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Sorption-spectroscopic and test methods for the determination of metal ions on the solid-phase of ion-exchange materials

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Abstract. Data on sorption-spectroscopic and test methods for the determination of metal ions on the solid-phase of ion-exchange materials published over the past decade are reviewed. The advantages and disadvantages of ion-exchange materials are discussed. The detection limits and selectivity of these techniques are described. The bibliography includes 151 references.

I. Introduction

In recent years, well-known organic reagents have been employed in sorption-spectroscopic and test methods more extensively than in conventional photometry. These techniques, with the use of the same reagent, allow simultaneous gain in sensitivity and selectivity and considerable reduction of the assay time. Remarkable progress in the analytical chemistry of organic reagents has become possible, in particular, owing to the advent of a new generation of instruments for measuring absorption and reflection of solid materials and organic reagents and complexes immobilised on these solids, *i.e.*, the analytical forms of the elements subject to determination, and of compact mini-pumps with controllable flow rates and novel materials as carriers. All these factors have stimulated the development of a great variety of sorption-spectroscopic techniques for the determination of inorganic compounds using organic reagents.

Various materials, *e.g.*, paper, foamed polyurethanes, silica, cellulose, poly(vinyl chloride) and caprone membranes, fabrics, ion-exchange resins, *etc.*, are used as a solid phase in sorption spectroscopy. This review considers the published data on the use of ion-exchange materials as a solid phase.

II. Sorption-spectroscopic methods

Ion-exchange materials have long been in use as sorbents for the concentration and separation of elements.[1–4] The history of selective sorption of metal ions on natural and synthetic materials has been described in a monograph.[1]

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Strongly acidic and strongly basic ion exchangers possess low selectivities. The main procedure for the enhancement of the selectivity of ion exchange materials is the introduction of complexing groups. Complexing sorbents can be synthesised by introducing covalently bound functional groups into the polymer[1–4] or by modification of ion-exchange and non-ionic resins with organic reagents based on ion exchange or adsorption.[5,6]

The sorbents with pendent chelating groups are well-known and have found wide application, though they have a number of drawbacks, such as difficulties of their synthesis, low reversibility of sorption – desorption processes, unsatisfactory kinetic characteristics, *etc.* On the other hand, these sorbents are efficient for the concentration and separation of elements with subsequent spectroscopic determination.

Modified ion-exchange resins prepared from conventional ion-exchange resins by sorption of organic reagents have found extensive use in recent years. Some characteristics of complexing sorbents for the concentration and separation of metal ions have been reviewed.[5] This review considers various types of ion-exchange resins and modifying reagents, their ligand capacity, methods for the determination of metal ions and areas of application of complexing sorbents. It was shown that the retention of a modifying reagent on an ion-exchange resin depends on the type of the modifying reagent, pH of the aqueous solution of the reagent, the nature of the ion-exchange resin and of the exchangeable anion, the structure of resin grains and the stability of the sorbent in different media. The conditions for desorption of the modifying reagent are also described. Other parameters determining the retention and selectivity of metal ion separation on complexing sorbents include the stability of metal complexes with organic ligands and pH of the test solution; the mechanism of the metal ion sorption on a complexing sorbent is similar to that of complexation in aqueous media.

The methods used for the preparation of modified ion-exchangers, their properties and applications are described in a review.[6] Such ion-exchangers are generally used for the selective and group concentration of elements, but their most valuable property is that they allow simultaneous concentration and determination of the corresponding elements. This has been employed in the most advanced directions of analytical chemistry, *viz.*, sorption-spectroscopic and test methods.

In the choice of optimum conditions for sorption-spectroscopic methods, one should take into account the fact that the behaviour of a complex compound in solution and on a solid phase may be different. The sensitivity and selectivity of the determination depend on the composition of the complex formed, on conditions of sorption and analysis, on the mode of immobi-

lisation of the reagent on the carrier, on kinetic features of the process and on many other factors.[7–10]

Depending on the method used to detect the analytical signal, sorption-spectroscopic methods for the determination of elements with the use of modified ion-exchange resins (solid-phase spectrometry) are subdivided into sorption-luminescent, sorption-photometric and diffuse reflectance spectroscopy.

Sorption-luminescent methods are based on the measurement of parameters of the generation or quenching of luminescence in reactions occurring on a solid phase. These methods are not considered in this review.

Sorption-photometric methods (solid-phase photometry) entail the measurement of optical densities of concentrated substances in cells relative to a swollen standard ion-exchange resin having the same degree of granulation, in cuvettes, on neutral glasses or perforated discs, *etc*., after a complex of the compound to be determined with the reagent has been formed on a solid phase. The methods based on the concentration of the ion to be determined either as such or as its complex on an original or a reagent-modified matrix with subsequent desorption of the complex compound and measurement of the optical density of the eluate, also refer to sorption-photometric methods.

Diffuse reflectance spectroscopy consists in the measurement of changes in the diffuse reflection of the solid phase containing a complex compound relative to an original or a reagent-modified solid phase. The latter two groups of sorption-spectroscopic techniques are closely interrelated and employ virtually identical terminology. The term 'sorption-photometric methods' is often applied to describe the methods involving measurement of the magnitude of diffuse reflection rather than optical density.

The absorption spectra of complexes in solution and the spectra recorded on a solid phase by using sorption-photometric methods are usually similar, which considerably simplifies comparison of their behaviour. The prospects for solid-phase spectrophotometry are considered in a review[9] which describes its main advantages, such as the possibility of simultaneous concentration and preparation of analytical forms of concentrated substances which are best suited for further analysis, enhanced stabilities of compounds in the sorbent phase in comparison with those in solutions, increased selectivity of action of chromogenic reagents due to greater rigidity of the molecule fixed on a polymeric matrix. Other advantages include the possibility of using both water-insoluble organic reagents immobilised on ion-exchange resins and reactions yielding poorly soluble compounds or colloidal systems, fast reaction kinetics, high degree of extraction and high variability of the solution volume to the adsorbent mass ratio. The reproducibility of experimental results depends on the procedures used for measurement of the analytical signal and sampling.

1. Solid-phase photometry

Solid-phase photometry (ion-exchange photometry or ion-exchange resin absorptiometry) was originally proposed for detecting trace quantities of elements.[11,12] The ions to be determined can be immobilised on a solid phase in three different ways, *viz*., (i) by sorption of the final complex, (ii) by sorption on an untreated ion-exchange resin followed by the formation of a complex on a solid phase and (iii) by sorption on an ion-exchange resin pretreated with a reagent. A design of a photometric cell suitable for a transparent ion-exchange resin for measuring optical density at appropriate wavelengths has been proposed. This method is characterised by high sensitivity and permits for measurement of microquantities of ions in complex mixtures. Thus the sensitivity of solid-phase photometry in the determination of bismuth exceeds that of conventional spectrophotometric procedures 320-fold. Solid-phase photometry was recommended for use in the analysis of natural waters without preliminary concentration of the elements to be determined.[11,12]

By virtue of higher sensitivity and selectivity which may be achieved by proper choice of a solid phase and a reagent, solid-phase photometry is advantageous over spectrophotometry in the determination of nitrite, fluoride and phosphate ions as well as of metal ions, such as zirconium, titanium, copper and uranium.[13]

In the analysis of geological materials, niobium is adsorbed as a complex with sulfochlorophenol C on the anion-exchange resin AB-17,[14] uranium(VI) is adsorbed on AB-17 modified with 2-(2-thiazolylazo)-5-diethylaminophenol.[15] The detection limit for uranium and niobium oxide is 0.1 μg ml^{-1}. Fe(II), Cu(II), Ni(II), Co(II) and Ti(IV) ions interfere with the determination of uranium. This method is time-consuming, since the sorption and masking of the interfering components take 30 min each.[15]

Vanadium(IV) and vanadium(V) are determined using Eriochromecyanine R immobilised on an anion-exchanger Sephadex DEAE-25. Vanadium(IV) is sorbed first and then vanadium(V) following its reduction with ascorbic acid. Light absorption of the solid phase is measured at 563 and 585 nm in a 1-mm cell; the detection limits of four- and five-valent vanadium is 1.6 and 1.4 ng ml^{-1}, respectively. This method is used for the analysis of natural waters.[16] Modification of the anion-exchanger Sephadex QAEA-2 with 5-bromosalicylhydroxamic acid resulted in a sorbent in which vanadium(V) forms a complex with an absorption maximum at 560 nm. A procedure has been developed for the determination of vanadium(V) with detection limits of 2.2, 1.3 and 0.5 μg $litre^{-1}$ in samples with volumes of 100, 250 and 1000 ml and with shaking time 20, 30 and 50 min, respectively. This method was used for monitoring crude oil and drinking water for vanadium.[17]

The use of the first derivative of the absorption spectrum in solid-phase determinations increases the sensitivity of the method and diminishes the background effect. The detection limit in the determination of molybdenum with pyrocatechol violet on a solid phase in the analysis of water, soil and plant tissues is from 2 to 8 ng ml^{-1}. The complex (1 : 1) is adsorbed on an anion-exchanger of the dextran type. A cell with an optical path of 1 mm is used and absorption is monitored at 716 nm.[18]

Phenylfluorone is used as a complexing reagent for the determination of molybdenum(VI) in sea water; the first derivative of the absorption spectrum of the complex on a nitrocellulose membrane filter is recorded at 536 nm. The concentration of molybdenum in sea water near the Japanese coast was found to be equal to 10.8±0.4 μg ml^{-1} (see Ref. 19).

The method of the first derivative in solid phase spectrophotometry was used for the determination of zirconium on the anion-exchange resin AB-17 modified with Eriochrome Black T,[20] and for the determination of lead as an iodide complex on the cation-exchange resin KU-2 modified with Basic Blue K.[21,22] The detection limits for zirconium and lead are 0.01 and 0.09 μg ml^{-1}, respectively.

Flow-injection analysis makes use of reagents immobilised on a solid phase. For example, in the determination of vanadium(V) in natural water, vanadium is first separated from accompanying components by column chromatography on Sephadex G-25, and then is made to react with 2-[2-(3,5-dibromopyridyl)azo]-5-dimethylaminobenzoic acid immobilised on the anion-exchange resin AG 1X2 in a flow of a formate buffer. The optical density of the complex formed is measured at 650 nm. The calibration curve is linear within the range of vanadium(V) concentrations from 2 to 10 μg $litre^{-1}$; the productivity of analysis is 5 to 6 samples per hour.[23]

Flow-injection systems can be used to determine nickel and zinc by solid-phase spectrophotometry owing to different sorption rates. Nickel and zinc complexes with 1-(2-thiazolylazo)-2-naphthol are adsorbed on silica gel C_{18}. Both complexes are adsorbed at a flow rate of 0.6 ml min^{-1}, but only the zinc complex is adsorbed at a flow rate of 1.5 ml min^{-1}. Analysis can be carried out at zinc and nickel concentrations from 0.1 to 2 mg $litre^{-1}$. The productivity of the method is 20 samples per hour. The procedure for the determination of zinc and nickel with the help of a flow-injection system was used in the analysis of copper alloys.[24]

2. Diffuse reflectance spectroscopy

It can be noted that there are much fewer studies in which changes in optical density are measured as an analytical signal than studies making use of diffuse reflection coefficients.

The advantages of immobilisation of analytical reagents on the surface of carriers over photometry of solutions were discussed in a review.[10] It was shown that the combination of sorption concentration with measurements of surface analytical signals makes it possible to reduce the detection limit of components that are detected by several orders of magnitude, while the use of adsorbents modified with specific organic reagents increases the selectivity of analysis. The same paper provides a classification of modified sorbents according to the type of the carrier and the modifying reagent and describes various procedures for the immobilisation of analytical reagents as well as different applications of the modified sorbents for analytical purposes. In particular, immobilisation of organic reagents from polar and non-polar solvents and their mixtures on different carriers under both static and dynamic conditions and after treatment of sorbents with high-frequency low-temperature plasma in the presence of the vapour of organic compounds is considered. Modification of sorbents with inorganic reagents is achieved by sorption or precipitation of metal hydroxides, oxides or salts on the surface. Composite materials based on modified sorbents are obtained in the casting of polyacrylonitrile fibres by filling them with finely dispersed sorbents.

The problem of what is to be called modified organic reagents, modified sorbents and immobilised reagents was raised in a study[25] where the terms 'modification' and 'immobilisation' referred to the analytical reagent rather than to the carrier. In their attempt to provide a more exact definition, the authors suggested that organic reagents were considered as modified if a second (or third) modifying (monomeric or polymeric) component reacts with an organic reagent and changes its properties, but no new chemical compound is formed. Upon immobilisation on a solid matrix, the reagent is modified with a polymeric ion-exchange resin. However, the majority of investigators use the following terminology: a reagent is immobilised on a carrier (solid phase), while the carrier (solid phase) is modified with the organic reagent.

The methodology of quantitative measurements in diffuse reflectance spectroscopy is described in the review.[26] This study deals with a description of the main factors which affect the accuracy and reproducibility of results of sorption-spectroscopic determination, *viz*., the particle size, moisture content and magnitude of the mirror reflection superimposed on the diffuse reflection resulting in the distortion of the spectrum. An attempt to relate the analytical characteristics of reactions occurring in solution to those occurring on a solid phase were undertaken in order to predict the possibility of conducting photometric reactions on a solid phase. However, the sensitivity of the sorption-photometric procedure from the optical characteristics of the reagent and the product of the photometric reaction in solution cannot be established *a priori*. Nevertheless, the authors presume that the known values of molar absorption coefficients of complex compounds in solution and the known sensitivity of the sorption-photometric method can be used to predict, with a lesser than 20% error the values of the diffuse reflection coefficients for other compounds with known molar absorption coefficients for the same matrix.[26]

A study of formation of mixed-ligand complexes of Zn(II), Cd(II), Pb(II) and Ag(I) on silica modified with thiourea derivatives revealed that the rate of formation of such surface complexes depends on the ratio of stability constants of metal–ligand complexes in solutions.[27]

Modified silica is used for the determination of osmium(VIII) and palladium(II) in wet dedusting sludge and washing acids[28,29] and for the determination of gold.[30] Gold is determined as the metal after thermal treatment of the sorbent and osmium is determined as the oxide. Analytical potentials of silica and foamed polyurethanes containing *N*-propyl-*N*′-[1-(benzothiazolyl-2-thio)-2,2,2-trichloroethyl]ureido or 4-adamantyl-2-(2-hydroxy-1-naphthylazo)thiazolyl (AOT) groups were examined for possible determination of Pt(IV), Pd(II), Au(III), Ag(I), Cd(II) and Hg(II). It was shown that Hg(II) (pH 6.0–8.5) and Cd(II) (pH 9.5–11.0) are quantitatively retained on the AOT-containing sorbent.[31]

It was demonstrated[32] that many regularities of formation of metal ion complexes with organic ligands on the surface of silica gel and in solution are identical for Fe(III), Cu(II), Co(II), Y(III) and La(III). In the case of easily hydrolysable ions, such as Zr(IV), Ti(IV), V(V), W(VI), Mo(VI) and kinetically inert platinum-group complexes, the irregularities are manifested in increased rates of complexation, enhanced complexing ability and formation of mixed-ligand complexes.

The sorption of dithizone (DT), 4,4′-bis(dimethylamino)thiobenzophenone, 4-(thiazol-2-ylazo)naphthol (TAN), 1,10-phenanthroline and high-molecular-weight quaternary ammonium salts (QAS) on silica gel (SG) and cellulose (C) was studied aimed at preparing solid-phase reagents for Hg(II), Ag(I), Pb(II), Zn(II) and Fe(III).[33–35] It was shown that such sorbents are stable in aqueous solutions in a broad range of pH. The optimum conditions for the formation of Cu(II), Co(II) and Zn(II) complexes with TAN–SG, of Ag(I), Hg(II) and Pb(II) complexes with DT–SG, of Co(II) and Fe(III) thiocyanate and Bi(III) tetraiodide complexes with QAS–SG and QAS–C were established. To this end, a variety of sorption-spectroscopic and test methods as well as reactive indicator papers have been devised for express control of these metal ions in natural, drinking and waste waters and biological fluids. The detection limit for these metal ions lies in the range of 0.2 to 10 μg litre^{-1} at a sample volume of 50–100 ml.

Optimum conditions for the sorption of Cd(II), Hg(II) and Pb(II) ions on Silochrom modified with 4-(thiazol-2-ylazo)resorcinol were found. These ions were sorbed from an acetate buffer pH 6.8–7.5 (15 ml) on the sorbent (0.3 g) upon shaking for 5–10 min. The concentration coefficient for Cd(II) and Pb(II) was 85, that for Hg(II) was 300. This procedure was used for the analysis of soils.[36]

The cobalt complex with 1-(2-pyridylazo)-2-naphthol (PAN) is adsorbed on an unmodified silica gel and is firmly retained on the sorbent after acidification with up to 0.5 M HCl. This procedure allows selective determination of 2 to 10 μg of cobalt in drinking and mineral waters. Ballast components are desorbed upon subsequent acidification. The sorption is performed from 100- and 300-ml sample volumes under static conditions; the mass of the silica gel is 0.2 g.[37]

1-(2-Pyridylazo)-2-naphthol immobilised on Silochrom C-120 is used for the determination of indium. The concentration coefficient for indium adsorbed from a 150-ml sample is 500.[38,39]

Immobilisation of aluminone on silica gels containing different groups, with different particle diameters and pore sizes was studied as a sensitive layer of an optical sensor for copper.[40] Immobilisation produced a favourable effect manifested as a longwave shift of the absorption maximum, a decrease in pH for the complexation and an increase in sensitivity and selectivity. A procedure for the detection of copper in foodstuffs with a detection limit of 0.015 μg ml^{-1} was developed.

Diffuse reflectance spectroscopy was used to study the completeness of sorption of Fe(II) and Fe(III) ions as complexes with cathechol-3,5-disulfonic acid on the anion-exchange resin AB-17.[41] This study demonstrated the possibility of separate determination of Fe(II) and Fe(III) ions; a test method was proposed for the determination of iron with a detection limit of 0.01 mg litre^{-1}. Fe(III) ions are determined at pH 3.5, while a sum of Fe(II) and Fe(III) ions, at pH 6–9. The measurements are performed at two wavelengths (500 and 540 nm); the concentrations of Fe ions are calculated from the following equations:

$$\text{Fe(III)}: F_{500} = (5.7 \pm 0.05)\,c + (0.83 \pm 0.04),$$

$$F_{540} = (4.56 \pm 0.05)\,c + (0.66 \pm 0.04),$$

Fe(II): $F_{500} = (4.59 \pm 0.28)\,c + (0.77 \pm 0.33)$,

$F_{540} = (3.7 \pm 0.06)\,c + (0.04 \pm 0.03)$,

where F is the Gourevich – Kubelka – Munk function and c is the iron concentration (μg ml^{-1}). Iron ions are determined at concentrations from 0.03 to 6.4 μg ml^{-1}.

Colorimetric characteristics of coloured sorbates, *viz*., luminosity (L), colour coordinates (A, B), saturation (S), brightness (Y), colour tone (T), shading (E), *etc*., can be used for detecting analytical signals in diffuse reflectance spectroscopy in addition to the diffuse reflection coefficient (R) or the Gourevich – Kubelka – Munk function (F). The use of these colour characteristics as analytical signals makes it possible to determine dissociation constants of organic reagents and increases the sensitivity and accuracy of metal ion determinations. The use of ΔL and ΔY instead of ΔF (where Δ is the difference between the values of the corresponding coefficients for the complex and the reagent) decreases 4- to 20-fold the detection limit for cobalt, indium and nickel with immobilised reagents. According to sensitivity of determination, these values can be arranged in the following order: $\Delta F < \Delta A < \Delta S < \Delta L < \Delta Y$.[42–49]

The Gourevich – Kubelka – Munk function, which allows the establishment of a correlation between analytical signals in the same photometric reaction occurring both in a solution and on a solid phase, is the most frequently used as the analytical signal. The simplest way to express the analytical signal is to present it as a difference in diffuse reflection coefficients of carriers after the passage of control and test solutions at the optimum wavelength.

The intensities of analytical signals depend on the efficiency of sorption of metal ions from solutions and the completeness of conversion of sorbed metals into coloured complex compounds on a solid-phase. The signals, in turn, depend on the acidity of test solutions (Fig. 1 *a*), the mass of sorbent discs (Fig. 1 *b*) and the composition of the reagent solution.

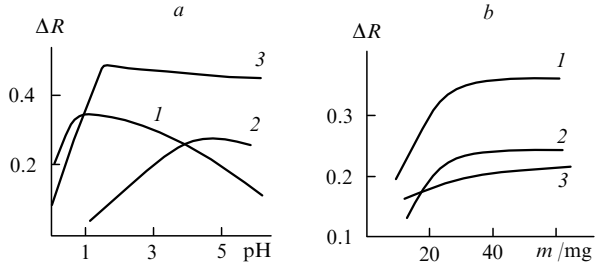


Figure 1. Dependence of the analytical signal of metal complexes on the solid phase of a fibrous sorbent filled with the cation-exchange resin KU-2 on the acidities of solutions (*a*) and the mass of the sorbent disc (*b*) in the determination of iron (*1*), nickel (*2*) and copper (*3*) with potassium thiocyanate, dimethylglyoxime and sodium diethyldithiocarbamate, respectively;
(*a*): c_M = 0.05 (Fe), 0.1 (Ni), 0.1 mg litre^{-1} (Cu); (*b*): c_M = 0.05 mg litre^{-1}.

3. Chemical optical sensors

Sorption-spectroscopic methods and immobilised organic reagents were used in the design of the so-called chemical optical sensors or sensitive elements.[50–85] There are several different interpretations of the term 'sensor'. Thus a chemical sensor is defined as a probe which provides direct information about the chemical composition of the environment. It consists of a physical transducer of analytical signals and a chemically selective layer.[52] Chemical sensors are the main elements of a new generation of analytical devices, such as sensor analysers, which, together with a sensitive element, comprise sample injectors and various devices for the processing of signals and displaying the results, *viz*., the concentration of the tested substance.[53, 54] In other studies,[55, 56] a sensor is referred to as a primary device which selectively responds to changes in definite properties of the environment by converting this information into the corresponding electrical signals, *e.g*., optical signals. We define a sensor as a sensitive element of a sensor analyser.

Sensors are supposed to be recoverable systems, *i.e*., they must easily be reset after the assay is completed. Therefore, the material used as a solid phase should first of all be mechanically and chemically stable. Fibrous materials filled with ion-exchange resins largely meet these requirements.

These materials are cast from suspensions of finely dispersed ion-exchange resins in a solution of polyacrylonitrile in dimethylformamide. Pressing of suspensions through spinnerets produces thin porous polyacrylonitrile fibres filled with ion-exchanger particles. The diameter of a polyacrylonitrile fibre is 30 to 40 μm, the size of carrier particles is 5 to 10 μm, the degree of filling is 50 mass % – 75 mass %. By virtue of their fibrous structure and high degree of dispersion of filling agents, such materials manifest remarkable kinetic properties.

Carriers represent white or light-yellow 0.1 – 0.2 mm thick fibrous plates having a density of 40 to 80 g m^{-2} which are stable in strongly acidic, neutral and weakly alkaline media. These plates are used to manufacture discs. Depending on their diameter, 10 or 20 mm, thickness and degree of filling, the mass of discs varies from 10 to 50 mg.

Prior to use, carriers (in the form of plates or prefabricated discs) are washed with 2 M HCl up to a negative reaction for Fe(III) with thiocyanate ions and then with water up to a negative reaction for chloride ions with silver nitrate and dried in air. Such carriers can be stored at room temperature for an indefinitely long period of time. Prior to use, plates are shaped into discs and swollen in water for at least 24 hours.

Immobilisation of analytical reagents is performed in a static or a dynamic regime. In the former case, the discs are kept in aqueous or aqueous – organic solutions of reagents (10^{-5} – 10^{-6} M) for 5 – 15 min and then washed with water. The concentration of the immobilised reagent varies from 10^{-6} to 10^{-4} mol litre^{-1} g^{-1}. In the latter case, the reagent solution is dripped or pumped through the carrier disc placed in a cell with a sintered-glass filter using a peristaltic pump.

Filled fibrous sorbents can be used in both modified (*i.e*., after immobilisation of the organic reagent) and in the original (colourless) form.

Ions to be determined are concentrated in different ways, *viz*., directly from the test solution with subsequent detection on a solid phase, by concentration of a complex compound formed in the solution and by sorption of the ion in question on a carrier with an immobilised reagent.

Apparently, sorption of a preformed complex is the least appropriate solution of the problem of increasing the sensitivity and selectivity of the method. The advantages of discs with immobilised reagents are as follows: full readiness of the so-called sensitive element for the assay, simplicity and lack of necessity to prepare reagent solutions. Of their disadvantages one may relate limited durability and storage life; nor in all cases can they be recovered.

The obvious merits of colourless discs are that they are easily recovered and that the same discs can be used for the determination of different elements. Another advantage is that the storage life of carriers is not limited. Their demerits are as follows: the necessity to prepare reagent solutions and the need for an additional procedure, the so-called 'development', *viz*., sorption of a reagent on a carrier after concentration of the ion in question.

On the whole, the main attraction of fibres filled with ion-exchange resins is the possibility to vary the degree of their filling and the nature of the ion exchanger and the reagent depending on a concrete selectivity problem. In contrast with other carriers, these materials represent both the sites for colour reactions and the means for concentration of ions to be tested and removal of

ballast components. They are resistant to mechanical actions and manifest high sorptive and kinetic properties, which ensures a high level of sensitivity, which can be attained by passing any volume of test solutions. The use of fibrous materials ensures easy sorption of reagents and tested ions (*e.g.*, by immersion of the carrier into the solution or by passing the solution through the carrier) and easy separation of the solid phase from the solution (*e.g.*, by decanting under static conditions or by pumping under dynamic conditions). This, in turn, allows easy automation of flow sorption-spectroscopic procedures and, if necessary, test operation without any devices based on visual detection.

Studies of fibres filled with ion-exchange resins used as sorbents follow two main lines which include sorption-spectroscopic determination of metal ions based on changes in their diffuse reflection upon complexation with organic reagents on a solid phase (carrier) and elaboration of test methods.

These studies were undertaken with the view of constructing recoverable systems which utilise exclusively fibrous sorbents with immobilised reagents as optical sensors. However, despite its indisputable advantages, this approach significantly restricts the potentials of a new carrier. It was found that organic reagents immobilised on carriers are not always effective in analytical reactions or they change their colour upon immobilisation. Regeneration of optical sensors with immobilised reagents is a complicated task. On repeated regeneration, organic reagents are either destroyed or washed off from the carrier with a regenerating solution. Nevertheless, in some cases sensitive elements can be recovered. Thus in the determination of lead with Xylenol Orange [51] and in the determination of uranium with Arsenazo I,[64] the same sensitive element (the optical sensor) can be used for up to 20 assays. Most frequently, optical sensors cannot be regenerated at all, *e.g.*, a sensitive element for thorium with Xylenol Orange.[51] It is economically more advantageous to replace a sensitive element used as a chemical optical sensor than to regenerate it.

Two types of sensitive elements or chemical optical sensors are presently being developed, *viz.*, fibrous materials filled with ion-exchange resins with and without organic reagents immobilised on them. In the latter case, the analytical reaction with an organic reagent is accomplished after sorption of the tested ion.

In the choice of a particular organic reagent, preference should be given to the most well-studied and accessible reagents possessing good analytical characteristics. Organic reagents containing acid groups are immobilised on materials filled with anion-exchange resins; while those containing basic groups are sorbed on cation-exchange resins. In a few studies, sorption was performed on ion-exchange fabrics with phosphate or vinylpyridinium groups.

Fixation of reagents on solid carriers occurs mainly due to the ion exchange mechanism and partially due to adsorption, formation of hydrogen bonds and other interactions.

Electron and EPR spectroscopy was used to study the properties of 1-(2-pyridylazo)-2-naphthol (PAN) immobilised on polyacrylonitrile fibres filled with finely dispersed ion-exchange resins and its complexes with copper(II).[66] In this study, fibres filled with different ion-exchange resins, *viz.*, KU-2, KB-4, AB-17 and A-5, were employed. The parameters of EPR spectra of copper complexes on a solid phase in the pH range of 1–8 were calculated. It was shown that immobilisation of PAN on a solid phase changes its state (*viz.,* the spread of individual ionic forms of the reagent is shifted and widened) and spectroscopic properties. If the concentration of the reagent exceeds 10^{-5} mol litre^{-1} g^{-1}, this undergoes association on the surface of the carrier. The main contribution to the retention of PAN on these ion-exchange resins is due to ionogenic groups of the carrier; however, under certain conditions, adsorption begins to play a leading role, as is the case with the adsorption of PAN on KU-2 in alkaline media.

The role of the nature of the carrier in complexation is rather complicated and ambiguous and is manifested primarily in its competing interaction with metal ions. By using different carriers, one can vary the concentration of the immobilised reagent on the surface and thus control its reactivity.

The second type of chemical optical sensors proved to be more advantageous than first type sensors. Their additional advantages are as follows. Since sorption and determination are separated by certain time interval, it is possible to introduce masking complexing agents in the concentration and determination steps, which considerably increases the selectivity of the reactions. Also, this particular type of sensor makes use of the original, colourless carriers. This circumstance has stimulated the development of new spectroscopic solid-phase methods (*e.g.,* determination of cations on a solid phase), which consists, for example, in the sorption of metal cations in the form of colourless or weakly coloured anionic complexes on anion-exchange resins and their subsequent detection in the most contrasting colour reaction. Thus the sensitivity of determination of Fe(III) with thiocyanate on the anion-exchange resin AB-17 increases considerably if iron is sorbed in the form of complexes with tartaric or glycolic acids (Fig. 2).[67,68] Comparative data on iron determination with thiocyanate following sorption from solutions of glycolic acid on KU-2- or AB-17-containing fibres testify to a significant increase in selectivity. The selectivity factors are equal to 10 and 20 for Zn, 20 and 50 for Cd, 5 and 200 for the uranyl ion, $\ll 1$ and 10 for Bi and 100 and 3000 for oxalates and phosphates, respectively.

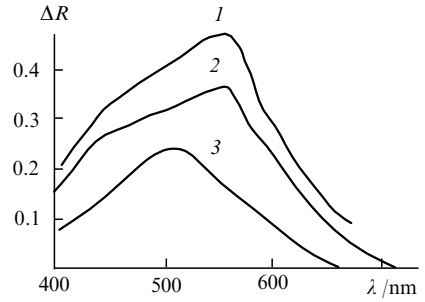


Figure 2. Reflection spectra of the iron thiocyanate complex formed upon sorption of Fe(III) from 0.01 M solutions of glycolic (*1*) and tartaric (*2*) acids and without addition of anions (*3*) on a fibrous material filled with the anion-exchange resin AB-17; $c_{Fe} = 0.2$ μg ml^{-1}.

The new methodology has made possible solid-phase determination of thorium with Arsenazo III. The latter is the best reagent for thorium; however, it changed its colour upon sorption on a carrier, which prevented the assay. If thorium in the form of the oxalate complex is sorbed on fibres containing an anion-exchange resin, it can be determined in the form of the complex with Arsenazo III on a solid phase in strongly acidic media. In this approach, the detection limit is 0.2 ng ml^{-1} (the sensitivity of photometric determination of thorium with Arsenazo III is 0.01 μg ml^{-1}). Uranium, zirconium, titanium, lanthanum, iron, fluorides and phosphates do not interfere with the determination.[69,70]

Fibrous adsorbents filled with ion-exchange resins (AB-17, A-5, KU-2) and the styrene–divinylbenzene copolymer containing no ionogenic groups were studied as possible carriers for a sensitive element for mercury with 4-phenylazo-3-aminorhodanine.[79] It was found that the reagent is tightly bound only to carriers containing ionogenic (both cationic and anionic) ion-exchange groups. However, the sensitive reaction of mercury with the immobilised reagent occurred only on fibres with the cation-exchange resin KU-2. A method has been developed for detecting mercury in waters with the detection limit of 0.02 μg ml^{-1}.

Sensitive optical elements for uranium, mercury and lead have been proposed, which are based on the formation of complexes with Arsenazo III, dithizone and hexaoxacycloazochrome, respectively.[80] In these studies, polyamide, poly(ethylene terephthalate) and cellulose membranes were used as carriers.

These membranes are made of transparent or semi-transparent materials and are resistant to dilute alkalis and acids. Immobilisation of reagents is carried out in a static or a dynamic mode. In the dynamic mode, the solution is allowed to pass over the membrane surface if the pore diameter is less than 0.45 μm. In the case of larger pores, the solution is filtered through the membrane. The ranges of direct determination in water are 0.01 to 0.10 for uranium, 0.005 to 0.05 for mercury and 0.05 to 0.5 mg litre^{-1} for lead.

The possibility of selective determination of uranium(VI) at the level of 2×10^{-8} mol litre^{-1} in the presence of a 100-fold excess of thorium by diffuse reflectance spectroscopy has been demonstrated.[81, 82] In these studies, polycaproamide and nylon membrane filters were used as matrices. The diffuse reflection coefficient, R, is fixed at 660 nm for uranium and 680 nm for thorium and the uranium concentration is determined from a system of equations:

$$R = \varepsilon_U c_U l + \varepsilon_{Th} c_{Th} l,$$

$$c = c_U + c_{Th},$$

where R is the diffuse reflection coefficient, ε is the molar adsorption coefficient, c is the concentration (mol litre^{-1}) and l is the membrane thickness.

The conditions of sorption of azorhodanines, tyrodine and sulfonitrophenol M on polymeric carriers, *e.g.*, caprone mem-

Table 1. Some characteristics of sorption-spectroscopic methods for the determination of metal ions using fibrous materials filled with ion-exchange resins.

Ion (I)	Fibre (fabric)	Sorption conditions	Reagent	Detection limit /mg litre^{-1}	Selectivity factor		Ref.
					M	[M/I]	
Cu(II)	KU-2	pH 1, $C_6H_8O_6$	PAN	0.03	Zn, Cd, Hg, Pb, V, Al, Mn, Ni	> 1	72
	KU-2	0.04 M HNO_3	DETC + EDTA (pH 8.5)	0.002	Zn, Cd, U	100	76
					Fe(III), Ni	50	
					Co	10	
Fe(III)	KU-2	0.1 M HNO_3	KSCN	0.01	Ni	200	76
					Co	50	
					Cd	20	
					Zn	10	
					U(VI)	5	
					Cu	2	
Ni(II)	KU-2	pH 4.5	DMG, 2% NH_3	0.005	Cd, Zn	100	76
					Bi	10	
					Fe(III), Cu, Co	5	
Ag(I)	KU-2	pH 3	Rhodazole X	0.005	Fe, Ni, Co, Zn, Pb,		85
					Pd, Ca, Mg	100	
					Cu	10	
					Hg	2	
Hg(II)	KU-2	pH 1	PAAP	0.02	Pb, Cr, Cd, Ni, Co, Zn	> 10^3	79
					Fe, Cl^-	> 10^2	
					Cu	50	
Pd(II)	KU-2	0.01 M HNO_3	NDEA, pH 2–3	0.0005	Au, Pt, Ru	100	77
					Rh, Ir	1000	
Pb(II)	A-5	pH 5	KO	0.004	Al, Ni, Cu, Zn, Sn	4	51
U(VI)	A-5	pH 6	Arsenazo I	0.007	Fe(II)	100	64
					Fe(III), La	20	
					Al, Th	10	
					Zr	1	
V(V)	AB-17	pH 3.5, NaF, H_2O_2	PAR, 0.1 M HCl	0.002	Zn, Mn, Cr(III), Al	> 100	78
					Fe(III), Cr(VI)	50	
					Cu	20	
					Mo	5	
Cr(VI)	AB-17	pH 2	DPC, 0.05 M H_2SO_4	0.0005	Ca,W,Fe(III), Cr(III), Hg	> 10^3	71, 74, 87
					V, Zn, Co, Ni, Al,	> 10^2	
					Cu, Mo, Mn, Pb, Cd		
Th(IV)	AH-31	$H_2C_2O_4$, pH 2	Arsenazo III, 4 M HCl	0.0002	F^-, PO_4^{3-}	> 10^3	70
					Fe(III)	300	
					La,Ti	50	
					Zr	10	
					U(VI)	5	
Zn(II)	F(I)	pH 10, $Na_2B_4O_7$	DT + DETC + + $Na_2B_4O_7$	0.02	Fe(III), Cu, Co, Ni, Pb	> 1	75
Co(II)	F(II)	pH 5	PAN, 0.05 M HCl	0.0005	Fe(III), Mn	100	73
					Cu, Zn	10	
					Ni	5	

Notes. Abbreviations: PAN, 1-(2-pyridylazo)-2-naphthol; DETC, sodium diethyldithiocarbamate; EDTA, ethylenediaminetetraacetic acid; DMG, dimethylglyoxime; PAAP, 4-phenylazo-3-aminorhodanine; NDEA, *p*-nitrosodiethylaniline; XO, Xylenol Orange; PAR, 4-(2-pyridylazo)resorcinol; DPC, 1,5-diphenylcarbazide; DT, dithizone; F(I), fabric with vinylpyridine groups; F(II), fabric containing PO_3H_2 groups.

branes, fibrous materials filled with cation- and anion-exchange resins and fabrics with ionogenic groups, were studied in the development of sensitive elements for Hg(II), Cu(II), Ag(I), Au(III), Pt(IV) and Pd(II). It was shown that azorhodanines and sulfonitrophenol M immobilised on caprone membranes can be successfully used for the determination of these metal ions with the detection limit of 1 to 15 μg litre^{-1}.

A procedure has been developed [83–85] for the determination of silver based on its sorption on discs from polyacrylonitrile fibre filled with the cation-exchange resin KU-2 with subsequent detection with rhodazole X; the detection limit is 5 μg litre^{-1}.

The main characteristics of methods for sorption-spectroscopic determination of metal ions which employ fibrous materials filled with ion-exchange resins and fabrics carrying ionogenic groups as solid phases are summarised in Table 1.

III. Instruments

Optical sensors for recording analytical signals are used in mini-devices of the well-known companies 'Specord', 'Spectroton', 'Pulsar' and 'Multitest', in mini-photometers 'Merck', *etc*. Recent publications describe two more devices. One of them was developed at the Institute of Analytic Instrumentation of the Russian Academy of Sciences and represents a small-size chemosensor analyser designed for the determination of pH and concentration of metal ions; its operation is based on the principle of reflective photometry of chemosensors made of optically transparent polymers containing organic reagents.[86] Its designers sought to build a specialised instrument for implementation of one or several similar analytical procedures with the aid of sensors having a universal configuration. This approach permits one to perform the measurements in three different regimes, *viz*., measurements of light absorption of the tested object ($-\log R$) relative to the diffusely reflecting substrate or an analogous object with the known characteristics. The second and third regimes are intended for procedures utilising definite types of sensors and allow for calibration. Chemosensors for measuring pH and concentrations of Fe(III), copper and rare-earth metal ions at the level of 2×10^{-3}–2×10^{-5} mol litre^{-1} have been developed.

The apparatus ($150\times130\times80$ mm) has a weight of 1 kg (the volume of the samples varies from 5 to 70 μl) and can be used for measuring reflective properties of coloured reagent papers and multilayer sensitive elements. The measurements are performed at wavelengths from 530 to 700 nm. The duration of the exposure of the sensitive element to the sample is 90–120 s. The apparatus operates on alternating current or utilises the energy of internal accumulators.

The second instrument, *viz*., the optical sensor analyser OSA-TM developed at the Scientific-and-Industrial Corporation 'Kvant' (Rostov-on-Don), is intended for environmental monitoring of natural, drinking and purified waste waters for heavy metals at the MPC and lower levels under both laboratory and field conditions.[87] It is designed as a colorimetric densitometer and is used for measuring diffuse reflection coefficients of optical sensors in flow-through cells as well as for measuring optical densities of coloured solutions in cells for liquid samples. This apparatus ($370\times220\times100$ mm) has a weight of 4.5 kg and operates on alternating current or utilises the energy of accumulators. It is supplied with an integral flow-through optical cell, a peristaltic pump, a microprocessor with push-button control and eight light filters operating at 400–750 nm. Its operation is based on the detection of changes in colour (*e.g*., reflection wich optical sensors or the optical density of the tested solution) as a result of interaction of metal ions with analytical reagents. The analytical signals are shown on a digital display as the transmission (reflection) coefficient, optical density and concentration of metal ions in the tested solution.

The potentials of OSA-TM are exemplified [87] in the determination of chromium(III) and chromium(VI) in surface waters. Chromium(III) is measured photometrically with Arsenazo III, while the concentration of chromium(VI) is determined in a flow-through cell with anion-exchanger filled fibres using complexation with 1,5-diphenylcarbazide on the solid phase. A method was proposed for the simultaneous determination of chromium(III) and chromium (VI) in sanitary–general-purpose water up to 1 : 5 ratio at the concentration of Cr(III) > 0.2 MPC and that of Cr(VI) > 0.1 MPC. The duration of one assay is 10 to 20 min.

A procedure for sorption-spectroscopic assay utilising optical sensors is simple with this instrument. A carrier disc (∅10 mm) is placed in a flow-through cell and the test solution is pumped through the disc at a rate of 10 ml min^{-1} under optimal sorption conditions. If unmodified carriers are used, the reagent solution is pumped through under optimum assay conditions after which the diffuse reflection coefficient is measured.

The main advantage of the OSA-TM analyser is that it allows both routine photometric measurements and measurements in flow-through optical cells where the sorption of the tested ion occurs. The reaction of the ion takes place on a solid phase and is followed by measurement of the analytical signal. A combination of these three processes in a single flow-through cell not only simplifies the procedure but also increases significantly the reproducibility of experimental results owing to the omission of one step, *i.e*., the transfer of the optical sensor from the sorption cell to the measuring cell, which excludes any fluctuations in the sensor wetness. The use of the instrument allows for rapid presentation of experimental results in units of concentration. The construction of the instrument with a flow-through optical cell became possible due to development of optical sensors in which fibrous materials filled with ion-exchange resins or fabrics containing ionogenic groups are used as carriers.

IV. Test methods

Numerous versions of test methods are being actively developed.[88–104] The materials used as carriers for sorption-spectroscopic assays, such as reagent papers, foamed polyurethanes, silica gel, membranes, ion-exchange resins, *etc*., are also employed in test methods. Indicator test systems, *e.g*., from 'Merck', are currently known.

Some densitometric characteristics for express tests have been obtained which are based on the use of reactive reagent papers [96] and are designed for the determination of certain elements with the help of reflective electronic mini-photometers equipped with light-emitting diodes operating at wavelengths of 567±15 and 660±10 nm and a modified device for concentration of 10^{-7} mass %–10^{-5} mass % of components in aqueous media.

The main requirements for test reactions are as follows:[101] high sensitivity (not lower than MPC); high light-transition contrast; proximity of the optimum acidity of assays to the acidity of the tested solution; stability of external effects for a sufficiently long time and upon exposure to light; the possibility to preserve the test form after positive response for subsequent quantitative assay under laboratory conditions; and selectivity.

The methodological aspects of detection and processing of analytical signals in colorimetry have been reviewed.[48,101] The general colour discrimination criterion (ΔE) is the main parameter in making a test scale. In order to increase the sensitivity of a test reaction, special parameters, such as whiteness (W) for colourless sorbents and yellowness (G) for blue-coloured complexes have been introduced. The calibration test scale is built up from the known dependence of the general colour discrimination on the concentration of the tested element. One unit of ΔE corresponds to one colour discrimination threshold; therefore, the concentrations of tested elements are selected in accordance with the corresponding magnitude of ΔE. A reliable sense of difference in light flux intensities is reached if this difference is at least 10%. Therefore, discrete values of colour discrimination with $\Delta E > 10$ are especially preferred in the case of diffuse reflection. If the tested sample loses its colour or is bleached in the course of an

analytical reaction, its whiteness is used for building up a test scale:

$$W = 100 - \Delta E.$$

The lower threshold of tested concentrations in any test method is defined as general colour discrimination (10 arbitrary units) between the original test sample (E_0) and the test sample following its reaction with the tested element (E):

$$E - E_0 = 10 \text{ or } W_0 - W = 10.$$

In the building up of a test scale, one should not go beyond the limits of saturability (ΔS) of the tested sample (20% – 60%) which corresponds to the upper threshold of tested concentrations.

The contrast of a colour reaction is enhanced after application of optical bleaching compounds onto the matrix surface; their operation principle is fluorescence. The presence of these compounds does not influence chemical and analytical characteristics of immobilised reagents. In their presence, reagents are rapidly and evenly distributed over the matrix surface and are well retained in acid media under both static and dynamic conditions. For example, the detection limit in the determination of uranium(VI) with Arsenazo III and application of optical bleaching is 0.001 μg ml^{-1}. The colour of the complex compound is bright green, whereas in the absence of the bleaching agent the complex has a grey-blue colour and has a detection limit of 0.1 μg ml^{-1} (see Ref. 102).

A portable field test system for the determination of numerous elements in water, soil and rainfall has been developed.[103, 104] This assay includes the following steps, *viz*., measurement of the lengths of coloured or bleached zones on reactive reagent papers cut into stripes and pasted into a polymeric film one end of which is brought into contact with the tested fluid, visualisation of colour intensity, measurement of the area of the coloured or bleached zone and visualisation of colouring of the tested fluid after application of reagent papers. The range of tested concentrations is 0.001 – 1000 mg litre^{-1}.

1. Reagent test papers

The majority of publications devoted to test methods deal with reagent papers.[88–121] Heavy metals on the whole are determined with the help of a device which is similar to that used for air sampling (the detection limit is up to 10^{-7} mol litre^{-1}) which employs test papers impregnated with potassium tetraborate and PAN.[107] Rapid tests for the determination of toxic elements in water are carried out on papers, films or glasses with the detection limits of 0.05 for Cu(II), 0.2 for Fe(III), 0.5 for Co(II), 0.03 for Mn(II) and 0.03 mg litre^{-1} for V(V) (see Ref. 108).

Iron ions are determined on reactive test papers with detection limits ranging from 0.02 to 0.2 mg litre^{-1} depending on the method (see Refs 109 – 111). A tape method was proposed for the determination of Fe(III) (0.5 – 3.5 mg litre^{-1}) on papers impregnated with the anion-exchange resin Amberlite IRA 400 modified with sodium ethylenediaminedi(hydroxybenzylphosphonate).[112]

Immobilisation of pyrazole-containing formazanes and hydrazones on the base-paper increases their sensitivity with respect to transition metals. Express tests for determining Cu(II), Ni(II) and Co(II) at the level of 10^{-7} mass % – 10^{-8} mass % have been developed.[113] Test paper impregnated with Michler's thioketone, potassium dihydrogenphosphate, sodium thiosulfate (in order to reduce copper and remove active chlorine) and Triton X-100 was proposed for the determination of copper in drinking water (the detection limit is 0.05 mg litre^{-1});[114] test paper containing the nickel complex with 2-nitroso-1-naphthol, diphenylguanidine, thiourea and ammonium fluoride was used for the determination of cobalt.[115]

An express test method for the determination of manganese in drinking water is carried out on paper containing a multicomponent reagent. This analysis is based on the measurement of the time interval during which the indicator zone changes its colour as a result of oxidation of Malachite Green with potassium periodate (KIO_4) catalysed by manganese(II) ions. The detection limit is 0.03 mg litre^{-1} (see Ref. 116).

Zinc ions are determined in foodstuff using reagent test paper (FMOPF-6C) at pH 8.0. The effect of copper ions is eliminated by addition of thiourea.[117] Reagent test paper was recommended for use as indicators for multicomponent assay of water:[118]

Ion	Concentration range /mg litre^{-1}	Ion	Concentration range /mg litre^{-1}
Pb(II)	0.001 – 0.1	Bi(III)	0.001 – 0.1
Cu(II)	0.001 – 0.1	Fe(II)	0.01 – 0.2
Fe(III)	0.01 – 0.2	Hg(II)	0.2 – 2
Cr(VI)	0.1 – 5		

Lead ions are determined using a reagent test paper (RTP) metal test after its fast separation from Cu, Fe and Zn in aqueous solutions (pH 6.0), emulsions and suspensions using the sensor filter of a pocket indicator ultrafiltration unit.[118]

Stripes of reagent paper are used for the quality control of water;[119] paper stripes impregnated with diphenylthiocarbazone are used for test determination of trace amounts (15 ppb) of lead in drinking water,[120] while paper stripes soaked with a covalently bound multidentate chromogenic reagent of the formazane type are used for the determination of mercury with a detection limit of 0.05 mg litre^{-1} (see Ref. 121).

The detection limit in enzymic determinations of mercury and organomercurials on foamed polyurethanes, paper and chitosan with immobilised peroxidase is 10^{-5} μg ml^{-1}, *i.e*., below the MPC for mercury.[122–127] A sorption-catalytic procedure for the determination of manganese [128] is based on preliminary concentration of manganese(II) ions on cellulose filter paper with chemically bound diethylenetriaminotetraacetate groups (DETATA) and subsequent catalytic oxidation of 3,3′,5,5′-tetramethylbenzidine with KIO_4. The optimum conditions for this reaction in solution and on filter paper were found to be different. Preliminary concentration of manganese on DETATA-paper allows for a nearly 10-fold decrease in the detection limit (up to 6×10^{-6} mg litre^{-1}) and expands the range of tested concentrations up to $5 \times 10^{-6} - 2.5 \times 10^{-3}$ mg litre^{-1}. The selectivity of the assay is higher in this case: after preliminary concentration from a 20-ml sample, determination of 1 ng of manganese is insensitive to a 1000-fold molar excess of other ions. This method is applied in the analysis of tap and river water.

An express test for the detection and determination of vanadium, which catalyses the oxidation of *p*-diethylaminoaniline with bromate, on glass or poly(methyl methacrylate) at pH 4 – 5 has been developed. The detection limit decreases in the presence of ferrone which potentiates the catalytic effect of vanadium. This determination is selective with respect to many metals. The interference of Fe(III) ions is eliminated with fluorides. The detection limit for vanadium is 0.09 mg litre^{-1} (see Ref. 129).

The approaches used in test methods are very diverse. For example, in one of them the analyte is concentrated in a limited area on a hydrophobic surface by evaporation and the element is detected by colour reaction or fluorescence. This procedure is used to determine aluminium with Xylenol Orange in tap water at pH 8.0 or with lumogallione at pH 7.0 (the detection limit is 2.7 ppb) (see Ref. 130).

Molybdenum is determined by an ion-exchange drop reaction with azide with the detection limit of 2 μg in 0.09 ml of the sample using the anion-exchange resin Bio-Rad AG 1X8.[131] In the determination of chromium(VI), five to ten beads of the anion-exchange resin Amberlite IR-120 (H-form) are placed onto a white plate and Malachite Green is added (drop reaction). The green colouring of the resin surface observed after 10 min points to the presence of chromium; the detection limit is 1.6 μg.[132]

Iron ions are determined on the anion-exchange resin AB-17X8Cl with the detection limit of 0.01 μg ml^{-1} (see Ref. 41). Polyester fabric based on poly(ethylene terephthalate)

is used as a substrate for an array of multipurpose indicators. This procedure permits complete elimination of cross contamination of reagent paper stripes with chemical reagents from adjacent stripes.[133]

2. Silica gel

Test methods on silica gel have attracted attention in the past decade.[8, 34, 49, 134–140] It was found[49] that the optical characteristics of Fe(III), Cr(VI), Mn(II), Ni(II), Cu(II) and Zn(II) complexes with PAN on Silochrom C-120 are very similar to those in solution. Thus sorption of 1-(2-pyridylazo-)-2-naphthol and 4-(2-pyridylazo)resorcinol (PAR) from aqueous solutions of various acidities was investigated and the conditions for the preparation of modified adsorbents with predetermined capacity with respect to azo compounds were established. Sorption of PAN and PAR on Silochroms C-80 and C-120 was studied under static conditions.[134] A procedure has been developed for the determination of the reagents in the sorbent phase. The indirect assay consists in the measurement of changes in light absorption of solutions after immobilisation. Alternatively, azo compounds are determined upon oxidation with cerium(IV) in the modified sorbent phase. Maximum modification of the silica surface is observed at pH < 3. The protonated form of PAR is the most intensively adsorbed on silica hydrated to the greatest degree. The completely dissociated form of PAR is not adsorbed by the silica surface. The degree of adsorption of PAN at pH 4.0 decreases as the proportion of acetone in the tested solution increases. At an acetone concentration of 60 vol. %, PAN is not adsorbed on silica surface. Complete adsorption of PAN with Silochrom C-120 usually takes 20 minutes.

It was found that the efficiency of sorption of azo compounds depends on the structure of the silica, its porosity and specific surface. With an increase in specific surface, sorption of the reagent increases. At lower specific surface, the greater part of the reagent diffuses into the sorbent and the pore sizes thus become critical. It was found that adsorbents with a low capacity with respect to the reagent (*e.g.*, < 25 μmol g^{-1}) are more preferable for use in test methods (see Ref. 134).

The colorimetric method was used for separate determination of Cu [$(0.4-22.0)\times10^{-6}$ mass %] and Zn [$(3.8-39.0)\times10^{-6}$ mass %] in natural water on PAN-modified silica.[48] Cobalt was determined with PAN immobilised on silica gel[135] using a test method based on colour discrimination by luminosity (the detection limit is 0.004 μg ml^{-1}); its quantitative determination was performed using the Gourevich–Kubelka–Munk function (the detection limit is 0.03 μg ml^{-1}). It was found that on going from diffuse reflection coordinates (ΔF) to sorbate colour coordinates (ΔL) with a test reagent, the sensitivity and reproducibility of determination of cobalt increase 4- and 1.5-fold, respectively. 4-(2-Thiazolylazo)resorcinol immobilised on silica gel was recommended[136] as the test reagent for Co(II), Pd(II) and U(VI) (the detection limits are 0.02, 0.005 and 0.03 μg ml^{-1}, respectively).

Test methods for the determination of Co(II), Cu(II) and Zn(II) with 1-(2-thiazolylazo)-2-naphthol, for the determination of Ag(I), Hg(II), Pb(II) with dithizone and for the determination of Co(II), Fe(III) and BiI_4^- thiocyanates with quaternary ammonium salts on silica gels and cellulose have been developed.[34]

The optical and colorimetric characteristics of immobilised 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol and its complexes were obtained in the analysis of sorption of indium and uranium(VI) ions on Silochrom C-120. Test methods for the determination of indium with a detection limit of 0.002 μg ml^{-1} (see Ref. 44) and uranium with a detection limit of 0.25 μg ml^{-1} (see Ref. 137) have been developed; subsequent determination of uranium by diffuse reflectance spectroscopy in the sorbate phase reached a detection limit of 3.5 ng ml^{-1}. The optimum conditions for the formation of uranium(VI) complexes with PAR immobilised on KU-2, foamed polyurethane and Silochrom C-120 were established as pH of 5.8–8.2 and an equilibration time of 20, 20 and 15 min, respectively. An advantage of PAR immobilised on KU-2 is that it elicits analytical signals of greater magnitude and produces a broader plateau on the optical density versus pH of the complex solution curve. This reaction is selective in the presence of cyclohexanediaminetetraacetic acid; the detection limit is 0.1 μg ml^{-1} (see Ref. 138).

A linear-colouristic method[141–143] is based on the linear dependence of the length of the coloured zone of the display tube on the concentration of the tested compound. In this procedure, hydrophobic carriers, such as silica gels Diasorb-C_{16} and Diasorb-phenyl, are modified with known analytical reagents. The dimensions of the coloured zone depend on the nature of the carrier, quantity of the adsorbed reagent, internal diameter of the display tube, flow rate and pH of the sample. By varying tube diameter, one can change the concentration range of the tested element. The detection limits for various elements vary from 10^{-8} to 10^{-6} mol $litre^{-1}$.

Silica gel modified with lead diethyldithiocarbamate can be used as the indicator powder for the determination of copper ions with a detection limit of 1.5×10^{-8} mol $litre^{-1}$ in the presence of 1000-fold excess of Ni(II), Zn(II), Cd(II) and Co(II).[141] PAN and Xylenol Orange immobilised on silica gel are used for the determination of copper and iron.[142] At equal concentrations of these ions ($< 5\times10^{-6}$ mol $litre^{-1}$), two differently coloured zones are formed in the tube filled with silica gel Diasorb-phenyl-PAN, *viz.*, crimson (Cu) and green (Co).[142] The possibility of determination of cobalt and Fe(III) in the same sample at the MPC level with the use of a tube filled with silica gel Diasorb-C_{16} modified with 1-nitroso-2-naphthol was demonstrated.[143] This method is characterised by ease of tube preparation and rapidity of analysis.

The possibility of direct determination of trace amounts ($10^{-9}-10^{-5}$ mol $litre^{-1}$) of heavy metals in water, soil extracts and other natural subjects by the sorption-colouristic method was considered.[144] Coloured zones are produced upon frontal chromatographic sorption of Hg(II), Cd(II), Pb(II), Co(II), Cu(II), Bi(III), Sb(III) and Fe(III) on microcolumns packed with cellulose and polystyrene-based ion-exchange resins modified with polar residues (*e.g.*, sulfides of zinc, cadmium and manganese as well as hexacyanoferrates of calcium and lead) and organic reagents.

3. Foamed polyurethanes and membranes

The polymeric matrix of foamed polyurethanes, which have a membrane structure, contains both polar groups and hydrophobic fragments. This makes foamed polyurethanes helpful tools in test methods for the determination of metal cations, polycyclic hydrocarbons, phenols, heteropolyacids, surfactants and other compounds.[93, 123, 138, 145]

A number of test reactions on foamed polyurethane carriers have been developed for determination of several elements (the colour scale ranges, Δc, are indicated):

Element	Cr	Ni	Co	Ti	Fe
Δc /mg $litre^{-1}$	0.1–1	0.1–40	0.04–6	0.01–0.5	0.004–0.6

1,5-Diphenylcarbazide and dimethylglyoxime are used for the determination of chromium and nickel, respectively; potassium thiocyanate is used for the determination of cobalt, titanium and iron.[93]

Immobilisation of chitosan HRP on foamed polyurethane gives a more active and stable sorbent than on a polystyrene plate or on paper. Oxidation of *o*-dianizidine proved to be the most efficient indicator reaction which made it possible to decrease the detection limit for mercury to 25×10^{-3} ng ml^{-1}. The rate of the indicator reaction is monitored visually by fixing the moment of appearance of red-coloured oxidation product. Thiourea was used to enhance the inhibitory effect of mercury. This method is not only highly sensitive, but also highly selective: only 10^5-fold excess of Cd(II), Pb(II) and Bi(III) interfere with the determination.[123]

Optimum conditions were established for complexation of uranium(VI) with PAR immobilised on foamed polyurethane,

KU-2 and Silochrom C-120. The detection limit is 0.1 μg ml^{-1} (see Ref. 138).

Test methods employing poly(vinyl chloride) and caprone membranes were recommended for the determination of Hg(II), Ag(I), Cu(II), Au(III), Pd(II) and Pt(IV) in the presence of at least a 10-fold excess of Fe(III), Ni(II), Co(II), Zn(II), Cd(II), Be(II), Al(III) and alkaline-earth metals with detection limits from 1 to 15 μg $litre^{-1}$. Immobilised azorhodanines and Sulfonitrophenol M were used as reagents.[85]

A highly sensitive field test for the determination of chromium(VI) in water at the level of < 1 μg $litre^{-1}$ is based on the formation of a coloured chromium complex with 1,5-diphenylcarbazide in 0.1 M sulfuric acid and its sorption on an ion-exchanger incorporated into the membrane.[146] The intensity of coloration is proportional to the chromium concentration in the range from 0.05 to 50 μg $litre^{-1}$. In 50-ml samples, chromium is determined with a detection limit of 10 ng $litre^{-1}$.

4. Fibrous materials filled with ion-exchange resins

Fibrous filled materials are perfect carriers for visual assays. They allow for simultaneous concentration and determination of tested elements as well as for variation in the nature of the adsorbent depending on a concrete experimental task. The tested ions may first be adsorbed on original, colourless materials and are then 'developed'. Alternatively, adsorbents with immobilised reagents can be used. Carriers can be used under both static and dynamic conditions; they are resistant to mechanical and chemical actions.

Fibrous materials filled with ion-exchange resins and fabrics with ionogenic groups are used as carriers in visual determinations of metal ions using known colour reactions with organic reagents.[69, 74, 99, 147–151] The tested element is selectively concentrated on a solid phase; the use of highly sensitive and highly selective reagents facilitates its determination in drinking water at the MPC and lower levels.

In addition to remarkable kinetic properties (*e.g.*, ease of sorption and high filtration rates), fibrous materials endowed with ion-exchange properties manifest high stabilities in aggressive media. Therefore they can be used for sorption and determination of metal ions under drastic conditions in the presence of large concentrations of masking substances and in highly acidic media. These materials are distinguished by handling convenience, are easily transferred with pincers and do not lose their shape upon stirring, heating in solution, drying, *etc*.

Express tests are based on colour reactions of metal ions with reagents on a solid phase. Fibrous materials filled with ion-exchange resins used as carriers and fabrics with ionogenic groups in the form of discs 1–2 cm in diameter serve not only as the reaction sites but also as sorbents for the concentration of tested ions (and thus increasing the sensitivity of the reaction) and their separation from ballast substances. The use of carriers containing specific groups allows one to lower the detection limit and to increase the selectivity. In addition, these express methods employ well-known, organic reagents that have proved to be efficient in photometric assays and are commercially available which significantly simplifies their introduction into routine analytical practice.

The analytical procedure is simple and easily accessible. Reagent solutions are added dropwise to a tested solution (10 ml) to ensure optimum sorption conditions after which the carrier disc is introduced. The solution is agitated for 5–7 min and then decanted with the disc held back by a glass rod. One to three drops of the reagent solution are dripped onto a colourless unmodified disc and the colouring of the disc is compared with the calibration colour scale obtained under identical conditions. In some cases, the scale, enclosed in a polyethylene film, is preserved for a sufficiently long period of time. Carrier discs can be regenerated with acids and re-used after washing with water. Some characteristics of modern test methods for visual assessment of metal ions utilising fibrous materials filled with ion-exchange resins and fabrics with ionogenic groups are summarised in Table 2.

Table 2. Some characteristics of test methods for the determination of metal ions which utilise fibrous materials as a solid phase.

Ion (I)	Fibre (fabric)	Sorption conditions	Detection conditions	Selectivity factor		Change in disc colour	Colour scale /mg $litre^{-1}$	MPC /mg $litre^{-1}$	Ref.
				M	[M/I]				
Fe (III)	KU-2	0.1 M HNO_3	KSCN	Ni	200	white → red	0.1–1	0.3	99
				Co	50				
				Cd	20				
				Zn	10				
				U(VI)	5				
				Cu	2				
Cu(II)	KU-2	0.01–0.05 M HNO_3	DETC + + EDTA	Cd, Zn, U(VI), Mn(II)	100	white → yellow	0.05–1	1	99
				Fe(III), Ni	50				
				Co	10				
				Bi	5				
Ni(II)	KU-2	pH 5–6	DMG	Cd, Zn	100	white → red	0.1–1	0.1	99
				Bi	10				
				Fe(III), Cu, Co	5				
Pd(II)	KU-2	0.01 M HNO_3	NDEA	Ni, Cu, Zn, Cd	10^4	yellow → red	0.05–0.5	–	77, 147
				Co, Rh, Ir	10^3				
				Fe(III), Au, Pt, Ru	10^2				
V(V)	AB-17	pH 2.5, 0.05% H_2O_2	PAR, 1 M HCl, 50–60 °C	Ni	500	yellow → violet	0.1–1	0.1	148, 149
				Cu	200				
				Mo, Cr(VI)	50				
				Fe(III)	20				
				V(IV)	2				

Table 2 (continued).

Ion (I)	Fibre (fabric)	Sorption conditions	Detection conditions	Selectivity factor		Change in disc colour	Colour scale /mg litre^{-1}	MPC /mg litre^{-1}	Ref.
				M	[M/I]				
Cr(VI)	AB-17	0.01 M H_2SO_4	DPC	W(VI), Cr(III), H_2O_2	$>10^3$	white → pink	0.01 – 0.25	0.05	74, 99
				V(V), Zn	500				
				Ni, Co, Al, Hg, Fe(III)	200				
				Pb, Cd	100				
				Cl^-, SO_4^{2-}	$>10^4$				
Cr(VI) + + Cr(III)	AB-17	oxidation of Cr(III) to Cr(VI)		determination of Cr(VI) against Cr(III) and a sum of chromium ions		the same	0.01 – 0.25	0.05	99
Mo(VI)	AB-17	pH 3 – 5, $C_6H_8O_6$	Phenyl-fluorone, 0.5 M HCl	Fe(III)	600	orange → crimson	0.02 – 0.4	0.25	149
				Cr(VI)	100				
				Sn, Zr	20				
				V(V), Th	10				
Th(IV)	AN-31	0.004 M $H_2C_2O_4$, pH 2	Arsenazo III, 6 M HCl	F^-, PO_4^{3-}	$>10^3$	pink → grey-green	0.01 – 0.1	–	69
				Fe(III)	300				
				La, Ti	50				
				Zr	10				
				U(VI)	5				
U(VI)	AN-31	pH 6, acetate buffer	Arsenazo I	La, Fe(III)	20	pink → blue	0.1 – 1	0.05	64, 147
				Th, Al	10				
				Ti(IV)	2				
				Zr	1				
U(VI) + + Th(IV)	AN-31	0.01 M $NaHCO_3$, 0.001 M EDTA, pH 9 – 10	Arsenazo III, 7 M HCl	Th : U	1 : 3 – 3 : 1	pink → green	0.02 – 0.24 (sum)	–	150
				Zr	3		0.01 – 0.12 (thorium)		
Zn(II)	F(I)	pH 9 – 10, borate buffer	DT + DETC	Fe(III), Cu, Co, Ni, Pb	> 1	orange → crimson	0.1 – 0.5	1.5	99
Co(II)	F(II)	pH 5 – 6, acetate buffer	PAN	Fe(III), Mn	100	orange → green	0.05 – 0.5	0.1	99
				Cu, Zn	10				
				Ni	5				

Studies with two or three elements or with one element in different oxidation states are being developed during the past decade. For example, both Cr(VI) and Cr(III) ions can be determined following oxidation of Cr(III) by heating with ammonium persulfate in 0.05 M H_2SO_4 followed by decomposition of the excess of the oxidant by boiling with subsequent sorption of Cr(VI) ions on discs prepared from fibres filled with an anion-exchange resin and their detection with 1,5-diphenylcarbazide, which gives a pink coloration. The solution is divided into two parts one of which is used for the determination of only Cr(VI) ions and the other one, for the determination of both Cr(III) and Cr(VI) ions after which the concentration of Cr(III) ions is determined from the difference between the two measurements.[99]

If uranium(VI) and thorium(IV) are present in solution in 1 : 3 to 3 : 1 ratios, they can be determined in the same sample with Arsenazo III in the presence of a 3-fold excess of zirconium. Sorption is performed from a carbonate medium in the presence of ethylenediaminetetraacetic acid; the assay is carried out after acidification with 6 – 7 M HCl. The overall concentration of uranium and thorium is determined judging from the coloration of wet discs; thorium is determined judging from the coloration of dried discs. The coloration of the uranium complex with Arsenazo III disappears upon drying due to a decrease in acidity.[150]

V. Conclusion

At present, the detection limits for metal ions attainable using sorption-spectroscopic and test methods reach 10^{-3} – 10^{-2} mg litre^{-1}. Enzymic test methods provide an exception, for they allow measurements of up to 10^{-5} mg litre^{-1}. However, by reason of high complexity of these reactions, the reproducibility of experimental results is rather low. In some cases, sorption-spectroscopic methods allow for a detection limit of 10^{-4} mg litre^{-1}.

As can be judged from the increasing number of publications, these methods are extensively developing along several different lines. The range of tested elements and carriers is expanding and novel procedures for the detection of analytical signals (*e.g.*, colorimetry, derived photometry, flow-injection analysis, *etc.*) evolve. New steps are having made on the road to multielement assays.

The equipment for sorption-spectroscopic assays is also being improved. The use of small-size instruments allows a more objective estimation of experimental results, on the one hand, though this increases the cost of assays on the other hand. Test methods intended for routine and versatile uses present particularly great interest in those cases where the most reliable tool is the human eye, especially because sometimes it detects differences in colour much better than any device. In this context, the simplest, easiest, highly contrasting and safe systems provide the most efficient test methods. Sometimes, the sensitivity and accuracy of sorption-spectroscopic methods is one order of magnitude higher than those of test methods. When these methods are used simultaneously, the concentration of toxic elements can be assessed by test methods; more accurate concentration measurements are accomplished by sorption-spectroscopic methods.

Modern test methods allow detections at the MPC level. Some ions, *e.g.*, mercury, selenium, cadmium, *etc.*, having detection

limits below 10^{-3} mg litre^{-1} present a problem. However, the main problem involved in sorption-spectroscopic and test methods is selectivity. In order to increase selectivity, one should make the carrier resistant to aggressive media, such as acids, alkalis, masking complexing compounds, oxidants and reducing agents used to eliminate the interfering effects of ballast components. There must also be a possibility to vary the nature of the carrier in order to increase the sorption of the tested ions and to prevent the sorption of ballast components.

In our opinion, ion-exchange materials have indisputable advantages over paper, membranes, silica gel and other materials. They are characterised by high mechanical and chemical stabilities, high capacity and good kinetic properties, which allows for a significant decrease in the detection limit by increasing the volume of the tested solution in those cases where the sensitivity of a colour reaction is not high enough. The array of active ionogenic groups is rather broad.

The use of fibrous ion-exchange materials eliminates such disadvantage of ion-exchangers as friability and ensures easy drying, washing and other procedures without any detriment to the carrier surface. This increases the reproducibility of experimental results and simplifies the automation of analysis. The use of fibrous materials filled with ion-exchange resins permits one to combine selective concentration of an element with its selective determination and thus solves the problem of selectivity, lowering of the detection limit and rapidity of analysis. In this sense, too, these materials hold much promise.

Recent trends in the development of sorption-spectroscopic and test methods are towards further improvement of assay methodology and synthesis of novel reagents and updating of the existing ones aimed at their use in combination with the solid phase. Some reagents often lose their ability to form complexes upon immobilisation on the carrier. The broadening of the range of carriers and their potentials, variation of the nature and degree of dispersion and filling of carriers may help to solve numerous problems connected with the increase in the sensitivity and selectivity of analytical methods. And, finally, it is necessary to update the existing mini-instruments and to design new ones including those which utilise fibre optics, flow-through cells and mini-computers providing for rapid analysis in an automated regime. This will favour progress in the design of sorption-spectroscopic and test methods and their application in the analysis of natural and industrial materials and environmental subjects.

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