	Mass spectrometry	289, 290
	Photoacoustic spectrometry	341, 343, 344, 347
	Ring-oven technique	248, 324, 325, 328
	Planimetry	206, 393, 394
Ruthenium	X-Ray fluorescence	259
	Ring-oven technique	326, 327
Rhodium	Spectrophotometry	304, 305
	Fluorescence	250
	Atomic emission spectroscopy	412
	Atomic absorption spectroscopy	265
	Mass spectrometry	289, 290
	Kinetic method	305, 383-386
	Ring-oven technique	325, 327
Palladium	Densitometry	194, 199
	Spectrophotometry	301, 302, 304, 305
	Fluorescence	250
	Atomic emission spectroscopy	412
	Kinetic method	305
	Ring-oven technique	325, 327, 328
Osmium	X-Ray fluorescence	259
Iridium	Fluorimetry	250
	X-Ray fluorescence	259
	Neutron-activation method	368
	Kinetic method	386
Platinum	Densitometry	194
	Spectrophotometry	305
	Fluorimetry	250
	Atomic emission spectroscopy	268
	Ring-oven technique	325

TABLE 4 (continued)

	Zero group of the periodic system (Xe)	
Xenon	Radiometry	112
	Lanthanum and Lanthanides	
Rare-earth elements	Neutron-activation method	137
	Autoradiography	103, 313
	Spectrophotometry	314
	Fluorimetry	250
Lanthanum	Spectrophotometry	312, 315
	Atomic emission spectroscopy	269
Cerium	Spectrophotometry	315
	Atomic emission spectroscopy	269
	Radiometry	104, 105
	Ring-oven technique	330
	Planimetry	394
Praseodymium	Spectrophotometry	103
	Atomic emission spectroscopy	269
	Radiometry	103
Neodymium	Spectrophotometry	315
	Atomic emission spectroscopy	269
Samarium	Spectrophotometry	315
Europium	Radiometry	104, 105
Terbium	Spectrophotometry	103, 313
	Atomic emission spectroscopy	269
	Radiometry	103
	Actinides	
Thorium	Ring-oven technique	248, 330
	Planimetry	394
Uranium	Spectrophotometry	306
	Radiometry	121
	Neutron-activation method	123
	Ring-oven technique	248, 330

	Planimetry	394
Plutonium	Radiometry	121, 363
Americium	Radiometry	120, 121
	Autoradiography	121
Curium	Radiometry	121
	Autoradiography	121

Table 5. Conditions of the element detrminations in the natural and industrial samples

Sample analyzed	Elements or iones determined	Sorbent	Mobile phase	Determination method	Limit of detection or range of determined concentration	RSD, %	References
1. Minerals, ores, rocks							
Monazite	R.E.E.	Silica gel with NH_4NO_3	Tributyl phosphate - methyl ethyl ketone - ethyl acetate - HNO_3	Spectrophotometry	-	-	315
Monazite, technical products, pure elements	R.E.E.	Silanized silica gel	Diisopropyl ether - trihexyl phosphate - HNO_3 (65%), 100:70:6	Visual	0.05-0.1 @[mu]g of rare-earth elements	-	449
Rocks	R.E.E	Silanized silica gel	Diisopropyl ether - triphenyl phosphate - conc. H_2SO_4, 100:80:90	Visual	0.01-0.02 @[mu]g	-	414
	R.E.E. and Y	Fixion 50x8 (circular mode)	0.1M Oxalic acid - 2M NH_4Cl (pH 8-9)	Neutron activation	Eu 0.05; Sm 0.1 Tb 0.2; Yb 0.3 La 0.4; Tu 1.0 Ce 2.0; Nd 10.0 @[mu]g/g	5-20 when the concentration exceeds 5-10 times the limit of detection	137
Minerals	U	Kiselgel	Hexane - tributyl phosphate, saturated with 4.7M HNO_3, 100:1	Activation	0.02% U	-	369
Cinnabar	Te	Silica gel KSK with starch	Tribytyl phosphate - benzene, 3:7	Spectrophotometry after elution	$nx10^{-3}$% Te	10	135

Sulfide chalcopyrite ore	Ag	Chelating cellulose with azo-rhodanine groups	0.01M EDTA	Atomic absorption	-	15	263, 264
Sulfide minerals	20 elements	Silica gel, Amberlit LA-1	2 - 10M HCl	Visual	-	-	450
Minerals from Pakistan	Many cations of 5 analytical groups	Alumina, gypsum, Silica gel	Acetone - 4M HCl - acetyl acetone, 9:0.6:0.4, or 9.6:0.3:0.1. Acetone - 4M HCl, 9.2:0.6, or Acetone - conc.HCl, 9.4:0.6	Visual	-	-	451
25 minerals	15 elements	Silica gel, Amberlit LA-1	2 - 10M HCl	Visual	-	-	452
2. Natural and industrial waters							
Natural and potable water, biological fluids	Se	Silica gel	Chloroform with bytylhydroxy toluene (0.01%)	Fluorescent	250 fg	-	453
Waters	Al, Be, Cr, various chelates	Silica gel	Ethanol with 1N HNO_3, 99:1	Fluorimetry for Al and Be, photometry for Cr	Al 0.1 ppm, Be, Cr 1.0 ppm	-	245
Sea water and sea weeds	Co, Cu, Ni, Fe	Alumina (circular mode of TLC)	-	Ring-oven technique	Ni 10, Cu 8, Co 5, Fe 5 ng	5-12	324
Natural water	Ca, Mg, Fe, Al, Mn,	Microcrystalline	For cations: water - conc HNO_3 - EDTA - dioxane -	Visual or fluo-	Ca 10mg/L; Mg and Fe 10^3,	-	454

TABLE 5 (Continued)

	Cl^-, SO_3^{2-}, SO_4^{2-}, PO_4^{3-}, F^-, NO_3^-	cellulose	antipyrine (4, 4, 0.1, 200, and 2mL, correspondingly) or saturated water solution of simm-collidine in 0.4M HNO_3; for anions: ethanol - pyridine - water - conc.ammonia, 15:5:4:1	rescence	Al 20, Mn 300, F^- and Cl^- 5000, SO_3^{2-} 10^5, SO_4^{2-} $2x10^4$, PO_4^{3-} $2.5x10^4$, NO_3^- 10^4 ng/L		
Water	Fe, Co, Ni, Cu, Mn, Pb, Sn, Hg, Bi, Al, Be, Cr	Silica gel	Methanol - 3M HCl, 99:1, ethanol - 1M HNO_3, 99:1, or n-butanol - benzene - 1M HNO_3 - 1M HCl, 50:46: 2.7:1.3	Visual (dithizonates)	Fe, Cu, Hg, Cd, 0.1, Al, Be 1.0, Cr 8, other 0.5 ppm	-	134, 455
Waste water from galvanic workshops	Zn, Fe, Cu, Ni	Fixion 50x8	4M NH_4CH_3COO, pH 7.3	Visual, densitometry	0.3-6 mg/L	9-14 for visual, 6-12 for densitometry	408
Technological and waste waters from galvanic workshops	Fe, Co, Ni, Cu (diethyldithiocarbaminates)	Silufol (strips of special shape)	Acetone and chloroform	Visual	5-10 values of maximum permissible concentration	-	409
Waste water from galvanic workshops	Co, Ni, Cu, Zn, Cr, Fe, V	Chelating cellulose with azopyrocatechol groups	n-Bytanol - acetone - glacial acetic acid - 50% NH_4OH - water, 7:5:3:3:2	Visual	20-400 mg/L	-	410
		3. Metals, alloys, technical materials					
Platinum and gold-based alloys of noble me-	Pt, Pd, Rh, Au	DEAE-cellulose	3M Sodium chloride	Visual, atomic emission spectroscopy	Pd, Rh, Au, $1x10^{-4}$%, Pt $5x10^{-5}$%	10-20	412

tals							
Molybdenum-based alloy	Ta	Silica gel impregnated with 5-10M HCl	Water - acetone solutions of HCl	Atomic emission spectroscopy	≥0.5% Ta	6	270
Molybdenum alloys with yttrium and lanthanium	Y, La	Cellulose LK impregnated 0.2M solution of trioctylamine chloride in toluene	0.1M HCl	Spectrophotometry after elution	Mo : La(Y) from 100:1 to 1000:1	4	312
Alloys of nonferrous metals	Pb, Cu, Bi, Co, Sn, Ni, Zn	Alumina (unfixed layer)	Acetone - 3M HCl, 2:3	Planimetry	Bi 6, Sn 4, @[mu]g, Zn, Pb 200; Co, Ni 100, Cu 20ng	≤7	456
Steel	Cr	Microcrystalline cellulose	Acetone - conc. HCl - water, 8:1:1	Fluorimetry, photometry	-	-	457
Ferroalloys	Fe, Zn, Co, Ni, Mn, Ca, Cr, Mg.	Alumina	-	Visual with colour drop reaction	Cr 1.56x10^4, Mg 910, Ca 360, Fe 340, Mn 185, Ni 87, Co 38, Zn 9 ng	-	458
Semiconducting alloy Sn-Au	Au	Silica gel with starch	0.1 M HCl	Polarography after elution	Au 300 ng/mL	2.8	380
Didymium, polyrit	Ce (IV)	Silica gel KSK	Tributyl phosphate - benzene, 1:10	Radiometry on ^{144}Ce and spectrophotometry	-	-	105

TABLE 5 (Continued)

Technical tripolyphosphate and products of acid-thermal treatment of phosphorite	Pyrophosphate	Silica gel KSK with maize starch	n-Propanol - trichloroacetic acid - 25% NH_4OH, 95:20.5:0.4	Densitometry	1.1-4 mg/L	5	215
		4. Pure substances, salts, reagents					
High-purity platinum	Rh	DEAE-cellulose (anticircular mode of TLC)	5M Sodium chloride	Atomic absorption spectrometry	10 ng	20	265
Preparations of Lantonoids of various purity	Fe, Cu, Zn, Hg, Co	Silica gel KSK with starch	Acetone	Visual	$nx10^{-2}$-$nx10^{-1}$%	-	104
Salts of uranil nitrate	Rare-earth elements	Silica gel KSK with starch	Tributyl phasphate - benzene, 5:95	Spectrophotometry after elution	$nx10^{-5}$-$n10^{-3}$%	-	314
Cadmium sulfide	Cu	-	-	-	$2x10^{-3}$%	-	207
Solutions of ^{113m}In	^{113}Sn	-	-	-	-	-	119
		5. Biological objects					
Biologi-	Se	Silica gel	Chloroform - butylhydro-	Fluores-	250 fg	-	453

cal fluids, natural water, potable water		(HPTLC)	xytoluene (0.01%)	cence		
Biological objects	Na, K, Mg	Silica gel with starch	Ethanol - glacial acetic acid	Densitometry	-	3-4	21a
Biological specimens, air samples	Cd, Co, Ni, Zn, Hg.	Silica gel with diatomaceous earth, 5:3	Benzene - chloroform - carbon tetrachloride - heptane, 5:2.7:2:2	Colorimetry after elution	1 @[mu]g	8-12	295
Biological tissues	Fe, Co, Ni, Cu, Zn, Mn, Rh, Sn, Cd, Pb	Silica gel	Kerosene - toluene - acetic acid, 66:33:85	Mass spectrometry	-	-	290
Blood and tissues	Fe, Cu, Co, Ni, Zn	Alumina for Fe, Co, Ni, Cu; cellulose for Zn	Methyl isobutyl ketone - pentyl acetate, 2:1	Circular TLC	-	5	459
Biological tissues	Se	Silica gel	Ethyl acetate - toluene, 1:4, for normal-phase TLC Ethanol - water - acetic acid, 65:35:1, for reversed-phase TLC	Fluorimetry, densitometry, autoradiography	0.1 ng	2	460
Human urine	Hg	Silica gel 960 (Merck)	Chromosolv	Densitometry	0.5 ng	-	209
6. Vegetable materials, foodstuffs							
Oats, cereals	Ni, Co, Cu	Silica gel G	Acetone with 0.5% conc. HCl	Reflectance spectroscopy	10-50 ng	2-5	219
Cotton	Mg	Alumina	Acetone - n-butanol - am-	Visual	100-300 ng	-	461

TABLE 5 (Continued)

seeds, their peels, cottonoil cake			monia - water, 65:20:10:5				
Syrup	NO_3^-	Silufol F-254	n-Propanol - conc.ammonia, 2:1	Densitometry	≈1% NO_3^-	6	216
Vegetable juices	NO_3^-	Silufol	Acetone - water, 10:1	Visual	10-15 mg/L	-	415
Foodstuffs	Ortho-, pyro-, tri-, and tetraphosphates	Kiselgur G (Merck)	Isopropanol - water - 20% ammonia (75:25:0.3) with 4% trifluoroacetic acid	Densitometry	Ortho-1.0, pyro-0.5, tri-0.25, tetra-0.13 @[mu]g	-	214
Caviar	Boron	Silica gel G (Merck)	Ethanol - benzene	Visual	-	-	462
		7. Pharmaceuticals and cosmetic preparations					
Medicines	Ag	Silica gel	Chloroform - benzene, 20:3	Densitometry	50 ppm	-	193
Pharmaceuticals	Mn	Silica gel	Pyridine - methyl isobutylketone - chloroform, 20:4:1	Densitometry	-	-	204
Eluate from generator with $^{99}MoO_4^-$ for producing ^{99m}Tc	^{99m}Tc	Cellulose Watman CC41	Methanol - water, 9:1	Radiometry	-	-	463
Radioactive pharmaceuticals labelled	^{99m}Tc	Silica gel G (Merck)	Methyl ethyl ketone or 0.9% NaCl solution	Radiometry	-	-	395

with ^{99m}Tc							
Medicines	Hg	Kiselgel G (Merck)	Benzene	Spectrophotometry of dithizonate	100 ng	-	303
Sodium chromate for injections labelled with ^{51}Cr	^{51}Cr	Silica gel, cellulose, etc.	Water - ethanol - conc. ammonia, 125:50:25	Radiometry	-	-	464
Various radioactive pharmaceuticals	^{51}Cr, ^{131}I, ^{113m}In, ^{92}P ^{203}Hg, ^{57}Co ^{75}Se, ^{198}Au ^{99m}Tc	Silica gel, Istman Kodak	0.1M NH_4OH, 0.1M NaOH, 1M HCl; methanol; 0.9% NaCl; chloroform - toluene (4:1); ethanol - NH_4OH (7:3); acetone - water - HCl, (7:2:1).	Radiometry	-	-	465
Vitamins, soaps	Co, Pb, Zn, Cu, Ni, Hg	Silica gel	Chromosolv	Densitometry	0.5 ng	-	209
Shampoo	S	-	-	Spectrophotometry	≈1%	5	212
Lipstick	Hg	Silica gel	Cyclohexane - benzene, 1:2	Densitometry	10 ng	-	192
8. Miscelaneous objects							
Magnetic fraction of interstellar dust particles	Fe, Co, Ni	Silica gel KSK	Acetone - 3M HCl, 99:1	Densitometry	-	9-22	206
Nuclear fuel	Rare-earth elements	-	-	Radiometry	-	-	313

TABLE 5 (Continued)

Mineral oils	Pb	Microcrystalline cellulose	Acetone - 10M HCl - water 7:1:2	Fluorimetry	200-300 ng	-	243, 244
Air	Pb	Amberlit CG-120, cellulose	Solution for collecting Pb from air	Visual	-	-	466

Yamane et al. determined 14 metal ions in the form of their dithizonates, 8-hydroxyquinolinates and 2-methylquinolinates.[134,245,455] Toxic metals (Zn, Cu, Ni, Pb, Hg, Cd) can be preliminary extracted with chloroform from a water sample in the form of diethyldithiocarbamates at pH 4.6. Then these metals are separated by TLC on a thin layer of Kiselgel SIL N-HP (Macherey-Nagel & Co.), with the mixture of benzene and hexane (5:1) as mobile phase. The visual identification of these metals can be carried out after their transformation into the dithizonates by spraying the chromatogram with a dithizone solution.[468]

Ion-exchange TLC was applied to the determination of Zn, Fe, Cu, and Ni in waste water of halvanizing workshops.[408] The preliminary concentration of the determined elements was carried out by coprecipitation on magnesium hydroxide. The metals were determined in the chromatographic zones by visual or densitometric techniques. A semiquantitative method was proposed for the determination of heavy metals (Fe, Co, Ni, and Cu) in technological and waste waters at the level of 5 to 10 maximum permissible concentrations. The diethyldithiocarbaminates of the determined elements were separated on Silufol plates in the shape of stripes and determined directly on the plates using a visual semiquantitative method.[409]

Heavy metals (Co, Ni, Cu, Zn, Cr, Fe, and V) were determined by TLC in waste waters of halvanizing shops in the concentration range from 20 to 400 mg/L. A chelating cellulose-based sorbent containing azopyrocatechol groups was used.[410] The following mixtures of elements were separated: Fe - Cr, Fe - Zn, Fe - Co, V - Co, V - Zn, Ni - Co, Ni - Zn, Cr - Cu, Cr - Ni, Cr - V, Cr - Co, Cu - Co, Cu - Zn, Fe - Co - Cr, Fe - Co - Zn, Cr - Ni - Co, Cr - V - Co, and V - Co - Zn. The sorption zones were colored without additional spraying of the chromatograms. The element contents were determined semiquantitatively from the intensities of zone color. The limit of detection was 0.05 to 2 μg of an element in the zone.

Metals, Alloys, Technical Materials. A method for the determination of tantalum in molybdenum-based alloys (0.5% and more) was developed.[270] The tantalum was separated from molybdenum using water - acetone solutions of HCl as mobile phase. The amount of tantalum in the concentrate obtained was determined by atomic absorption spectrometry.

TLC was employed for test-analysis of platinum- and gold-based alloys.[412] Anion-exchange DEAE cellulose was used as sorbent. The zones of alloy components (Pt, Pd, Rh, Au) were visualized by spraying the chromatograms with a sulfochlorophenol azorhodanine solution. The elements were determined semiquantitatively by comparison of the sizes and color intensities of the separated zones with the scale obtained with the use of reference solutions. Atomic emission spectroscopy was used for the quantitative determination of the elements in the zones.

The quantitative densitometric determination of magnesium in aluminum-based alloys was carried out by TLC on the mixed layers of cellulose and an ion-exchanger Amberlite IRP-69. The zone visualization was performed using an ethanol solution of 8-hydroxyquinoline.[469]

Pyrophosphate contents of technical tripolyphosphate and products of acid thermal processing of phosphorite were determined with RSD 5% by TLC in combination with densitometry.[215] Binary alloys of yttrium (or lanthanum) with molybdenum were analyzed using anticircular TLC in combination with spectrophotometric determination.[312]

Technical preparations of rare earth elements (such as "didim" and "polyrit") were analyzed to determine Ce (IV) by use of TLC and radiometry (144 Ce) or spectrophotometry with arsenazo III.[105] This method made possible to separate Ce (IV) from trivalent rare earth elements.

A semiconductor alloy of Sn - Au was analyzed by use of TLC and oscillographic stripping polarography. The gold was determined after its separation from the matrix (tin) by TLC on a thin layer of silica gel.[380]

The employment of a combination of TLC and sampling by anode dissolution makes it possible to determine chromium in steel fluorimetrically.[457] A special design of electrode was developed for sampling by electrolysis. The technique of ascending TLC on an unfixed layer of alumina was applied to the determination of Pb, Cu, Bi, Co, Sn, Ni, and Zn in alloys of nonferrous metals.[456] It is possible to carry out the quantitative separation of Pb^{2+} from Hg_2^{2+}, Hg^{2+}, Tl^+, Bi^{3+}, Sn^{4+}, Sb^{3+} by TLC with the use of chelating mobile phases containing DMSO[428] in the case of analyses of Pb-containing alloys.

The determinations of Fe, Zn, Co, Ni, Cr, Mn, Ca, and Mg in ferrites were performed with the use of visual detection.[458] Sodium, potassium, calcium, and magnesium were determined in clays and in burned brick.[470]

Pure Substances, Salts, and Reagents. Rhodium was determined in pure platinum (99.99%) by electrothermal atomic absorption after its separation from the matrix and concentration anticircular TLC on DEAE-cellulose.[265] Trace common elements (Fe, Cu, Hg, Ca, Zn) were detected in high-purity rare-earth metals (99.95% and more pure) at concentrations of 10^{-2} to 10^{-1}%.[104] Rare-earth elements in the range $n \times 10^{-5}$ to 10^{-3}% can be determined in high-purity uranil nitrate by use of TLC. The sample weight varied from 0.05 to 5 g depending on analyte concentrations.[314] Down to 0.002% of copper was determined in CdS by TLC separation combined with densitometry.[207] Coprecipitation with HgS was employed for copper preconcentration.

Daughter ^{113m}In was separated from parent ^{113}Sn by TLC on a thin layer of Kieselgel with the mobile phase methanol-2 *M* NaCl-1 *M* HCl (45:5:0.5).[119] The initial ^{113}Sn remains in the lower part of the plate, whereas ^{113m}In migrates to the upper part. Both elements are detected using a color reaction with ditizone or pyridylazonaphtol. Such a technique can be employed to control the purity of ^{113m}In solutions.

Biological Samples. A procedure was developed for the fluorimetric determination of selenium in biological fluids and waters.[453] Densitometric measurements at 530 nm were used for the determination of Na, K, and Mg in biological fluids.[21a] The colorimetric determination of Cd, Co, Ni, Zn and Hg was performed after their separation by TLC and elution from the corresponding zones with chloroform.[295] Mass spectrometry was applied to the determination of Fe, Co, Ni, Cu, Zn, Mn, Rh, Sn, Cd, and Pb in biological tissues after isolation by TLC in the form of tetraphenyl porphyrin complexes.[290] Some metal ions were isolated and identified by TLC in samples of human placenta.[471]

Foodstuffs and Plant Materials. The methods for the analysis of foodstuffs using TLC are reviewed.[472] A combination of TLC and reflectance spectroscopy was used for the determination of nickel, cobalt, and copper in oats and in other cereals.[219]

The densitometric determination of the ortho-, pyro-, tri-, and tetraphosphates in foodstuffs was carried out after their separation by TLC.[214] The qualitative detection of boron in the form of boric acid in caviar was carried out by TLC on a thin layer of silica gel with the mobile phase consisted of ethanol and benzene (1:10).[462] Acetic acid, NH_4OH, and sulfuric acid (1:1) served as reagents for visualization.

Nitrate ions were separated from other oxyanions (ClO^-, IO^{4-}, BrO_3^-, CrO_4^{2-}, MnO^{4-}, SeO_3^{2-}, SeO_4^{2-}, VO_3^-, etc.) on Silufol-

254 plates with the use of a mixture of n-propanol and concentrated ammonia (2:1) in the analysis of plant materials (e.g., molasses).[216]

A visual technique was proposed for the semiquantitative estimation of the concentration of nitrate ions in vegetable juices. The colored zones of nitrate on thin-layer chromatograms after treatment with diphenylamine were compared with a scale obtained with the use of reference solutions under identical conditions.[415] The lowest limit of detection of nitrate ions in the analyzed sample was 0.1 μg in the individual zone that corresponded to the nitrate concentration 10 mg/L in the test juice. This technique can be used for the determination of nitrate in any vegetable products including Cruciferae and colored products such as carrot and beet, since the colored substances are separated from the zone of nitrate ions in the course of the chromatographic process.

Pharmaceuticals and Cosmetic Preparations. Silver can be determined in medicines densitometrically after its separation as dithizonate on a thin layer of silica gel.[193] The excess dithizone and the dithizonates of other metals do not interfere with the silver determination. Mercury can also be determined in various medicines as dithizonate using TLC on Kieselgel G (Merck).[303]

To determine manganese densitometrically in pharmaceuticals, sample solution is mixed with pyridine and methanol solution of PAN. The chelate formed is extracted with chloroform after allowing to stay for 30 min in the dark. The chelate forms a red sport on a thin layer of silica gel of the use of the mixture pyridine-methyl isobutyl ketone-chloroform (20:4:1) as mobile phase. The densitometric measurements are carried out at 570 nm.[204]

An aqueous emulsion of shampoo containing 1% of free sulfur was analyzed densitometrically at 295 nm with an RSD of not more than 5%.[212]

Mercury was determined densitometrically in a lipstick.[192] The sample was dissolved in $CHCl_3$. Acetic acid and dithizone were added and the solution was allowed to stay for 30 min in the dark. The formed mercury dithizonate can be well separated from dithizone and dithizonates of other metals by TLC.

Technetium-99 used in medicine in the form of TcO_4^- is usually produced by elution with 0.9% NaCl solution from a generator containing $^{99}MoO_4^-$ on an aluminum support. The radiochemical purity of the eluates obtained from various ^{99}Tc-generarors was controlled by TLC.[463] TLC on silica gel (Merck) in a sandwich-chamber was used for the control of radiochemical purity of the radioactive pharmaceutical preparations labeled with ^{99}Tc.[395] The radiometric determination of ^{99m}Tc was carried out using a scanner or a scintillation chamber; technecium was also determined planimetrically. TLC was also used for the separation of ^{99m}Tc from neutron-irradiated ammonium molybdate. The separation of ^{99}Mo and ^{99m}Tc radionuclides was carried out on a thin layer of cellulose MN 300. The radiochemical purity of a sodium chromate preparation for hypodermic injections labeled with ^{51}Cr was controlled by TLC;[464] $^{51}Cr^{3+}$ was separated from $^{51}CrO_4^{2-}$ on thin layers of silica gel, cellulose and other sorbents.

A rapid TLC technique was described for the determination of radioactive contaminants (^{51}Cr, ^{113m}In, ^{203}Hg, ^{57}Co, ^{32}P, ^{131}I, ^{75}Se, ^{198}Au, ^{99m}Tc) in various radioactive pharmaceuticals.[465]

Miscellaneous Samples. Fe, Ni, and Co were determined in the magnetic fraction of interstellar dust by densitometry after TLC separation.[206] The dust particles were collected in the area of the Tunguska meteorite fall; the particles represented spherules 160 μm in diameters and 3 to 10 μg in weight.

Two-dimensional TLC was applied to the separation of rare-earth elements for their determination in irradiated nuclear fuel.[313]

Lead was determined in oils using a technique that combined TLC for its isolation and fluorimetric measurement of the element content in the chromatographic zone.[243,244] Chromatographic plates with a thin layer of an ion-exchanger Amberlite CG-120 were used for fast visual determination of the lead dust in air.[466] The lead was preliminary collected on filter paper and than dissolved in a buffer solution. Some metal ions were determined in wool fabric by TLC with visual estimation of zones after their visualization by a solution of sodium diethyldithiocarbamate.[473]

CONCLUSION

We do hope that this review will be useful for the community of chemists working in the fields of inorganic analytical chemistry, microanalysis, pharmaceutical chemistry, radiochemistry, medicine, forensic chemistry, umpire analysis, etc. The principal publications are discussed which characterize the present state-of-the-art and recent achievements in the field of the quantitative TLC of inorganic ions. The review enables the reader appreciate the role and importance of TLC for inorganic analysis and radiochemical studies. This paper should make easier the search of needed publication both on the techniques of quantitative estimation of chromatograms and on the analyzed samples and the elements to be determined.

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