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Immobilisation of analytical reagents on support surfaces

O A Zaporozhets, O M Gaver, V V Sukhan

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Abstract. The use of analytical reagents immobilised on the surface of sorbents in sorption-spectroscopic methods of analysis is surveyed. The bibliography includes 131 references.

I. Introduction

At present, analytical methods which can be used not only under stationary laboratory conditions, but also at the site of sampling are attracting more and more attention of researchers.[1,2] These methods should be highly sensitive and selective and also permit quick, easy and cheap analysis. Determination of traces of substances is preceded, as a rule, by their extractive concentration, ion-exchange separation,[3,4] *etc*. It is known [3] that efficient extraction of traces of elements by a small volume of an organic solvent from a large volume of the aqueous phase is hampered by the mutual solubility of these phases and by the difficulty of their separation. Ion-exchange materials are used most frequently for separation rather than for concentration of substances,[5] because, prior to the analysis, the absorbed ions must be eluted, and this implies dilution and, hence, decreases the sensitivity of the analysis. Better results can be achieved by measuring an analytical signal of the analyte directly on the surface of an ion-exchanger or another sorbent.[6]

There is a linear correlation between the absorption of light by a solid sorbent and the concentration of a substance adsorbed on its surface.[7] The method based on this correlation, which is referred to as solid-phase spectrophotometry, permits the sensitivity of analysis to be increased substantially compared to that achieved when the light absorption of the analyte is measured after its elution to a solution. Currently, sorption-photometric, sorption-luminescence and sorption-X-ray fluorescence techniques are being successfully developed; the procedures include concentration of the component to be determined from the liquid or gaseous phase onto a solid matrix, which is accomplished by its reaction with a reagent fixed on the surface, and subsequent measurement of spectral characteristics of the solid phase, in particular, of its reflection coefficient. Equations relating the diffuse reflection coefficient of a matrix to the concentration of a substance adsorbed on its surface for thick layers of finely dispersed weakly absorbing samples (Kubelka – Munk function) and for a thin adsorbent layer (for example, for paper chromatography) have been proposed.[8 – 10] The measurements can be carried out directly on the surface of the sorbent.

Sorption concentration in combination with measurement of an analytical signal on the surface makes it possible to decrease the limits of detection of elements by several orders of magnitude,[5,8 – 11] while the use of sorbents modified by specific analytical reagents increases the selectivity of analysis.

Sorbents modified with chromophoric reagents are used in visual test methods which are indispensable for quick analysis of environmental objects, especially, for tentative (rough) analysis.[1,2]

To transfer an analyte to the sorbent phase, various procedures are used: (a) the ion to be determined is first absorbed by an ion-exchange resin and then 'visualised' by a reagent that forms a coloured compound with the sorbate; (b) the analyte is converted initially into a complex by interaction with an organic or inorganic reagent or into an ion associate in solution, and then it is sorbed by an ion exchanger or by a non-modified sorbent; (c) the analyte is extracted from solution by a sorbent modified with an appropriate organic or inorganic analytical reagent. The latter method is the most promising, especially for the environmental control, for two main reasons. Firstly, the formation of a coloured compound in the sorbent phase is less dependent on the ionic strength of the solution than that in the solution bulk. Secondly, the reagent, which has an influence on the chemical equilibrium in the system under analysis, virtually does not pass from the sorbent surface to the aqueous phase.

In recent years,[12] it has been shown that chemical and analytical properties of immobilised reagents, especially the complex-forming ability, often differ markedly from those in solution. The chemical interactions in a two-phase system 'an analyte in solution – an analytical reagent fixed on the surface of a solid support' have not been adequately investigated.

Thus, the use of organic reagents fixed on a solid matrix is a new line in modern analytical chemistry that develops at the boundary between the analytical chemistry and surface chemistry.

II. Classification of modified sorbents

Sorbents modified with various reagents and meant for analytical purposes can be classified according to the type of either the support or the modifying agent used. Various sorbents are used as supports: ion-exchange resins, cellulose, poly(vinyl chloride)

O A Zaporozhets, O M Gaver, V V Sukhan Taras Shevchenko Kiev State University, ul. Vladimirskaya 60, 252033 Kiev, Ukraine.
Fax: (38-044) 224 41 88. Tel.: (38-044) 221 02 11.
E-mail: ZUBENKO@caf3.chem.univ.kiev.ua (V V Sukhan)

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membranes, fibres and, most frequently, highly dispersed silicas.[3,13] Chelate-forming organic reagents,[15–41] metal salts,[42–46] natural compounds[47–50] and some micro-organisms[51,52] have found the widest application as modifiers.

The possibilities of the target-directed variation of the chemical and analytical properties of sorbents by modifying them with various reagents are almost limitless. A number of techniques can be used to fix an analytical reagent on a matrix. One of them is a synthetic method involving the so-called covalent grafting of a modifying reagent.[53] Another method is impregnation of a matrix with a solution of a modifier.[54] The most convenient way consists in immobilisation (or fixing) of a modifying reagent on the surface of a support using adsorption, electrostatic interaction, hydrogen bond formation or other types of interaction.[12,55]

The main advantage of modified sorbents prepared *via* covalent grafting is their chemical and mechanical stability. Difficulty and complexity of modification and regeneration of systems of this type should be regarded as their drawbacks.

Impregnation of sorbents with analytical reagents is much less labour-consuming. However, the resulting sorbents are not very suitable for operation under dynamic conditions and are relatively unstable; therefore, they do not ensure sufficient reproducibility of analytical results.

At present, there exists a broad range of sorbents with analytical reagents immobilised on their surface. They are chemically and mechanically stable and are easily modified and regenerated. Sorbents of this type are best suited to the requirements for visual test systems.

III. Methods for the immobilisation of analytical reagents

1. Sorption of organic reagents from polar aprotic and protic solvents

This method is used most frequently for immobilisation of reagents under both static and dynamic conditions. Water, acetone, dimethylformamide, alcohols and their mixtures with water are used as solvents. Some examples of modification of sorbents by this method are presented below.

Silica gel has been modified with 8-hydroxyquinoline (HQ) by stirring the sorbent, first, with formaldehyde and acetic acid for 1 h and then with a solution of HQ in anhydrous ethanol for 2 h at 60 °C.[24,56]

Immobilisation of 1-(2-pyridylazo)-2-naphthol (PAN) on silica gel has been carried out under static conditions by stirring an ethanolic solution of the reagent with a weighed portion of the sorbent for 4 h.[40] The modified sorbent was washed with water and dried for 12 h at 80–100 °C and then for several hours at 80 °C under reduced pressure. The content of PAN in silica gel obtained in this way was 4 μmol g^{-1}. When silica gel was modified under dynamic conditions,[57] a solution of PAN in a 2 : 8 ethanol–water mixture was passed through a column with the sorbent using a peristaltic pump or a syringe.[57] The excess of the reagent was removed by elution with a solution of HNO_3.

Immobilisation of PAN on the surface of a styrene-divinylbenzene copolymer has been carried out in static and dynamic regimes from a methanolic solution.[58]

To modify silica gel with Eriochrome Black T, an ethanolic solution of a modifier was poured over a weighed portion of the sorbent, and the mixture was stirred with a magnetic stirrer for 30 min, and then filtered, washed with water and dried.[59] Modification of silica gel with polyhydroxyflavones has been carried out in a similar way.[60]

4-(2-Thiazolylazo)resorcinol (TAR) has been applied on the surface of Silocrome C-120 from acetone solutions.[61] The Silochrome was treated with 1 M solution of sulfuric acid and washed with water to create a weakly acidic medium. After that, a solution of TAR was introduced, and the system was allowed to stand for 1 day with occasional stirring. The sorbent was washed with water and dried in air.

Organic reagents have also been applied from aqueous solutions. For example, to modify the AB-17 × 8 anion exchanger with 1-(2-thiazolylazo)-2-naphthol-3,6-disulfonic acid (TAN-3,6-S), a weighed portion of the sorbent was shaken for 30 min in an aqueous solution of the reagent at pH 5.7. The modified ion exchanger was washed with water and dried in air.[62,63]

Membrane ultrafilters have been modified by immersing them in a mixture of water with a solution of the corresponding organic reagent in dimethylformamide (DMF).[64] The optimum time needed for the modification of the poly(vinyl chloride) film 'Vladipor' with 4,4′-bis(dimethylamino)thiobenzophenone from a 50% DMF solution was only 10–15 min.[65] The modified films were thoroughly washed and stored in the dark in twice distilled water.

Sorption of a chemiluminescent reagent lucigenin on the surface of various silicas has been carried out from aqueous solutions.[55,66] The maximum uptake was achieved on non-functionalised silicas, silica gel (1.6×10^{-5} mol g^{-1}) and Silpearl (3.4×10^{-5} mol g^{-1}), over a period of 5 min.

2. Sorption of organic reagents from non-polar aprotic solvents and their mixtures

Modification of silica gel with quaternary ammonium salts has been carried out as follows. Silica gel was stirred with a solution of a reagent in hexane for 1 h and then dried for 2 h at 60 °C.[67,68]

Static modification of silica gel with di(2-ethylhexyl) phosphate (DEHPA) has been carried out by stirring the sorbent, dried preliminarily for 2 h at 160 °C, with a solution of DEHPA in a chloroform–heptane mixture (70 : 30).[37] Then the sorbent was dried in air until the solvent was completely removed.

A similar procedure was used to modify silica gel with the aza-analogue of dibenzo-18-crown-6; for this purpose, a solution of the crown compound in a heptane–chloroform mixture (1 : 1) was employed.[69]

3. Immobilisation of organic reagents from the gas phase

A method for the modification of sorbents by treating them in a high-frequency low-temperature plasma in the presence of vapours of organic reagents has also been proposed.[70] Polysorb-1 was used as the sorbent and propargyl alcohol, allylamine and acrylic acid were used as modifiers. The sorbents were treated for 30 min, and after that, they were washed twice with methanol by decantation and dried in air.

4. Immobilisation of inorganic reagents

Modification of sorbents with inorganic reagents is mostly carried out by sorption or precipitation of metal hydroxides, oxides or salts on their surface.

Immobilisation of calcium phosphate on silica gel has been performed by treatment of the sorbent with a solution of calcium hydroxide and, after drying, with a solution of sodium dihydrogen phosphate.[71] Then the material was dried once again.

Aluminium and iron hydroxides have been applied to the surface of activated carbon by precipitating them from a solution of the corresponding sulfate in the presence of coagulating agents based on polyacrylamide.[72]

To apply titanium and zirconium hydroxides on carbon, it has been preliminarily impregnated with solutions of salts of these metals; then the hydroxides have been precipitated with ammonia, and the sorbent dried in air at 105–115 °C.[73,74]

The modification of acetylcellulose by manganese oxide has been accomplished by treating the sorbent with a solution of potassium permanganate at 60 °C and pH 2.[75]

5. Composite materials based on modified sorbents

Modified sorbents serve as the basis for a number of composite materials.[76] For example, a composite material based on polyacrylonitrile fibre has been filled during moulding with a selective chelate-forming sorbent containing grafted heterocyclic amines[77] or with a strongly basic anion-exchange resin.[78] Discs of a

polyacrylonitrile fibre filled with finely dispersed ion exchanger have been additionally modified by immersing them into a solution of PAN in aqueous acetone [79] or into aqueous solutions of Xylylene Orange (XO),[80] arsenazo I [81] or *p*-nitrosodiethylaniline.[82] The resulting materials were stored wet.

Immobilisation of 4-phenylazo-3-aminorhodanine (PAAR) to a disc-shaped polyacrylic fibre filled with a finely dispersed KU-2 ion-exchange resin has been carried out in the following way.[83] Wet discs weighing 40–50 mg were washed with 50 ml of 0.1 M HNO_3 and with 10 ml of acetone, immersed into 10 ml of a 5×10^{-5} M solution of PAAR for 15 min and washed with 50 ml of 0.1 M H_2SO_4. The material was stored wet. The capacity of the sorbent with respect to PAAR was 5×10^{-6} mol g^{-1}.

IV. Analytical applications of modified sorbents

1. Organic reagents

a. Nitrogen-containing reagents

Sorption of gaseous compounds — hydrogen sulfide, carbon disulfide, methanethiol and sulfur dioxide — on silica gel impregnated with diethanol- and monoethanolamine has been studied.[84] The capacity of the sorbent with respect to diethanolamine amounted to 1.51–2.06 mmol g^{-1}. The sorption of gases is due to their chemical interaction with amines. Unlike acidic gases, CH_3SH is inert towards monoethanolamine and diethanolamine; therefore, it is adsorbed on modified silica gel much less efficiently than on the pure support.

A procedure for the determination of traces of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) in river water and in industrial sewage has been developed.[23] The method involves preliminary sorption of the metal cations on silica gel impregnated with *N*,*N*,*N*′,*N*′-tetrakis(2-aminophenyl)ethylenediamine and their subsequent desorption with a 0.13 M solution of tartaric acid at pH 3. The contents of metals are determined by spectrophotometry. The calibration plots are straight lines for concentrations of the metal ions ranging from 1×10^{-8} to 3×10^{-6} mol $litre^{-1}$.

It has been proposed to use *p*-nitrosodiethylaniline immobilised on discs of a polyacrylonitrile fibre filled with the strongly acidic KU-2 cation-exchange resin as a unit sensitive to the presence of Pd(II) ions.[82] Palladium ions are sorbed from solutions in a dynamic regime, and diffuse reflection spectroscopy is used for their determination. The response of the sensing element is formed over a period of 2–10 min at a palladium(II) concentration of 1×10^{-6} mol $litre^{-1}$, and the detection limit is 5×10^{-9} mol $litre^{-1}$. The use of immobilised *p*-nitrosodiethylaniline makes it possible to improve the selectivity and enhance the sensitivity of the determination of palladium and to extend the range of concentrations suitable for determination compared to that in the case of conventional photometric analysis.

The possibility of concentrating and determining Zn(II) and Cd(II) ions with the aid of an ion exchanger modified with phenylsulfonylaminoquinoline, which is fairly sensitive and relatively selective with respect to these metals, has been studied.[85] The contents of metal ions were determined by fluorometry.

A new solid-phase chemiluminescence reagent for the determination of V(IV) and Fe(II) ions has been obtained based on lucigenin (*N*,*N*-dimethyldiacridylium nitrate) immobilised on a silica gel or Silpearl surface.[55, 66] The limit of detection of V(IV) is 0.7 and that for Fe(II) is 0.8 mg $litre^{-1}$. One portion of the reagent makes it possible to carry out more than 200 analyses in a flow regime without additional regeneration.

An extraction and chromatographic procedure involving the use of silica gel modified with Aliquat 336S has been proposed for the determination of bismuth at pH 3 in a 0.01 M solution of citric acid.[86] At the final stage, bismuth is determined by spectrophotometry as an iodide complex. The procedure is suitable for the determination of bismuth in low-melting alloys containing also lead, zinc, antimony and tin.

A simple and rapid method for concentrating zinc ions as a complex with 4-(2-pyridylazo)resorcinol (PAR) using methyltrioctylammonium chloride and bromide immobilised on the surface of biphenyl with PAR has been proposed.[87] The content of zinc was determined by the atomic absorption method.

Sorption of high-molecular-weight quaternary ammonium bases on highly dispersed silica can be used for preparing solid-phase reagents possessing anion-exchange properties. The sorption of (didecylaminoethyl)tridecylammonium iodide (DDATD), *N*-methyl-*N*,*N*,*N*′,*N*′,*N*′-pentadecylethylenediammonium diiodide (PDEDA) and *N*,*N*,*N*,*N*′,*N*′,*N*′-hexadecylhexamethylenediammonium diiodide (HDHMDA) on silica gel Chemapol L 40/100 has been studied.[88, 89] The maximum amount of DDATD adsorbed is 0.4 mmol g^{-1}, while those of PDEDA and HDHMDA are 0.12 mmol g^{-1}. It was proposed to use DDATD on silica gel for the concentration and determination of Co(II), Cu(II), Zn(II), Bi(III) and Mn(II) as acido-complexes.[90, 91] This material is also suitable for the chemiluminescent and visual-test quantification of cobalt(II) in natural water (the detection limit is 2 mg $litre^{-1}$).

Visual tests for the analysis of cobalt and bismuth ions in drinking water at their contents close to the maximum permissible concentration have been developed.[36, 91] The tests are based on the formation of coloured ion associates by bismuth tetrathiocyanocobaltate and bismuth tetraiodide on a silica gel surface. The sorption can be carried out in both static and dynamic regimes. Macro- and micro-components of natural water do not interfere with the determination.

The DDATD–silica gel system modified with chromophoric and luminescence reagents (indicators) of the anionic type: Methyl Orange, Methyl Red, picric acid and fluorescein, is also of interest.[88, 89] In this case, ion associates of the composition DDATD : indicator = 1 : 1 are formed on the surface of the solid phase. Inorganic and low-molecular-weight organic anions do not displace the immobilised reagents from the surface. However, the indicators enter into exchange reactions with anionic surfactants and thus pass into solution. This provides the basis for a procedure for determining micro-quantities of sodium dodecyl sulfate in natural and waste waters. The indicator displaced to the solution from the sorbent surface is quantified by spectrophotometry or luminescence or by visual test methods.

To determine formaldehyde in air by high performance liquid chromatography, the air is pumped through a glass cartridge filled with silica gel impregnated with 2,4-dinitrophenylhydrazine.[92] As a result, hydrazone is formed on the sorbent surface; then it is eluted with methanol and determined by UV spectroscopy at a wavelength of 365 nm.

b. Macrocyclic ligands

Sorption under dynamic conditions of Cd(II), Co(II), Mg(II), Ni(II), Pb(II) and Zn(II) ions on silica gel modified with macrocyclic ligands, diaza-18-crown-6, octaethylporphyrin and 8,9,17,18-dibenzo-1,7-dioxa-4,10,13,16-tetraazacyclooctadecane, has been studied.[33, 69] At pH 6.7, Cd, Co and Mg are eluted from silica gel modified with diaza-18-crown-6 in the order Cd > Co > Mg, and at pH 4, Zn, Pb and Ni are eluted in the order Zn > Pb > Ni. In the case of modification by octaethylporphyrin and by 8,9,17,18-dibenzo-1,7-dioxa-4,10,13,16-tetraazacyclooctadecane, elution occurs in the order Mg > Co > Cd (pH 6.7) or Ni > Pb > Zn (pH 4). When two reagents are immobilised simultaneously on the silica gel, the sequences of retention of metal ions change: Co and Pb ions are eluted first.

Immobilisation of tetraphenylporphyrin and its complexes with Sn(IV), In(III) and Zn(II) on aminopropyl-silica gel (with a particle size of 10 μm) afforded sorbents for high performance liquid chromatography.[93] These sorbents ensure virtually complete chromatographic separation of the above metals in normal, reversed-phase and anion-exchange variants. Examples of anion-exchange separation of aromatic carboxylic acids and sulfonic acids have also been reported.

c. N,O-Reagents

8-Hydroxyquinoline (HQ) is among the most efficient extractants used for the determination of metal ions.[94] Since at present, there is a constant tendency to decrease the toxicity of the chemicals used in analytical procedures and the labour content of the procedures, it is no wonder that numerous studies devoted to the immobilisation of HQ on the surface of various sorbents and to their analytical applications have been published. Sorption of Al(III), Fe(III), Cd(II), Co(II), Cu(II) and Mg(II) from aqueous solutions by silica gel modified with HQ (HQ-SS) has been reported.[95] The kinetics of sorption of various metal ions are dissimilar. Thus at pH 6, quantitative sorption of Cu(II) is achieved over a period of 10 min, while Zn(II) is sorbed quantitatively over a period of 30 min. The HQ-SS sorbent is used to concentrate rare earth elements from natural waters and to separate them from barium.[31] The possibility of using this sorbent for the extraction of traces of metals from sea water[96] has also been shown. The extracted metals were detected by various modifications of mass spectrometry,[17, 25, 28, 32, 37] by atomic absorption spectroscopy in the on-line regime[28, 37] and by inversion voltammetry.[97] HQ-SS is used successfully in the analysis of organic compounds, in particular, nitrophenol and chlorophenol present in water at levels higher than their maximum permissible concentrations.[29]

To determine iron(III) ions in sea water in a flow regime, a sorbent based on HQ immobilised on the surface of a chelate resin has been proposed.[96] The iron ions were then desorbed and detected by the luminescence method.

It has been suggested to detect aluminium(III) and manganese(II) in the presence of iron(III) using C_{16}-silica gel modified with a mixture of octaethylpurpurin and 5-phenylazo-8-hydroxyquinoline taken in a ratio of 5 : 1.[98] The metal ions are quantified in the eluate by spectrophotometry in the presence of Xylylene Orange.

β-Hydroxynaphthylidene-*o*-aminophenol immobilised on the APA-8n anion-exchange resin has been used as a sensing element in an optical sensor for detecting Al(III) ions.[99] The chemical and analytical properties of this solid reagent and of the fluorescent complex with aluminium formed on the surface of the sorbent were studied. The advantages of using this solid reagent for the analysis of aluminium were shown.

The use of silica gel modified with 1-(2-pyridylazo)-2-naphthol (PAN) for the concentration and separation of Cu(II), Co(II) and Ni(II) ions, the contents of which in a solution are several mg per litre has been described.[40] The concentration factor exceeds 100. It has been shown[20] that copper(II) ions are sorbed at pH 5–7 under dynamic or static conditions with a concentration factor of 200. Copper(II) is determined after its desorption with a 0.1 M solution of thiourea or 0.03 M hydrochloric acid flowed at a rate of 0.3–0.4 $cm^3\ min^{-1}$. The presence of less than 0.1 mg of Cr(VI), 2 mg of Zn, 0.2 mg of Mn(II), 3 mg of Ca(II) and 3 mg of Mg(II) does not interfere with the determination of copper. The optimum conditions for the sorption of cobalt(II) ions with PAN–silica gel and for its subsequent quantification by diffuse reflection spectroscopy and by the visual test method have been established.[34]

A linear colorimetric method for the determination of Fe(III) and Cu(II) using PAN–silica gel has been proposed.[57] One millilitre of a solution of a sample with pH 3.0 (Fe) or pH 2.5 (Cu) is injected with a syringe into a tube with modified silica gel. The quantity of the metal is found from the length of the coloured zone using a calibrating plot. Sorption of Pb(II) ions by the same sorbent was also studied.[99]

Foamed polyurethane and ion-exchange resins modified with PAN are used for concentration of uranium(VI) prior to its determination by diffuse reflection spectroscopy.[35] It has been proposed to use an ion exchanger based on a copolymer of styrene with divinylbenzene modified with PAN to analyse river water for Cu(II), Zn(II), Fe(III), Cd(II), Ni(II) and Pd(II).[58]

A procedure for the concentration of zirconium and its subsequent determination by spectrophotometry in the solid phase using the AB-17 × 8 sorbent modified by Eriochrome Black T (ECB T) has been developed.[59] The capacity of the sorbent with respect to zirconium under static conditions is 18.2 mg g^{-1}, and the detection limit is 9.6 mg $litre^{-1}$.

Silica gel treated with a mixture of ECB T with liquid anion-exchange reagent Aliquat 336 is capable of concentrating traces of transition and alkaline earth metals from water.[95] Neither alkali metal ions nor ammonium ions are sorbed on this anion exchanger. The sorbed metals are eluted with dilute perchloric acid and determined by atomic absorption spectroscopy. The modified sorbent makes it possible to concentrate these metals by a factor of 250. This served as the basis of a procedure developed for concentrating Fe(II), Cu(II), Pb(II), Ca(II) and Mg(II) ions from water and from solutions of sodium, potassium and ammonium salts by column chromatography.

An optical-fibre fluorescence sensor for simultaneous determination of Al(III) and Ga(III) or Al(III) and In(III) has been developed. The method involves the use the Bio-Rad AG1-X4 anion-exchange resin modified with lumogallion.[100] The analysis is carried out in a dynamic regime. The minimum concentrations of Al, In and Ga that can be determined in this way are 0.02×10^{-6}, 3.0×10^{-6} and 0.2×10^{-6} mol $litre^{-1}$, respectively.

The optimum conditions for the sorption of U(VI) on the Silochrome C-120 silica gel with immobilised 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol were found.[101] A new test form for the determination of uranium in the sorbate phase by diffuse reflection spectroscopy was proposed. The detection limit is 35 ng in a 10-ml sample.

Xylylene Orange (XO) immobilised on the surface of a polyacrylonitrile fibre filled with a finely dispersed anion-exchange resin has been proposed as the sensing element of an optical sensor for detection of Pb(II) and Th(IV) ions.[80] The response of the sensing element is formed over a period of 1–10 min at lead(II) and thorium(IV) concentrations of 1×10^{-8}–3×10^{-6} mol $litre^{-1}$.

Discs of a fibrous material filled with a weakly basic anion exchanger with immobilised arsenazo I have been used to determine U(VI) ions.[81] The discs with arsenazo I are suitable for rapid quantification of uranium(VI), which is sorbed in the dynamic regime and then determined by diffuse reflection spectroscopy. The detection limit for uranium is equal to 3×10^{-8} mol $litre^{-1}$. As in the majority of cases, the immobilised reagent increases the sensitivity and selectivity of the analysis. In addition, the use of this method extends the range of concentrations that can be determined relative to that in the method involving the formation of complexes with arsenazo I in aqueous solutions.

Cellulose materials have been modified with ethylenediaminetetraacetic acid and used to determine Cr(III), Fe(II) and Pb(II) ions by atomic absorption spectroscopy.[102] The quantity of metal ions that pass from a solution to the surface of the sorbent depends on the duration of the contact between the phases and on the concentration of the metal in the solution. Lead ions are sorbed most efficiently.

Traces of vanadium(IV) and vanadium(V) in water are determined by atomic absorption spectroscopy after concentration and separation on columns filled with silica gel containing immobilised fluorinated β-diketones — benzoyltrifluoroacetone and thenoyltrifluoroacetone — and *N*-(2-aminoethyl)-γ-aminopropyltrimethoxysilane.[20] To determine the overall amount of vanadium(V) and (IV), a sample in an acetate buffer solution (pH 6) was passed at a rate of 10 $cm^3\ min^{-1}$ through a column filled with 1.5 g of modified silica gel. Then the sorbed material was eluted with 6 M hydrochloric acid, a $(1-10) \times 10^{-6}$ M solution of cobalt(II) serving as the internal standard. The separate determination of vanadium(V) and vanadium(IV) is based on the fact that they are sorbed differently at various pH. For the adsorption of V(V) ions, a solution with pH 3 was passed through a column with modified silica gel, and to extract V(IV) from the liquid phase, a

solution that had passed through the column was neutralised to pH 6 and then passed through a second column filled with the same sorbent. The detection limit for vanadium is 0.06 μg litre^{-1}. Iron(III) and copper(II) ions as well as ions of other metals present in high concentrations can be masked by complexone III. This procedure was used to determine 1–2 μg litre^{-1} of vanadium in river water.

It has been shown that silica gel modified with reagents containing ethylenediamine and ethylenediaminetriacetate functional groups can be used for the separation and concentration of vanadium(V) and vanadium(IV).[22] The separation is carried out using two columns filled with modified silica gel. The first column contains silica gel modified with a compound incorporating ethylenediamine functional groups, while the second column is filled with the sorbent modified with a compound with ethylenediaminetriacetate functional groups. At pH 2.5–3.0, only vanadium(V) is sorbed in the first column. When inductively coupled plasma atomic adsorption spectroscopy is used for quantification of vanadium(V), the detection limit amounts to 60 pg cm^{-3}.

The use of silica gel modified with zincon for concentrating Na, K, Mg, Ca, Al, Zn(II), Cd(II), Pb(II), Mo(II), Fe(III), Co(II), Ni(II) and Cr(III) ions from aqueous solutions of their salts at pH 1–9 has been proposed.[103] A procedure for the atomic-absorption determination of these ions was developed. Prior to the determination, the ions were eluted from the surface of the modified sorbent with solutions of hydrochloric or perchloric acid. Zincon is used both for the separation of these elements and for purification of solutions of some salts from Zn(II), Pb(II), Cd(II) and Cu(II) ions present as impurities.

A procedure for the anion-exchange concentration of Cu(II), Zn(II), Pb(II) and Cd(II) ions using an anion-exchange resin modified with sulfonate azo-dyes has been developed.[104]

According to a known sorption-photometric method for the determination of palladium, the AB-17 × 8 anion exchange resin modified with nitroxaminazo (NOA) is used as the sorbent.[105] The limit of detection of microquantities of palladium is of the order of 10^{-4} μg cm^{-3}.

A procedure for the on-line separation of Pb(II), Cu(II), Cd(II), Co(II), Zn(II), Ni(II) and Mn(II) ions has been developed.[106] The ions are sorbed on cartridges filled with sorbents based on silica gel (40 μm) with immobilised hydroxamic acid. The calibrating plots are linear over a wide range of concentrations (0.01–5.0 mg litre^{-1}). The detection limits for Cu(II), Co(II), Zn(II) and Ni(II) ions are 5–10 μg litre^{-1}, and those for Pb(II) and Cd(II) ions are 20 and 30 μg litre^{-1}, respectively. This modified sorbent was used for analysis of tap water.

Sorbents based on ODS C18 silica gel or XAD-4 resin containing immobilised *p-tert*-butylcalyx[4]arenetetrahydroxamic acid have been used for the pre-concentration of traces of transition metal ions.[15] The conditions for the sorption of Fe(III), Co(II), Pb(II), Cd(II), Mn(II), Ni(II), Zn(II) and Cu(II) ions in the pH range of 2–7 were studied. A procedure for chromatographic determination of copper(II), zinc(II) and manganese(II) in natural and other waters was elaborated.

d. S,N- and S-containing reagents

A method for the spectrophotometric determination of microquantities of Ag(I) and Pd(II) in water involving the use a of poly(vinyl chloride) film modified with 4,4′-bis(dimethyl-amino)-thiobenzophenone has been proposed.[65] In aqueous solutions of metal salts, the colour of the modified films changes due to the formation of complexes on the solid surface. The intensity of the colour depends on the pH, duration of shaking, the temperature of the solution and the concentration of the metal. The largest factor of concentration (1000) is achieved under optimum conditions, namely, a 500-ml sample, a surface area of the modified film of 12 cm^2, a shaking time of 60 min and a temperature of the solution under analysis of 40–60 °C. The limit of detection of silver is 0.5 μg litre^{-1} and that of palladium is 0.2 μg litre^{-1}.

A sensing element for the determination of Hg(II) has been produced by immobilisation of 4-phenylazo-3-aminorhodanine (PAAR) on discs of polyacrylonitrile fibre filled with finely dispersed KU-2 ion-exchange resin.[83] The colour of the complex with mercury develops over a period of 3–5 min (for an initial volume of 10 ml). The method makes it possible to determine mercury directly in a solution, the detection limit being 0.02 μg cm^{-3}. Ions of many transition metals that usually accompany mercury do not interfere with its determination. The use of PAAR applied on the solid phase increases the selectivity of the analysis by an order of magnitude with respect to that achieved when mercury is determined using PAAR in solution.

A sorbent based on the AB-17 × 8 anion-exchange resin modified with 1-(2-thiazolylazo)-2-naphthol-3,6-disulfonic acid (TAN-3,6-S) has been proposed for the determination of copper.[62,63] To extract micro-quantities of copper from aqueous solutions and from water–organic mixtures, sorbents with coverages of 43% and 8%, respectively, are used.[107] The sorption-photometric method for the determination of low concentrations of copper is more sensitive and selective than the known photometric method for the determination of copper with TAN-3,6-S in solution.

The optimum conditions for the absorption of Pd(II) by this sorbent were also elucidated.[108,109] The amount sorbed depends on the nature and concentration of mineral acids as well as on the coverage of the sorbent with the modifier and on the presence of organic solvents. The detection limit for palladium(II) is 1.25 μg cm^{-3}.

Sorption of Fe(III) ions on the AB-17 × 8 ion exchange resin in the chloride form modified with TAN-3,6-S has been studied.[110] The formation of complexes of Fe(III) ions with TAN-3,6-S immobilised on the sorbent surface was studied by spectrophotometry. It was found that the ratios of the components in the complexes formed in solution and in the phase of the sorbent are identical.[62,108]

Conditions for sorption of Ni(II) ions with this sorbent were studied over a wide pH range.[62] The composition and the stability constant of the nickel complex formed in the resin phase were determined by spectrophotometry. The influence of the stoichiometry of the nickel complex with the modifying agent on the kinetic properties of the sorbent was considered.

Group concentration of Cu(II), Ni(II), Zn(II) and Cd(II) ions on the AB-17 × 8-Cl anion exchanger modified with TAN-3,6-S creates conditions for the subsequent X-ray fluorescence determination of these elements in the concentrate.[111,112] A sorption-X-ray fluorescence procedure for the determination of microconcentrations of these metals present simultaneously was developed. The detection limit is 0.35–1.2 μg, and the concentration factor is 200.

The protolytic and optical properties of Silochrome C-120 with 4-(2-thiazolylazo)resorcinol immobilised on its surface have been studied. Chemical and analytical conditions for the interaction of this material with U(VI), Cu(II), Ni(II), Zn(II), Co(II), Pd(II) and Fe(II, III) ions were identified.[61] The sorbent is used for the test determination of Co(II), Pd(II) and U(VI) ions present in concentrations of 0.005–0.03 μg cm^{-3} by diffuse reflection spectroscopy and also for determination of palladium and uranium in real objects.

The AB-17 × 8 anion-exchange in the chloride form modified with 2-(2-thiazolylazo)-5-diethylaminophenol (TADEAP) has been proposed as the sorbent for the determination of U(VI) present in a concentration of about 10^{-5}% by solid-phase spectrophotometry.[113] The analysis is carried out for alkaline solutions of complex compositions without preliminary separation of uranium from the accompanying elements.

A method for detecting traces of cadmium and copper in salt sediments of sodium chloride has been reported.[26] The method includes ion-exchange pre-concentration of the elements to be analysed on silica gel modified with a thiol and atomic absorption spectroscopy.

Reagents with xanthate and dithiocarbamate functional groups immobilised on a silica gel surface have been used to concentrate traces of noble metals.[114] The Pd(II), Ag(I), and Pt(IV) ions are sorbed quantitatively on this material at pH 4–5 and 2–5. The ions are detected by the atomic absorption method after desorption.

e. O-Containing reagents

Silica gel modified with dodecylbenzenesulfonic acid has been used under dynamic conditions for ion-chromatographic separation of transition metal ions.[115] Solutions of strontium salts containing citric, tartaric, oxalic, pyrophosphoric and dipicric acids added for complex formation were used as the eluents. The optimum conditions for the selective determination of Cu(II), Ni(II), Pb(II), Co(II), Cd(II), Fe(II) and Mn(II) cations were chosen. The analysis requires 25 min.

Eriochromocyanine immobilised on the XAD-2 support can serve as an optical sensor for the determination of Al(III).[116] The content of this metal is found by diffuse reflection spectroscopy.

Extraction chromatography on columns filled with silica gel containing a mixture of high-molecular-weight and isomeric tertiary C_{10} carboxylic acids 'Versatic 10' immobilised on its surface is used to separate indium(III) from accompanying elements.[117] Indium(III) is sorbed quantitatively from acetate buffer solutions with pH 4.5–6.0 and is desorbed with solutions of mineral acids. Neither Fe(III), Ni(II), Co(II), Zn(II) and Cu(II) ions nor U(VI), Cr(III), Al(III), Tl(III), Ga(III), lanthanide, Zr(IV) and Th(IV) ions are sorbed under these conditions; they can be separated by choosing an appropriate mobile phase.[117] The researchers cited presented examples of the separation of Al(III)–In(III)–Ga(III)–Th(III), UO_2(II)–In(III)–Zr(IV) and La(III)–In(III)–Th(IV) mixtures.

To analyse environmental objects, a procedure has been proposed in which traces of Cd(II), Cu(II), Mn(II), Zn(II) and Fe(III) are concentrated by sorption from aqueous solutions with pH > 6 on silica gel modified with 3-methyl-1-phenyl-4-stearoyl-5-pyrazolone (with a coverage of 4.2%).[118] Desorption of metal ions is accomplished using 1 M hydrochloric acid, and the contents of metals in the eluate are determined by atomic absorption spectroscopy. This procedure was used to determine traces of Cu(II), Mn(II) and Zn(II) in tap water.

The analytical potentialities of morin immobilised on the KU-2 cation-exchange resin and on a dextran type sorbent, Sephadex G-25, have been studied.[60] These sorbents are suitable for selective determination of zirconium and tin in wastewater. The minimum concentration of Zr detected in this way is 1.0 μg cm^{-3} and that for Sn(II) is 0.5 μg cm^{-3}.

f. Algae

Sorption of toxic metal ions (Co, Ni, Pb, Cd, *etc.*) from aqueous solutions by silica gel modified with an alga *Chlorella vulgaris* has been studied.[51] The sorbent was used to concentrate metals, which were then quantified by atomic absorption spectroscopy.

A method for the immobilisation of marine algae cells on silica gel has been proposed.[52] The material thus obtained was used to extract lead from aqueous solutions by column chromatography. The lead is determined after its desorption with a mixture of nitric and hydrochloric acids. The adsorption capacity of the modified sorbent with respect to lead decreases by 15% after 20 adsorption–elution cycles. This sorbent also extracts almost completely micro-quantities of cesium from strongly saline solutions.

2. Inorganic reagents

Methods for the preparation and applications of inorganic sorption materials based on various supports — carbon, zeolites, sand, wood cellulose, *etc.* — have been considered in a review.[71] The accessibility of many of these supports, the ease of synthesis of sorbents based on oxides, hydroxides, ferrocyanides and other solid phases, their mechanical strength and high kinetic characteristics make these materials highly promising sorbents for processing of natural and waste waters, liquid radioactive wastes and various solutions.

a. Metal salts

A separate group of sorbents comprises materials modified with inorganic salts; they are meant for the analysis of compounds capable of being involved in complex-formation, precipitation or redox reactions with the salts fixed on the surface.

Chromatographic behaviour of a large number of inorganic anions on silica gel modified with 0.1% aqueous solutions of $CuSO_4$, $ZnSO_4$, $[Co(NH_3)_6]Cl_3$ and $NiCl_2$ has been studied.[44] Desorption is carried out using water–organic mixtures containing mineral acids, and detection is accomplished using thin-layer chromatography and various visualising reagents.

A method for the separation of Tl(III) from Cd(II), Al(III), Ni(II), Fe(III), Ag(I) and Pb(II) using silica gel modified with sodium molybdate dissolved in a formic acid–butanol mixture has been reported.[43]

A procedure has been proposed for the determination of aromatic sulfur-containing heterocyclic compounds in slate pitch. The method includes chromatography on columns filled with silica gel containing palladium(IV) chloride adsorbed on its surface.[42] The analysis is performed by UV spectroscopy or flame photometry.

Sorption of cesium ions on silica gel with immobilised potassium tetracyanocuprate has been studied under static conditions.[119] The rate of ion exchange between potassium and cesium increases as the capacity of the sorbent with respect to the above copper(I) complex decreases. The sorbent can also be used under dynamic conditions.

A method for preparing a sorbent based on iron(III) hexacyanoferrate(II) has been described.[120] Cellulose was treated with a mixture of solutions of potassium hexacyanoferrate(III) and iron(III) nitrate in a special mixing reactor. The capacity of the sorbent with respect to the modifying reagent was 300 to 600 mg cm^{-3}.

Inorganic sorbents based on potassium hexacyanoferrate(III) have been obtained using precipitation reactions.[121] The compositions and physicochemical and sorption properties of the materials depend on the conditions of their synthesis.

Oxidative and indicator systems based on modified silica gel have been used to determine nitrogen oxides in air.[46] The oxidative tube contained silica gel impregnated with an acid solution of potassium permanganate, while the indicator tube was filled with silica gel impregnated with potassium iodide, starch, sodium chloride and sodium thiosulfate.

Tin(IV), zinc(II) and aluminium(III) iodides applied on activated carbon are used to extract radioactive iodine from solutions.[71]

A number of sorbents based on potassium hexacyanoferrate(II) applied on a zeolite, an acrylic fibre or silica gel are used for treatment of radioactive wastewaters.[71]

Amorphous calcium phosphate applied on an acid-resistant porous support with an extensive surface is used as a sorbent for the concentration of heavy metal ions.

A sorbent possessing high selectivity with respect to strontium in calcium-containing solutions is prepared by treatment of coal with a solution of potassium permanganate containing 1.0 to 1.2 g $litre^{-1}$ of ammonia.[71]

b. Metal oxides and hydroxides

Oxide and hydroxide films immobilised on various inert matrices (sand, cellulose, activated carbon, various copolymers, *etc.*) constitute a large group of inorganic sorbents.

A sorbent based on manganese dioxide applied on a support is used for the sorption of Cu(II), Zn(II) and Pb(II) ions under dynamic conditions.[75]

To purify water from iron, it is filtered through the so-called 'black sand',[122] which is prepared by the successive treatment of sand with solutions of manganese chloride and potassium per-

Table 1. Chemical and analytical properties of analytical reagents.

Reagent	Sorbent	Capacity of the sorbent/ mmol g^{-1}	Analyte	Optimal pH	Detection limit/ mg cm^{-3}	Method of determination [a]	Ref.
KU-2 cation exchanger + *p*-nitrosodiethylaniline	Polyacryl fibre (40–50 μm)	5.0	Pd(II)	2–3	5.3×10^{-4}	DRS	82
Lucigenin	Silpearl	0.034	V(IV)		0.7	CL	55, 66
	"	0.034	Fe(II)		0.8	CL	66
DDATD	Silica gel	0.24	Co(II)	200	0.002	CL	89, 90
Aza-analogue of dibenzo-18-crown-6	"	0.005	Co(II)	< 7	0.02	AAS	69
	"	0.005	Cu(II)	2–8	0.01	AAS	69
HQ	"		Lanthanides	8	$(3-5) \times 10^{-4}$	MS	31
	Hydrophilic vinylic polymer		Fe(III)	9.5	2.8×10^{-6}	CL	96
β-Hydroxynaphthaldene-*o*-aminophenol	APA-8n	4.0	Al(III)	4.0–6.5	1.2×10^{-3}	CL	99
PAN	Silica gel		Co(II)	3–5	0.02–0.04	DRS	34
	Silochrome C-120		Cr(III)	2.5–4.5	0.1	DRS	39
	"		Mn(II)	5.0–7.5	0.05	DRS	39
	"		Fe(III)	5.0–6.5	0.3	DRS	39
	"		Ni(II)	6–9	0.03	DRS	39
	"		Cu(II)	5–8	0.1	DRS	39
	"		Zn(II)	7.5–10	0.03	DRS	39
KU-2 cation exchanger + PAN-2	Polyacrylic fibre (30–40 μm)	0.2	Cu(II)	5.7	0.032	DRS	79
ECB T	AB-17 × 8 (100–250 μm)	0.23 [b]	Zr(IV)	2	9.6×10^{-6}	SPSP	59
Lumogallion	Anion exchanger		Al(III) and Ga(III) or Al(III) and In(III)	3–8	5.4×10^{-4} 1.4×10^{-2} 5.4×10^{-4} 0.34	PL	100
Anion exchanger (5–10 μm) + XO	Polyacrylic fibre (30–40 μm)	0.06	Th(IV)		4.6×10^{-3}	DRS	80
	The same	0.03	Pb(II)		0.01	DRS	80
Anion exchanger + arsenazo I	"		U(VI)		7.1×10^{-4}	DRS	81
Zincon	"	0.1	Ca(II)	< 6			103
	"	0.1	Mg(II)	< 9			103
NOA	AB-17 × 8	2.5×10^{-3}	Pd(II)	6	$> 10^{-4}$	SPSP	105
TAN-3,6-S	AB-17 × 8 (100–250 μm)	1.6×10^{-3}	Ni	9	1.25	SPSP	62
	The same	0.016	Cu(II)	2		SPSP	107
	"	6.3×10^{-4}	Pd(II)	2.5–3.0	1.25	SPSP	108
	"	$> 1.6 \times 10^{-3}$	Fe(III)	3.8–4.3		SPSP	110
	"		Cu(II)	4–5		SPSP	112
TAR	Silica gel		Co(III)	4.0	0.005–0.3	DRS	61
	"		Co(II)	6.2	0.005–0.3		61
	"		Pd(II)	6.0	0.005–0.3	DRS	61
	"		U(VI)	7.4	0.005–0.3	DRS	61
TADEAP	AB-17 × 8-Cl	5.0×10^{-4}	U(VI)	6–9	$> 10^{-4}$	SPSP	113
Morin	KU-2 + Sephadex G-25	0.01–1.0	Sn(II)	0.2–1.3	0.5	CL	60
	"	0.01–1.0	Zr(IV)	0.3	1.0	CL	60
Algae	Silica gel	267 ± 6	Pd(II)	4.7		CC	52
$PdCl_2$	"		Organic compounds			GC	42

[a] DRS is diffuse reflection spectroscopy, CL is a chemiluminescence method, AAS is atomic absorption spectroscopy, MS is mass spectrometry, SPSP is solid-phase spectrophotometry, PL is photoluminescence, CC is column chromatography and GC is gas chromatography. [b] Capacity of the sorbent is expressed in mg g^{-1}.

manganate. This yields a sorbing layer of manganese dioxide. Sulfonated coal can be used instead of sand.

A flow injection procedure for the determination of organic reducing agents in water samples using lead(IV) oxide immobilised on a silica surface has been suggested.[45] The concentration of organic compounds in water is found from the quantity of Pb(II) resulting from the reaction of Pb(IV) with reducing reagents. The concentration of Pb(II) is determined by spectrophotometry using 4-(2-pyridylazo)resorcinol or by atomic absorption spectroscopy.

The sorbent obtained by precipitation of aluminium and iron(III) hydroxides from solutions of metal sulfates on activated carbon in the presence of coagulating agents based on polyacrylamide is also suitable for the extraction of heavy metal ions from water.[72] The $Al(OH)_3 : Fe(OH)_3$: carbon ratio in this material is 1 : 4 : 5 by weight. The capacity of the sorbent with respect to uranium amounts to 266 mg g^{-1}.

Sorbents consisting of aluminium(III), iron(III) and manganese(II) hydroxides applied on copolymers of styrene with divinylbenzene with various degrees of cross-linking are used to concentrate microelements from sea water.[123] The factors of concentration of metals depend on the thickness of the hydroxide layer and on the degree of porosity of the support. The material is suitable for sorption under dynamic conditions.

The sorption on iron(III) hydroxide applied on various supports is used to purify solutions from water-soluble compounds of arsenic.[71, 124] This procedure ensures extraction of traces of arsenic and arsenous acids, organic arsenic-containing acids and their derivatives.[71]

Composite sorbents prepared by deposition of titanium(IV) and zirconium(IV) hydroxides on the activated carbon BAU are selective with respect to phosphate and fluoride anions.[73, 74] A sorbent of this type absorbs 2.4 times as much phosphate ions per gram as granulated titanium hydroxide, all other factors being the same. The high capacity of these materials with respect to phosphate ions is retained in neutral and weakly alkaline media.[71]

A sorbent consisting of a thin layer of iron oxide applied on sand has been proposed for the extraction of copper ions from washings containing ammonia.[125]

To concentrate metal ions from sea water and industrial sewage, a sorbent has been proposed,[126] which consists of dispersed metal hydroxides, oxides or sulfides or of these compounds precipitated on or embedded into an organic or inorganic porous support (organic polymers, zeolites, molecular sieves). The synthesis of a sorbent based on zinc hydroxide and an organic support is described in the patent cited [126] as an example. Methods for preparing a composite sorbent for the extraction of heavy metal ions from sea water or wastewater have been developed.[127, 128] This material is based on a porous support, for example, an organic polymeric gel in which finely dispersed aluminium, iron, manganese, titanium or other metal oxides and hydroxides are introduced. The quantity of the inorganic compound introduced is more than 0.1 mole per litre of the gel. The preparation of composite sorbents based on polyacrylamide and hydroxides of the above metals is described as an example. The exchange capacities of the sorbents with respect to copper(II), nickel(II), mercury(II), chromium(III) and some other heavy metal ions were determined. Characteristic features of the composite adsorbents are their high stabilities, good adsorption properties and easy separation from water.

A procedure for modification of inorganic sorbents consisting of hydroxides or insoluble salts of multi-charged metal ions applied on porous supports such as carbon, active sludge and sawdust has been reported.[128] These sorbents can be used to remove non-ferrous metal ions from wastewater of electrochemical plants.

Extraction of heavy metal ions from sea water can be carried out using adsorbents based on activated carbon, poly(vinyl acetate) or a fibrous non-woven material modified by treatment with a hydrosol of titanic acid (with a concentration of 5% – 10 % and a size of colloidal particles of 1 – 100 μm).[71]

The sorption properties and stability of titanium-containing sorbents on a sawdust support have been considered.[129, 130] The kinetics of peptisation of a wood-supported titanium hydroxide layer in water were studied and some assumptions as to the nature of the bond between the sorbtion material and the support were made.[130]

The main chemical and analytical characteristics of the immobilised reagents described above are summarised in the general Table 1.

V. Conclusion

Analysis of the published data indicates that the new line of research associated with the use in chemical analysis of reagents immobilised on the surface of various supports is quite promising. These reagents increase the sensitivity and selectivity of determination of many elements.

The decrease in the detection limits is achieved due to the concentration of the components to be analysed from a relatively large volume of a solution into the phase of a sorbent. Unlike extractive concentration, the sorption methods do not require the use of organic solvents and, hence, they cause no health hazard. The sorbents themselves are non-toxic and are readily separated from solutions by filtration, which makes the analysis quicker.

The better selectivity of these methods results from the fact that in some cases, owing to some geometrical features of fixing of organic reagents on a support surface, their complex-forming properties, for example, dentate number, change upon immobilisation. It can be assumed that modified sorbents extract most efficiently those metal ions that react with the immobilised reagent to give ion associates or complexes with a metal : ligand ratio of 1 : 1. In this case, steric restrictions caused by fixing of the ligand on the surface of the sorbent are minimised.

The subsequent development of this branch of analytical chemistry requires that the chemical nature of immobilisation of reagents on the surface of solid supports be elucidated.[67, 131] At present, the reagents are mostly fixed on the surface of a matrix by ion – ion interaction; other types of interaction are used much more seldom. In the latter cases, the chemical nature of the interaction of reagents with the sorbent surface is usually ignored, and the way of immobilisation is selected empirically by changing the solvents. Study of the chemical nature of the interaction of various classes of reagents with the surfaces of supports and elucidation of the regularities of the complex-formation involving supported ligands would markedly extend the analytical potential of the sorption methods. It is also necessary to work out scientifically justified criteria that would permit 'solid-phase reagents' to be regarded either as organic reagents modified with a surface or as sorbents modified with analytical reagents; at the current stage of investigation, this consideration is sometimes difficult.

References

1. Yu A Zolotov *Zh. Anal. Khim.* **50** 1333 (1995) [a]
2. Yu A Zolotov *Zh. Anal. Khim.* **50** 1237 (1995) [a]
3. N M Kuz'min, Yu A Zolotov *Kontsentrirovanie Sledov Elementov* (Concentration of Traces of Elements) (Moscow: Nauka, 1988)
4. V K Runov, S V Kachin *Zavod. Lab.* **59** 1 (1993)
5. G D Brykina, D O Marchenko, O A Shpigun *Zh. Anal. Khim.* **50** 484 (1995) [a]
6. V K Runov, V V Tropina *Zh. Anal. Khim.* **51** 71 (1996) [a]
7. K Yoshimura, H Waki, S Ohashi *Talanta* **23** 449 (1976)
8. V K Runov *Ross. Khim. Zh.* **38** 36 (1994)
9. P Kubelka, F Munk *Z. Techn. Phys.* **12** 593 (1931)
10. S V Veack *Anal. Chim. Acta* **10** 48 (1954)
11. I N Ermolenko, M L Lognin, M Z Gavrilov *Zh. Anal. Khim.* **17** 1035 (1962) [a]
12. S B Savvin, A V Mikhailova *Zh. Anal. Khim.* **51** 49 (1996) [a]

13. G D Brykina, L S Krysina, V M Ivanov *Zh. Anal. Khim.* **43** 1547 (1988) [a]
14. K Yoshimura, H Waki *Talanta* **32** 345 (1985)
15. S Hutchinson, G A Karney, E Horne, B Linch, J D Glennon, M A McKervey, S Y Harris *Anal. Chim. Acta* **291** 269 (1994)
16. T Honjo, H Katayama, K Terada, T Kiba Fresenius *Z. Anal. Chem.* **330** 159 (1988)
17. J W McLaner, K Akatsuka, J W Lam *IPC Inf. Newslett.* **17** 639 (1991); *Ref. Zh. Khim.* 17 G 231 (1992)
18. P Cronkleton *Proc. Nebr. Acad. Sci., 1880–1992. NATS and TER--QUA, Div. Affiliat. Soc., Lincoln, 1993* p. 88; *Ref. Zh. Khim.* 15 G 34 (1994)
19. V M Ivanov, S A Morozko, S V Kachin *Zh. Anal. Khim.* **49** 857 (1994) [a]
20. S Tong, F Liu, K Li *J. Environ. Sci. (China)* **1** 121 (1989); *Ref. Zh. Khim.* 9 G 210 (1991)
21. K E Krakowiak, M L Braening, I M Reed, J S Bradshaw, R T Braening, J Bryon *Anal. Chem.* **63** 1014 (1991)
22. K Hirayama, S Kageyama, N Unohara *Analyst* **117** 13 (1992)
23. D Chambaz, W Haerdy *J. Chromatogr.* **600** 203 (1992)
24. U Pyell, G Stork *Fresenius Z. Anal. Chem.* **342** 281 (1992)
25. J W McLaner, M A Azeredo, J W Lam *IPC Inf. Newslett.* **18** 375 (1992); *Ref. Zh. Khim.* 7 G 187 (1993)
26. U Koklu, S Akman *Acta Chim. Hung., Models Chem.* **129** 825 (1992); *Ref. Zh. Khim.* 14 G 153 (1993)
27. C Airoldi, M R Santos, in *The 12th IUPAC Conference on Chemical Thermodynamics: The 47th Calorimetry Conference, Snowbird, UT (Abstracts of Reports)* (Paylo, 1992) Vol. I, p. 219; *Ref. Zh. Khim.* 12 G 232 (1993)
28. H E Grafne, Z Feher *Magy. Kem. Foly.* **98** 328 (1992); *Ref. Zh. Khim.* 6 G 163 (1993)
29. M R Montero-Escolar, C Moreno-Roman, M E Leon-Gonzales, Z M Polo-Dies *Anal. Proc.* **29** 358 (1992); *Ref. Zh. Khim.* 10 G 273 (1993)
30. Y Kuroda, Y Kato, H Ogoshi *Bull. Chem. Soc. Jpn.* **66** 1116 (1993); *Ref. Zh. Khim.* 16 G 145 (1993)
31. B K Esser, A Volpe, J M Kenneally, D K Smith *Anal. Chem.* **66** 1736 (1994)
32. J W McLaren, J W H Lam *ICP Inf. Newslett.* **19** 715 (1994); *Ref. Zh. Khim.* 9 G 178 (1995)
33. N V Semenova, E I Morosanova, I V Pletnev, Yu A Zolotov *Zh. Anal. Khim.* **47** 1596 (1992) [a]
34. V M Ivanov, S A Morozko, Yu A Zolotov *Zh. Anal. Khim.* **48** 1389 (1993) [a]
35. V M Ivanov, S Massuu *Vestn. Mosk. Univ., Ser. 2, Khim.* **34** 572 (1993) [b]
36. V V Sukhan, O Yu Nadzhafova, O A Zaporozhets, L I Savranskii *Khim. Tekhnol. Vody* **16** 139 (1994)
37. E I Morosanova, I V Pletnev, V Yu Solov'ev, N V Semenova, Yu A Zolotov *Zh. Anal. Khim.* **49** 676 (1994) [a]
38. O P Shvoeva, V P Dedkova, A G Gitlits, S B Savvin *Zh. Anal. Khim.* **52** 89 (1997) [a]
39. S A Morozko, V M Ivanov *Zh. Anal. Khim.* **50** 629 (1995) [a]
40. K Li, F Liu, W Dong, S Tong *Acta Sci. Nat. Univ. Pekinensis* **28** 202 (1992); *Ref. Zh. Khim.* 18 G 145 (1992)
41. G V Myasoedova, S B Savvini *Khelatoobrazuyushchie Sorbenty* (Chelating Sorbents) (Moscow: Nauka, 1984)
42. Y T Anderson *Anal. Chem.* **59** 2207 (1987)
43. M Ajmal, A Mohammad, N Fatima *Indian J. Chem. A* **28** 91 (1989); *Ref. Zh. Khim.* 11 G 119 (1990)
44. M Ali, T Sharad *Microchem. J.* **44** 39 (1991); *Ref. Zh. Khim.* 16 G 134 (1992)
45. B Ruchti, C Schramm, S Kubischko, B Neidhart *Fresenius Anal. Chem.* **342** 822 (1992)
46. Russ. P. 1 673 958; *Ref. Zh. Khim.* 11 G 171P (1992)
47. US P. 5 273 908; *Ref. Zh. Khim.* 3 G 269P (1995)
48. T N Shekhovtsova, S V Chernetskaya, N V Belkova, I F Dolmanova *Zh. Anal. Khim.* **49** 789 (1994) [a]
49. T N Shekhovtsova, S V Chernetskaya, E B Nikol'skaya, I F Dolmanova *Zh. Anal. Khim.* **49** 862 (1994) [a]
50. T N Shekhovtsova, S V Chernetskaya, N V Belkova, I F Dolmanova *Zh. Anal. Khim.* **50** 538 (1995) [a]
51. P Pascucci, Y Senddon, in *Pittsburgh Conference Presents, New Orleans, 1992 (Abstracts of Reports)* p. 1177; *Ref. Zh. Khim.* 16 G 138 (1993)
52. C A Mahan, Y A Holcombe *Anal. Chem.* **64** 1933 (1992)
53. V A Tertykh, L A Belyakova *Khimicheskie Reaktsii s Uchastiem Poverkhnosti Kremnezema* (Chemical Reactions with Participation of the Silica Surface) (Kiev: Naukova Dumka, 1991)
54. V M Ostrovskaya *Zh. Anal. Khim.* **32** 1820 (1977) [a]
55. V V Sukhan, O A Zaporozhets, N A Lipkovskaya, L B Pogasii, A A Chuiko *Zh. Anal. Khim.* **49** 700 (1994) [a]
56. I Kasahara, S Willie, R Sturgeon, S Berman, S Tagachi, K Yoto *Bunseki Kagaku* **42** 107 (1993); *Ref. Zh. Khim.* 16 G 27 (1994)
57. I M Maksimova, E I Morosanova, A A Kukhto, N M Kuz'min, Yu A Zolotov *Zh. Anal. Khim.* **49** 1210 (1994) [a]
58. J Chwastowska, E Mozer *Talanta* **32** 574 (1985)
59. M I Shtokalo, E E Kostenko, I Z Zhuk *Zh. Anal. Khim.* **46** 1093 (1991) [a]
60. L E Zel'tser, N G Vereshchagina, A V Bychenko *Zh. Anal. Khim.* **46** 2041 (1991) [a]
61. V M Ivanov, O V Kuznetsova *Zh. Anal. Khim.* **50** 498 (1995) [a]
62. T V Marchak, G D Brykina, T A Belyavskaya *Zh. Anal. Khim.* **36** 513 (1981) [a]
63. G D Brykina, N L Fillipova, L S Krysina, T A Belyavskaya *Zh. Fiz. Khim.* **54** 2075 (1980)
64. A T Pilipenko, A V Terletskaya, T A Bogoslovskaya, G S Matsibura *Khim. Tekhnol. Vody* **14** 412 (1992)
65. G S Matsibura, V O Ryabushko *Khim. Tekhnol. Vody* **16** 416 (1994)
66. O A Zaporozhets, V V Sukhan, N A Lipkovska *Analyst* **121** 501 (1996)
67. O A Zaporozhets, O Yu Nadzhafova, A I Zubenko, V V Sukhan *Talanta* **41** 2067 (1994)
68. V V Sukhan, L I Savranskii, O A Zaporozhets, O Yu Nadzhafova, B G Lantukh *Ukr. Khim. Zh.* **58** 990 (1992)
69. E I Morosanova, L S Seliverstova, Yu A Zolotov *Zh. Anal. Khim.* **48** 617 (1993) [a]
70. V G Berezkin, Zh R Tuzhilina, Yu A Gerasimov, A A Kalachev, E Yu Sorokina *Zh. Anal. Khim.* **50** 525 (1995) [a]
71. E A Kazantsev, V P Remez *Khim. Tekhnol. Vody* **17** 50 (1995)
72. DDR P. 141 622; *Ref. Zh. Khim.* 23 L 169P (1980)
73. A A Blokhin, M I Semenov, V P Taushkanov, E A Andronov *Zh. Prikl. Khim.* **51** 2491 (1978) [c]
74. M I Semenov, A A Blokhin, V P Taushkanov, in *Khimiya i Tekhnologiya Neorganicheskikh Sorbentov, Perm', 1979 (Mezhvuz. Sb. Nauch. Tr. PPI)* [Chemistry and Technology of Inorganic Sorbents, Perm, 1979 (Intercollegiate Collection of Scientific Reports from the Perm Polytechnic Institute)] p. 75
75. M Brandano, B Sueli, F Galembeck *Colloids Surf.* **48** 351 (1990)
76. D C Sherrington *High Value Polymers* (London: Royal Society of Chemistry, 1991)
77. O P Shvoeva, G P Kuchava, G V Myasoedova, S B Savvin, L N Bannykh, N G Zhukova, O N Grishina, M S Mezhirov *Zh. Anal. Khim.* **40** 1606 (1985) [a]
78. S B Savvin, L M Trutneva, O P Shvoeva *Zh. Anal. Khim.* **48** 502 (1993) [a]
79. O P Shvoeva, S B Savvin, L M Trutneva *Zh. Anal. Khim.* **45** 476 (1990) [a]
80. L M Trutneva, O P Shvoeva, S B Savvin *Zh. Anal. Khim.* **44** 1804 (1989) [a]
81. O P Shvoeva, L M Trutneva, S B Savvin *Zh. Anal. Khim.* **44** 2084 (1989) [a]
82. O P Shvoeva, L M Trutneva, E A Likhonina, S B Savvin *Zh. Anal. Khim.* **46** 1301 (1991) [a]
83. S B Savvin, L M Trutneva, O P Shvoeva, K A Efendieva *Zh. Anal. Khim.* **46** 709 (1991) [a]
84. E Vanderheyden, E F Vansant, J Ptulippaerts *Mikrochim. Acta* **2** 163 (1988)
85. R Compano, R Ferrer, J Guiteras, M D Prat, in *European Conference on Analytical Chemistry, Euroanalysis VIII, Edinburgh, Scotland, UK, 1993 (Abstracts of Reports)* p. V9
86. S K Sahoo *Talanta* **38** 789 (1991)
87. T Nagahiro, M Sakate, in *European Conference on Analytical Chemistry, Euroanalysis VIII, Edinburgh, Scotland, UK, 1993 (Abstracts of Reports)* p. P25

88. O A Zaporozhets, O Yu Nadzhafova, O I Zubenko, V B Ishchenko, V V Trachevskii, V V Sukhan *Ukr. Khim. Zh.* **61** 9 (1995)
89. O Yu Nadzhafova, O A Zaporozhets, V V Verba, V V Sukhan, in *Symposium on the Protochemistry and Photophysics of Coordination Compounds, Jagiellonian University, Krakow, Poland, 1995 (Abstracts of Reports)* p. 74
90. O Yu Nadzhafova, O A Zaporozhets, V V Sukhan, in *The XIIIth European Chemistry at Interfaces Conference, Kiev, Ukraine, 1994 (Abstracts of Reports)* p. 134
91. O A Zaporozhets, N M Zinchenko, O Yu Nadzhafova, V V Sukhan *Khim. Tekhnol. Vody* **17** 588 (1995)
92. M Colli, A Girony, V Molina, R Marchetti, M G D'Eril, C Lucarelli *Chromatographia* **32** 113 (1991)
93. M E Meyerhoff, C E Kibbey, J Xiao, G Martin, in *Pittsburgh Conference Analytical Chemistry and Applied Spectroscopy III, Chicago, 1994 (Abstracts of Reports)* p. 449; *Ref. Zh. Khim.* 3 G 245 (1995)
94. Z Marchenko *Fotometricheskoe Opredelenie Sledov Elementov* (Photometric Detection of Traces of Elements) (Ed. Yu A Zolotov) (Moscow: Mir, 1971)
95. S Przeszlakowski, R Kocjan, in *Euroanalysis V: The Vth European Conference on Analytical Chemistry, Krakow, Poland, 1984 (Abstracts of Reports)* p. 216; *Ref. Zh. Khim.* 20 G 139 (1988)
96. H Obata, H Karatani, E Nakayama *Anal. Chem.* **65** 1524 (1993)
97. Bor-Yian Daih, Hsuan-Yung Huang *Anal. Chim. Acta.* **258** 245 (1992)
98. Y A Zolotov, E I Morosanova, N V Semenova, I V Pletnev, in *European Conference on Analytical Chemistry, Euroanalysis VIII, Edinburgh, Scotland, UK, 1993 (Abstracts of Reports)* p. L41
99. L E Zel'tser, L A Arkhipova, A V Bychenko *Zh. Anal. Khim.* **50** 312 (1995) [a]
100. M K Carroll, F V Bright, G M Hieftje *Anal. Chem.* **61** 1768 (1989)
101. V M Ivanov, S A Morozko, M Sabri *Zh. Anal. Khim.* **50** 1280 (1995) [a]
102. J N Egila, S A Kareem, in *European Conference on Analytical Chemistry, Euroanalysis VIII, Edinburgh, Scotland, UK, 1993 (Abstracts of Reports)* p. P26
103. R Kocjan *Analyst* **119** 1863 (1994)
104. M Pesavento, M Bascape, in *European Conference on Analytical Chemistry, Euroanalysis VIII, Edinburgh, Scotland, UK, 1993 (Abstracts of Reports)* p. L4
105. G D Brykina, A Chandra, V P Khvostova, T A Belyavskaya *Zh. Anal. Khim.* **39** 1859 (1984) [a]
106. N Ryan, J P Glennon *Anal. Proc.* **29** 21 (1992)
107. G D Brykina, T V Marchak, L S Krysina, T A Belyavskaya *Zh. Anal. Khim.* **35** 2294 (1980) [a]
108. T V Marchak, G D Brykina, L S Krysina, T A Belyavskaya *Zh. Anal. Khim.* **36** 2361 (1981) [a]
109. G D Brykina, T V Marchak, L S Krysina, V T Khvostova, T A Belyavskaya *Zh. Anal. Khim.* **37** 1841 (1982) [a]
110. G D Brykina, T V Marchak, L S Krysina, T A Belyavskaya *Zh. Anal. Khim.* **38** 1463 (1983) [a]
111. G D Brykina, N L Stepanova, A V Stefanova, L S Krysina, T A Belyavskaya *Zh. Anal. Khim.* **38** 33 (1983) [a]
112. G D Brykina, N L Stepanova, T A Belyavskaya *Zh. Anal. Khim.* **37** 208 (1982) [a]
113. G D Brykina, G F Agapova, V F Kalinina, L S Krysina *Zh. Anal. Khim.* **3** 1461 (1988) [a]
114. M Aihara, H Watanabe, M Kiboku *Anal. Sci., Pt. 1, Suppl.* **7** 87 (1991); *Ref. Zh. Khim.* 18 G 149 (1992)
115. O N Obrezkov, O V Krokhin, A V Pirogov, S N Semenova, O A Shpigun *Zh. Fiz. Khim.* **68** 1880 (1994) [d]
116. M Ahmad, R Narayanasswamy, in *European Conference on Analytical Chemistry, Euroanalysis VIII, Edinburgh, Scotland, UK, 1993 (Abstracts of Reports)* p. O2
117. P S Majumdar, U S Ray *J. Indian Chem. Soc.* **68** 152 (1991); *Ref. Zh. Khim.* 6 G 180 (1992)
118. A Tong, Y Akama *Anal. Sci., Pt. 1, Suppl.* **7** 83 (1991); *Ref. Zh. Khim.* 18 G 148 (1992)
119. L S Pan, V V Vol'khin, M V Zil'berman, in *17-ya Vsesoyuz. Konf. po Khimii i Tekhnologii Redkozemel'nykh Shchelochnykh Elementov, Apatity, 1988 (Tez. Dokl.)* [The 17th All-Union Conference on the Chemistry and Technology of Rare-Earth Alkaline Elements, Apatity, 1988 (Abstracts of Reports)] p. 104
120. L L Voloshenko, B A Zaitsev, E N Malinina, in *Khimiya i Tekhnologiya Neorganicheskikh Sorbentov, Perm', 1979 (Mezhvuz. Sb. Nauch. Tr. PPI)* [Chemistry and Technology of Intercollegiate Sorbents, Perm, 1979 (Intercollege Collection of Scientific Reports from the Perm Polytechnic Institute)] p. 71
121. V P Remez, M V Gridnevskii, M P Remez, in *Ispol'zovanie Prirodnykh Tseolitov Sokirnitskogo Mestorozhdeniya v Narodnom Khozyaistve, Cherkasy, 1991 (Tez. Dokl.)* [The Use of Natural Zeolites of the Sokirnitskii Deposit in the National Economy, Cherkasy, 1991 (Abstracts of Reports)] p. 44; *Ref. Zh. Khim.* 2 L 259 (1992)
122. L A Kul'skii, I T Goronovskii, A M Koganovskii, M A Shevchenko *Spravochnik po Svoistvam, Metodam Analiza i Ochistke Vody* (Handbook of the Properties, Methods of Analysis, and Purification of Water, Part 1) (Kiev: Naukova Dumka, 1980)
123. I V Sheveleva, V A Vasilevskii, O L Khristoforova, O E Presnyakova, in *Neorganicheskie Resursy Torya* (Inorganic Resources of the Sea) (Vladivostok, 1978) p. 34
124. S Maeda, A Ohki, Y Tsurusaki, T Takesita *Spar. Sci. Technol.* **25** 547 (1990); *Ref. Zh. Khim.* 13 B 2798 (1991)
125. M M Benjamin, in *Proceedings of the 77th ESF Annual Technology Conference, Orlando, 1990 (Abstracts of Reports)* Vol. 1, p. 213
126. Jpn. P. 54-40 238; *Ref. Zh. Khim.* 22 L 205P (1980)
127. Jpn. Appl. 54-8185; *Ref. Zh. Khim.* 20 I 386P (1980)
128. A A Kopyrin, A K Pyartman, A V Bekrenev, in *Teoriya i Praktika Elektrokhimicheskikh Protsessov i Ekologicheskie Aspekty ikh Ispol'zovaniya, Barnaul, 1990 (Tez. Dokl.)* [Theory and Practice in Electrochemical Processes and Ecological Aspects of Their Use, Barnaul, 1990 (Abstracts of Reports)] p. 241
129. E V Zheltonozhko, S A Perminov, V P Remez, A S Shubin, in *13-i Vsesoyuz. Seminar "Khimiya i Tekhnologiya Neorganicheskikh Sorbentov" (Tez. Dokl.)* [The XIIIth All-Union Seminar 'Chemistry and Technology of Inorganic Sorbents' (Abstracts of Reports)] (Minsk: Institute of Physicochemical Problems of the Belorussian State University, 1991) p. 22
130. E V Zheltonozhko, A S Shubin, S A Perminov, V P Remez *Zh. Prikl. Khim.* **64** 910 (1991) [c]
131. V V Turov, O A Zaporozhets, O Yu Nadzhafova, V V Sukhan *Teor. Eksp. Khim.* **32** 376 (1996) [e]

[a] — *J. Anal. Chem. (Engl. Transl.)*
[a] — *Moscow Univ. Bull. (Engl. Transl.)*
[a] — *Russ. J. Appl. Chem. (Engl. Transl.)*
[a] — *Russ. J. Phys. Chem. (Engl. Transl.)*
[a] — *Theor. Exp. Chem. (Engl. Transl.)*