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Ion exchangers based on modified mineral carriers

G V Kudryavtsev, S Z Bernadyuk, G V Lisichkin
Moscow State University

ABSTRACT. Methods for the synthesis of ion exchangers based on modified mineral carriers, such as chemical modification of the surface by organosilicon compounds, adsorption and chemical modification of the surface by low-molecular-weight and polymeric organic compounds, the polymerisation of monomers on the surface of mineral carriers, and the hydrolytic polycondensation of organosilicon compounds, have been examined. A list of the most widely encountered commercial sorbents has been given. The possibilities provided by the use of ion exchangers based on mineral carriers for the sorption and separation of inorganic ions, in the high-performance liquid chromatography of organic compounds and biopolymers, and also in catalysis, have been demonstrated.

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I. Introduction

Until recently, two main classes of ion exchanger were known: synthetic organic polymers containing ionogenic functional groups, and inorganic materials, primarily silica, aluminium oxide, and zeolites. The extensive practical application of organic polymeric ion exchangers is due to their universal action, the high concentration of ionogenic groups, the ease of regeneration, and the possibility of varing widely the nature and concentration of the functional groups and hence the sorptive and catalytic characteristics of these materials. The advantages of inorganic ion exchangers are their mechanical strength, their stability to heat and radiation, and the fact that they do not swell in solvents. In general, it can also be said that they have better mass-exchange characteristics, as is clearly seen by comparing the sorptive properties of meso-porous and large-pore mineral materials and organic sorbents with a gel structure. In addition, certain types of inorganic ion exchanger have unique catalytic properties.

At the same time, the development of chemistry and biochemisty has raised problems, for the solution of which both known classes of ion exchanger have proved unsuitable. For example, the use of organic ion exchangers in the intensively developing high-performance liquid chromatography is prevented by their poor average mass-exchange characteristics and the fact that the volume of the sorbent layer in the chromatographic column is not constant. Although mineral sorbents do not have these disadvantages, they can be used to solve only a restricted range of problems, because of the non-uniformity and narrow variability of the surface properties.

It has thus become necessary to create materials of a new type, combining the advantages of the previously known classes of ion exchanger. The mechanical and mass-exchange characteristics of these materials should be determined primarily by the rigid wide-pore mineral framework of the carrier, and their ion-exchange characteristics by the nature of the attached functional groups. The production of these materials has involved the modification of the surface of inorganic materials by organic compounds containing ion-exchanger functional groups.

The ion exchangers being considered form part of an extensive class of modified mineral carriers which find varied applications in sorption, chromatography, catalysis, and other branches of science and technology. The methods of preparation, properties, and applications of these materials have been described in a large number of publications (see for example the published monographs[1–11] and reviews[12–19]), but no general review of ion exchangers based on modified mineral carriers has been published. Such a review is appropriate, because of the specific characteristics of the synthesis of these materials and the fields of application in which only these materials are used, such as high-pressure ion chromatography, the ion-exchange chromatography of proteins and other natural compounds, and acid–base and phase transfer catalysis.

The present review describes methods for obtaining ion exchangers based on mineral carriers, some of their properties, and their applications in sorption, catalysis, and chromatography.

II. Methods for obtaining ion exchangers based on modified mineral carriers

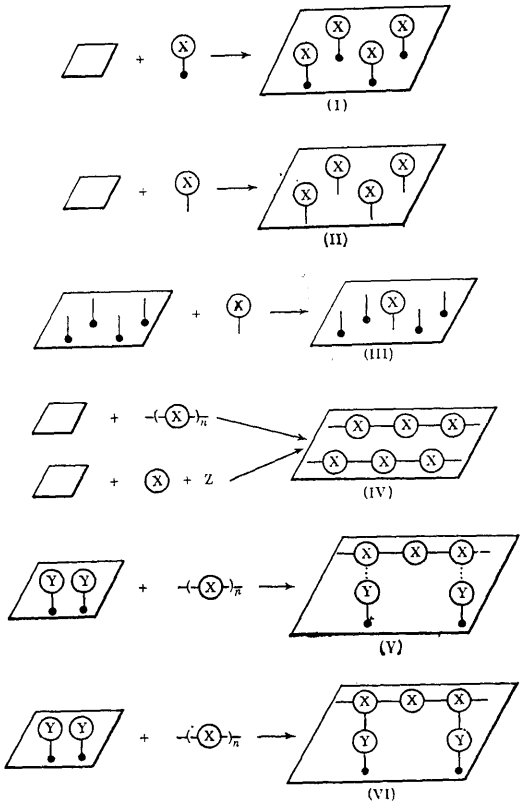
A large number of functional groups capable of taking part in ion exchange have been attached to the surface of mineral carriers. It was decided to restrict the present review to a narrow range of classical ion exchangers. Thus the cation exchangers examined include strongly, moderately, and weakly acidic materials containing sulphonic, phosphonic, and carboxylic acid groups, and the anion exchangers include strongly basic materials with quaternary ammonium and phosphonium groups and weakly basic materials with mono- and polyamine groups. The last sorbents, and also phosphonic and carboxylic acid cation exchangers, in a number of cases may show complex-forming power. The properties and applications of these sorbents associated with complex formation are not examined in the present review. Other materials excluded from the present review are modified mineral carriers with grafted tertiary phosphines or ionogenic molecules of aminoacids, dithiocarbamates, dithiocarboxylic acids, hydroxamic acids, and other compounds for which complex-forming properties or affinity are most characteristic.

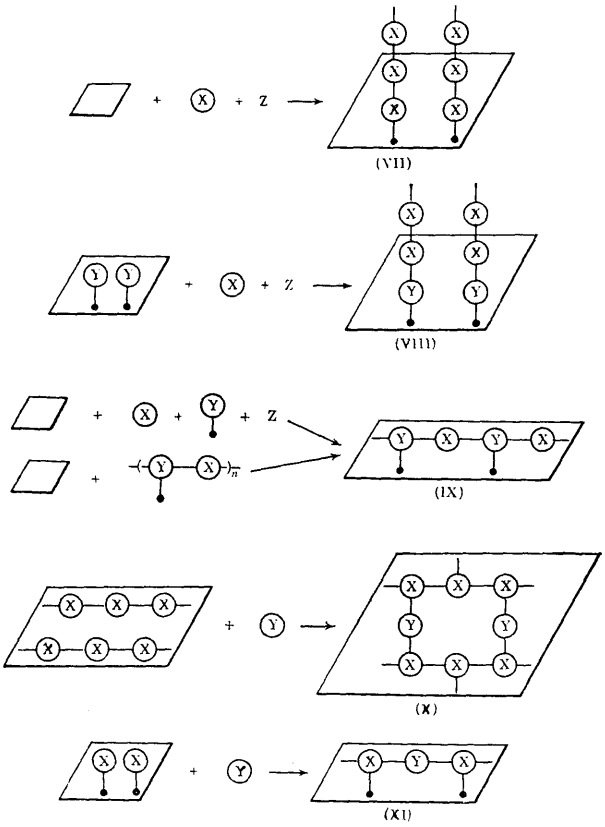
A wide range of mineral materials are used as carriers for the attachment of organic compounds, primarily silica, and also aluminium,[20–24] titanium,[22–26] zirconium,[22,27] tin(IV),[25,26,28] ruthenium(IV),[25,29] etc. oxides. The great majority of studies have been devoted to the attachment of organic compounds to silica, since this material has been extensively studied, is easily modified, and is readily available. Subsequently, except in certain special cases, the discussion will deal with the modification of the surface of silica. It should be noted that the approaches to the modification of the surface of different oxides are identical, and in most cases are based on the reaction with the hydroxyl groups of the surface. The regular features of the modification established for silica can in a first approximation be extended to other oxide carriers.

Ionogenic groups cannot be attached directly to the surface of mineral carriers, because of the instability (primarily to hydrolysis) of the bonds Si–O–C, Si–N, Si–S, Si–O–S, Si–P, Si–O–P, etc. This makes it necessary to introduce an organic "binder" joined to the carrier surface, and then to attach ion-exchanger groups to it by strong covalent bonds.

A large number of methods for modifying the surface of mineral carriers have now been developed, making it possible to vary the nature of the organic modifying layer (monomeric, polymeric) and the nature of the bond between the carrier and the organic modifier (covalent, ionic, hydrogen bonds, topological fixation). The variety of methods of preparation and structures formed on the surface is illustrated in Scheme 1. Additional possibilities for the synthesis of modified mineral carriers are provided by the conversion of attached functional groups X into other ion-exchanger groups.

Scheme 1





= the surface of the mineral carrier;

● = the anchoring group forming a covalent bond with the carrier;
– = a hydrocarbon chain;

Ⓧ = an ionogenic group or molecule containing an ionogenic group;

Ⓨ = a cross-linking molecule or group with no ion-exchange properties;

Z = initiation (in polymerisation).

The synthesis paths represented in the scheme are based on the use of prepared mineral carriers. An alternative method for obtaining modified silicas is by the hydrolytic polycondensation of organosilicon compounds.

Specific examples of the synthesis of ion exchangers based on modified mineral carriers can now be considered.

1. Covalent attachment of monomeric organic compounds (structure I)

Modification of the carrier surface by organosilicon compounds has been most widely used to synthesise ion exchangers based on silica:

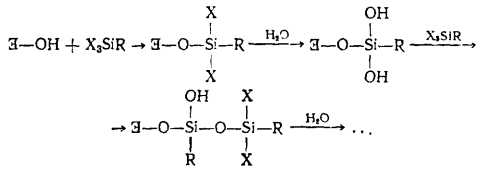
$$\exists\text{—OH} + XX^1X^2SiR \rightarrow \exists\text{—O—}\underset{|}{\overset{|}{Si}}\text{—R},$$

where ∃ represents the surface of the mineral carrier, X (and possibly X^1 and X^2) = Cl or OAlk, and R represents an organic group, which may include the required functional group.

The attachment of organosilicon compounds to the carrier surface may give two types of grafted-layer structure: "brush" and "polymeric". When the brush structure is formed, the molecules of the modifier are attached to the carrier surface as a result of their reaction

with the hydroxyl groups of the carrier, giving a uniform monomolecular layer. The surface concentration of grafted compounds is determined by the size of the XX^1X^2Si anchor group, and for ion exchangers with the brush structure it does not exceed 2–3 molecule nm^{-2}. For carriers with $S_{sp} = 100\ m^2\ g^{-1}$, this quantity is ~ 0.4 mmol g^{-1}, which is much lower than that for organic polymers.

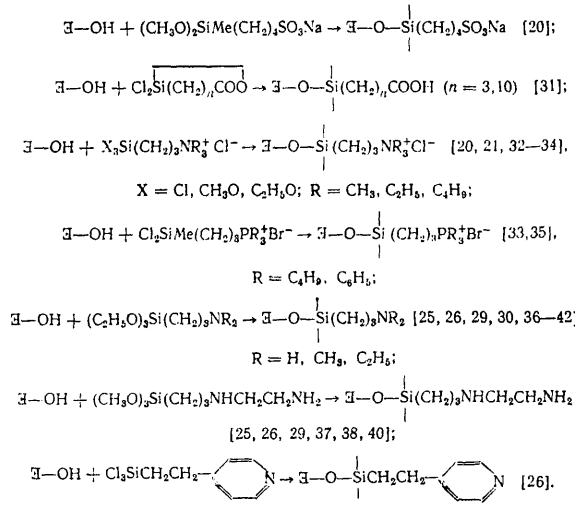
The surface concentration of grafted organic compounds can be increased by carrying out the modification in the presence of water. The following processes take place, giving the grafted layer a polymeric structure:



Sorbents with a polymeric structure have a higher surface concentration of grafted organic molecules, compared with sorbents with a brush structure, but when more than four molecules nm^{-2} are attached to the surface, a uniform covering cannot be expected.[30]

Not all hydroxyl groups of the carrier surface react with organosilicon compounds. Residual silanol groups, which show weakly acidic ion-exchange properties and are also capable of bringing about the specific adsorption of many organic molecules, in many cases have an unwanted influence on the properties of ion exchangers particularly when they are used in high-performance liquid chromatography (HPLC). The surface concentration of silanol groups can be decreased by using so-called monofunctional monomers $XSiMe_2R$ or by carrying out additional silanisation by small silanising agents, usually trimethylchlorosilane or hexamethyldisilazane.

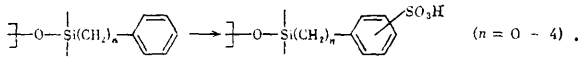
In principle, all the ion exchangers considered can be obtained by single-stage modification of the carrier surface:



Of the modifiers listed, however, only the organosilicon derivatives of amines, primarily γ-aminopropyltriethoxysilane (trade mark AGM-9), are readily available. Research workers therefore prefer first to attach a relatively simple and readily available organosilicon compound to the surface, and then to introduce into it the required ion-exchange group, using familiar reactions of organic synthesis.

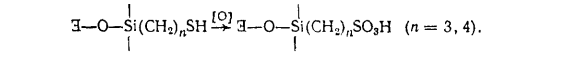
The yields of the reactions on the surface are usually not quantitative, and this leads to the presence of functional groups of different types. When selecting a method for synthesising an ion exchanger, it is preferable that the original functional groups to be subjected to subsequent transformations, and also the intermediate products of their transformation, should not have ion-exchange properties.

Strongly acidic cation exchangers are most frequently obtained by sulphonating aromatic compounds attached to the surface:[43–48]



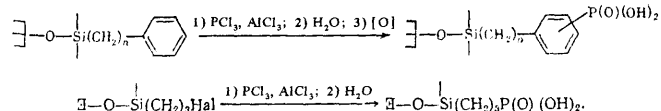
The advantages of this method are the availability of the original organosilicon modifiers and the high degree of sulphonation, which reaches 100% when chlorosulphonic acid is used as sulphonating agent.

The oxidation of grafted thiols is equally effective:[49,50]



Other methods of synthesis include radical chlorosulphonation of attached alkyl groups,[49] the reaction of grafted halogenoalkyl groups with sodium sulphite[51] or ammonia,[49] the reaction of a grafted glycidyl ester with sodium sulphite,[52] and the oxidation of a grafted isothiouronium salt.[20]

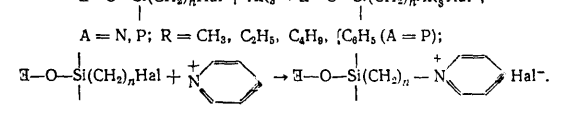
The following methods can be recommended for synthesising phosphonate cation exchangers:[53,54]



The attachment and hydrolysis of esters of alkyl or phenyl hydrogen phosphates[55,56] and the chlorides of alkyl hydrogen phosphates[57] have also been described.

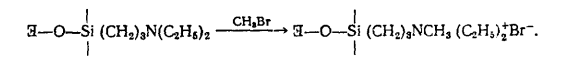
The best method for obtaining carboxylic acid cation exchangers is by the acid hydrolysis of attached esters[44,58,59] and nitriles,[46,58] where the yields are quantitative.

The most widely used method for synthesising strongly basic anion exchangers is by the reaction of attached halogenoalkyl groups with tertiary amines,[45,46,60,61] phosphines,[33,35,62] or pyridine:[61]



When an aromatic compound is grafted initially to the silica surface, it is first chloromethylated, for example with methyl chloromethyl ether in the presence of zinc chloride, and then aminated.[48,63] The advantage of the method is the high yield (>80%) at all stages of the transformation.

It is possible in principle to synthesise strongly basic anion exchangers by the exhaustive alkylation of attached amines, for example:[33]



However, since there is no guarantee that the reaction on the surface will be quantitative, the product may contain not only the required tetra-alkylammonium compounds but also alkylamines, which also have ion-exchange properties.

The method of synthesis on the surface in the production of weakly basic anion exchangers is usually employed to attach polyamine groups:[40,64]

$$\equiv Si{-}O{-}Si{\equiv}\,(CH_2)_3Hal + NH_2(CH_2CH_2NH)_nH \rightarrow \equiv Si{-}O{-}Si{\equiv}\,(CH_2)_3NH(CH_2CH_2NH)_nH.$$

Extensive synthetic possibilities are provided by the use of silica specimens modified by epoxy-groups.[52] The sorbents are obtained by treating silica with γ-glycidoxypropyltrialkoxysilanes followed by reaction with compounds capable of opening the epoxy-ring:

$$\equiv Si{-}OH + (RO)_3Si(CH_2)_3OCH_2CH{-}CH_2 \rightarrow$$

$$\rightarrow \equiv Si{-}O{-}Si{\equiv}\,(CH_2)_3OCH_2CH{-}CH_2 \xrightarrow{HX} \equiv Si{-}O{-}Si{\equiv}\,(CH_2)_3OCH_2CHOH{-}CH_2X,$$

$$X = N(C_2H_5)_2,\ OCH_2CH_2N(CH_3)_2,\ OCH_2CH_2N(C_2H_5)_2,$$
$$(NHCH_2CH_2)_nNH_2,\ OCH_2COOH,\ SO_3H.$$

When silica with grafted epoxy-groups is treated with water at pH 3, the product is a sorbent with grafted diol groups (X = OH). This sorbent and its derivatives are widely used in the chromatography of biopolymers, since there is no non-specific adsorption of proteins. It may also be noted that the oxidation of a grafted alcohol by a mixture of sodium metaperiodate and potassium permanganate in a weakly alkaline medium provides a convenient method for obtaining weakly acidic carboxylic acid cation exchangers.

The advantages of the method involving the covalent attachment of monomeric organosilicon compounds also include the possibility of obtaining polyfunctional sorbents (so-called multi-phases); chromatographic separation on these sorbents involves the coordinated combination of reactions of two or more types between the substances being analysed and the sorbent. The need for sorbents of this kind arises most frequently in the analysis of biopolymers, where the use of only one method of separation (for example reversed-phase or ion-exchange methods) does not give the required selectivity. To solve this problem, the carrier surface is modified using a mixture of organosilicon compounds, and the required functional groups are introduced to give sorbents of the following type:[65–68]

$$\equiv Si{-}O{-}Si(CH_3)_2(CH_2)_nCH_3$$
$$\equiv Si{-}O{-}Si(CH_3)_2(CH_2)_3R$$

$$R = C_6H_4SO_3H,\ N^+(CH_3)_2CH_2C_6H_5.$$

The best ratio of "hydrophobic" and ion-exchange interactions in the separation can be achieved by varying the quantities of the original organosilicon compounds. These results often cannot be achieved simply by mixing two different sorbents.

An alternative method of varying the contributions of the "hydrophobic" and ion-exchange interactions in retention is by changing the length of the hydrocarbon chain connecting the ionogenic group to the carrier surface.[69] This method gives sorbents with highly reproducible properties, but the need for the special synthesis of a set of organosilicon modifiers restricts its application.

A promising method for synthesising ion exchangers with variable ion-exchange capacity has been proposed;[70] the first stage involves the exhaustive modification of the silica surface by diol groups (using γ-glycidoxypropyltriethoxysilane), and in the second stage these groups are acylated using the cyclic anhydrides of dibasic acids. The concentration of carboxyl groups introduced can be varied to give the best ion-exchange retention of proteins; the complete shielding of the surface by the diol groups ensures that non-specific adsorption of proteins does not take place.

The covalent attachment of monomeric organosilicon compounds to the surface of mineral carriers ensures uniformity of the sorption centres and high reproducibility and predictability of the synthesis. In the case of sorbents with a brush structure, the modifier forms a lining in all the pores of the carrier consisting of a thin regular layer, allowing the diffusion of the substances from the solution into the interior of the particle and ensuring a high rate of mass exchange. This gives modified sorbents of this type a dominant position in HPLC. At the same time, these sorbents have a number of disadvantages.

Firstly, these sorbents have a low stability to hydrolysis. Modified silica specimens in which the grafted layer has a brush structure are not recommended for use at pH < 1 and pH > 9. The degradation of weakly basic anion exchangers is often observed on prolonged use even at pH > 7. The hydrolytic stability of sorbents in the alkaline range up to pH 10 can be increased by using other inorganc carriers, in particular aluminium oxide and aluminated or zirconated silica specimens.

Secondly, the exchange capacity of these sorbents is several times lower than that of ion exchangers based on organic polymers. This represents a significant obstacle to their use in technological sorption processes, and restricts their sphere of application to mainly analytical problems.

Thirdly, their synthesis is relatively complicated, and the use of organosilicon compounds which in many cases are expensive and difficult to obtain increases their cost considerably, compared with their organic-polymer analogues.

Thus the search for other methods for synthesising ion exchangers based on modified mineral carriers is continuing.

2. The attachment of monomeric organic compounds by adsorption (structures II and III)

The adsorption of organic ionogenic compounds on the surface of a mineral carrier is undoubtedly the simplest method for synthesising the sorbents being considered. The earliest studies in this field (see for example Ref.71), however, revealed its main disadvantage, namely the low stability, due to the continuous elution of the deposited substance into the solution. This stimulated the development of methods for the covalent attachment of organic compounds to the surface.

Nevertheless, recent experience has shown that adsorption systems can be used successfully even in HPLC. The surface modifier is a compound which is firmly adsorbed on silica, for example tetraethylenepentamine,[72] or a compound which has a low solubility in the eluant, for example cetyltrimethylammonium bromide or n-hexadecylpyridinium chloride when working with aqueous eluants.[73] Silica with adsorbed tetraethylenepentamine has been used to separate carbohydrates and polyalcohols at pH 8–9; even under these conditions, it was necessary to add the modifier to the eluant to keep the column characteristics constant. Silica with adsorbed long-chain ammonium salts shows practically no change in its characteristics when used to separate mixtures of inorganic anions.[73]

An increase in the stability of adsorption-bonded systems can be achieved by using reversed-phase sorbents as the original carrier, for example silica specimens modified by octyl- or octadecylsilanes. The thin hydrophobic layer grafted to the surface ensures the strong retention of ionogenic substances containing long-chain alkyl groups: $C_nH_{2n+1}SO_3Na$,[74] $C_nH_{2n+1}OSO_3Na$,[74,75] $(C_nH_{2n+1})_4N^+Cl^-$,[74,75] and

$C_{16}H_{33}N(CH_3)_3^+Cl^-$.[76,77] This method is essentially the limiting case of ion-pair chromatography. The modified columns are made from organic materials. Aqueous solutions are mainly used as eluants in the chromatographic analysis. Under these conditions, high stability of the column operation is achieved; according to Ref.77, the exchange capacity remains unchanged during continuous operation for at least 80 d in the separation of mixtures of inorganic anions.

This method for obtaining sorbents is attractive chiefly because of the ease of variation of the nature and sorption characteristics of the ion exchangers based on the most readily available reversed-phase columns.

3. The attachment of polymers

The greatest variety of possible sorbent structures among the ion exchangers being considered is provided by mineral carriers with organic polymers attached to their surface. Initially, the interest in these materials was due to the possibility of their application as polymer fillers.[8,15,16,24,78–99] In recent years, these materials have been used increasingly as sorbents and catalyst carriers.[22,28,100–121]

The interest of research workers in materials of this class is due to the following potential advantages over mineral carriers with covalently attached monomeric organic compounds: 1) higher stability of action, resulting from the multi-point attachment of the polymeric modifier to the surface or from the more effective shielding of the surface; 2) the greater sorptive capacity, resulting from the increase in the proportion of the organic component; and 3) the simpler (in some cases) synthesis, which makes it possible to avoid the use of organosilicon modifiers.

Two main approaches are used in the production of these materials: modification of the surface by prepared polymers[22,100,104,112–121] and polymerisation of monomers on the surface.[24,28,41,78–99,101–103,105–111,122]

Modification by prepared polymers (structures IV–VI, IX, X). The simplest version of the modification is the adsorption of organic polymers on the surface of a mineral carrier to give so-called film or pellicular sorbents.[123] The best results are obtained using heterochain nitrogen-containing oligomers based on polyethyleneimine (PEI),[112–116] which are firmly adsorbed on the surface of hydroxyl-containing carriers. By changing the molecular mass of the oligomer used, it is possible to vary the thickness of the grafted layer over a wide range, beginning from the values characteristic of brush structures. For example, the use of branched PEI oligomers with a molecular mass of 600 gives layers with a thickness of 3–4 nm;[115] the best selectivity in the separation of oligonucleotides is shown by silica specimens with pore dimensions of 70–100 nm, modified by PEI with a molecular mass of 35 000.[121]

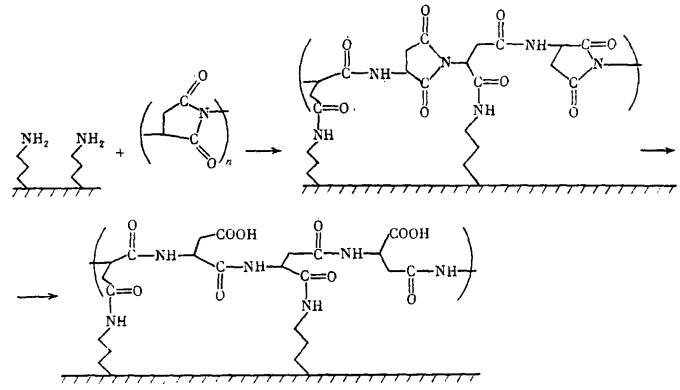
PEI attached by adsorption will obviously be transferred to the solution to some extent, particulary on treatment with acidic eluants. To increase the stability of action of these systems, Regnier and co-workers[112–115] proposed the cross-linking of the adsorbed oligomers using bifunctional and polyfunctional reagents: dibromoalkanes, epichlorohydrin, and cyanuryl chloride. The compounds most widely used for this purpose contain two or more epoxy-groups, which react with amines under mild conditions, and, when the epoxy-ring is opened, give additional alcohol groups which increase the hydrophilic nature of the sorbent. A similar approach was used in Ref.118, where adsorbed polyvinylpyrrolidone was cross-linked by the thermal decomposition of dicumyl peroxide or by using radiation.

When the adsorbed oligomers have been cross-linked, the particle of inorganic carrier is included in a "network" of organic polymer by so-called topological fixation; the components cannot be separated without complete breakdown of the sorbent. The sorbents with the greatest hydrolytic stability have been obtained by using titanium or aluminium oxides, or zirconated silica, as carrier: when these sorbents are kept at pH 14 for 24 h, only slight transfer of PEI to the solution is observed.[22]

Sorbents containing cross-linked PEI have the properties of weak anion exchangers, but they can easily be converted into strongly basic anion exchangers by quaternisation using methyl iodide[113] or into weakly acidic cation exchangers by reaction with halogenocarboxylic acids or with the anhydrides of dibasic carboxylic acids.[116,124]

To obtain film ion exchangers based on non-porous particles, the charged macro-particles are brought into contact with positively charged particles with colloidal dispersion. As a result of super-equivalent adsorption, the macro-particles acquire a charge opposite to the original charge. On these macro-particles it is possible in turn to deposit other micro-particles of opposite charge. Thus in Ref.104, particles of Amberlite XE-225 (a strongly basic polymeric anion exchanger) with dimensions of 100–500 nm were deposited from solution on glass particles with dimensions of 24–52 μm, followed by negatively charged particles of Ludox-AM with dimensions of 15 nm; these operations were repeated three times, to give an anion exchanger with a specific surface of 0.5 $m^2 g^{-1}$. Because of the low specific surface of these sorbents, their sorptive capacity is low and does not exceed $n \times 10$ μg-equiv g^{-1}, which is much lower than that of sorbents with a brush structure and, more particularly, the sorbents with adsorbed PEI described above.

To ensure stronger bonding of the oligomers to the carrier surface, in a number of cases the original carrier has been chemically modified using organosilicon compounds capable of forming covalent bonds with the functional groups of the oligomers.[116,119,120] Thus in Ref.116, PEI was attached using grafted carboxyl groups; in Ref.120, polyaspartic acid was attached to the surface of aminopropylsilica by the chemisorption and subsequent hydrolysis of polysuccinnimide.



Sorbents with an analogous structure are also obtained by modifying the carrier with polymers containing organosilicon anchor groups, for example polyethyleneimine containing $(CH_3O)_3Si(CH_2)_3$ groups[125] or a copolymer of 4-chloromethylstyrene and vinylmethyldichlorosilane.[117] The presence of active chlorobenzyl groups in the copolymer provides a method for synthesising a wide range of cation and anion exchangers. An advantage of this method of grafting is that the characteristics of the original polymer are usually well known.

Polymerisation on the surface (structures IV, VII–IX, XI). The polymerisation of monomers on the surface of mineral materials is one of the most general methods of synthesising modified mineral carriers.[8,15,16] The simplest method involves polymerisation on the surface of non-modified carriers. Weakly acidic cation exchangers are

synthesised by polymerising acrylic acid[24,28,79,103,122] (in the polymerisation of methyl methacrylate[24,84,86,93] or acrylonitrile,[24] subsequent hydrolysis is necessary). Extensive synthetic possibilities are provided by the polymerisation of styrene;[100–103,122] sulphonation of the polymer layer on the surface gives sulphonic acid cation exchangers,[100–103, 122] and chloromethylation followed by amination gives strongly basic anion exchangers.[100,122] A promising monomer is chloromethylstyrene.[126–128] In some cases,[100–103,126–128] these vinyl monomers are copolymerised with divinylbenzene.

Various methods are used to initiate polymerisation: mechanochemical treatment,[80,81] ultraviolet irradiation,[90,129] and electrical discharge.[82] In most studies, polymerisation has been carried out using special initiators and using radiation. In the first case, the adsorption of the monomer on the carrier surface is accompanied by the adsorption of benzoyl peroxide,[24,100] t-butyl peroxide,[101] azobisisobutyronitrile,[28,127,128] or ammonium persulphate.[24] In the second case,[84–88,93] two methods are used: irradiation of the carrier with an adsorbed layer of monomer, or post-radiation grafting, where the carrier is subjected to the action of radiation and then treated with the monomer. The lifetime of the reaction centres on the surface may reach 20 d.[130]

All these cases give the homopolymer and a so-called non-extractable polymer, the proportion of which may reach 90–100%. For polymerisation under the influence of radical initiators or an electrical discharge, covalent bonds are not formed between the polymer and the carrier, and the modifying layer is held on the surface by adsorption forces or geometric factors. On mechanochemical treatment or the action of radiation or ultraviolet light on systems with adsorbed quinone,[90] radicals such as $\equiv Si-O^{\cdot}$,[15,16,80,90,93] which initiate polymerisation, may be formed on the carrier surface. In this case the polymer is joined to the surface by an $Si-O-C$ bond, which is not stable to hydrolysis and which is decomposed by the action of small quantities of moisture, so that it cannot be said that covalent bonds are formed between the polymer and the carrier surface.

An effective procedure which makes it possible to use milder polymerisation conditions in the surface layer and at the same time guarantees the formation of a strong carrier–polymer covalent bond involves the preliminary modification of the carrier by organosilicon compounds. The most widely used methods are those involving the attachment of vinyltrichlorosilane[91,93,105–109] and other vinyl derivatives[94,96] to the carrier surface. Treatment with γ-rays or radical initiators is then used to bring about the polymerisation of acrylic acid,[106,108,109] methyl methacrylate,[93,94] styrene,[94,96,105,107–109] or vinylpyridines[91] on the surface of the modified carrier. In a number of cases, cross-linking of the grafted polymer chains is brought about by carrying out the polymerisation in the presence of divinylbenzene.[105]

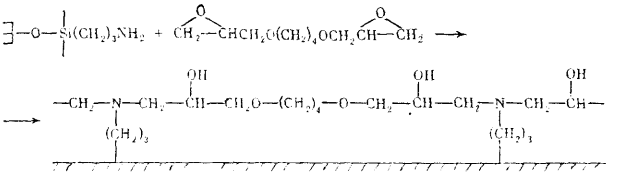
It is possible to attach to the surface not only vinyltrichlorosilane but also other organosilicon compounds capable of initiating radical polymerisation, in particular peroxides[23,92,97,131] and ozonides.[98] A method has also been described for attaching to the carrier surface compounds with the general formula $Cl_2(CH_3)Si(CH_2)_3X$, where $X = N(CH_3)_2$, $N(C_2H_5)_2$, and $OCOCCl_3$, with subsequent graft polymerisation of methyl methacrylate or styrene under the influence of visible light (λ = 400–500 nm) in the presence of manganese carbonyl,[95] fluorenone, or related organic compounds.[37]

A fundamental and as yet not fully resolved problem concerns the structure of the grafted layer in these materials. Analysis of data obtained by different authors indicates that only a small proportion of the silanol groups of the surface or grafted organosilicon compounds initiate the growth of a polymer chain. This leads to "islet" modification of the surface, and complete covering of the surface by the organic polymer requires a large quantity of the monomer, up to 3–6 effective monolayers (see for example Ref.84). In the initial stage of the polymerisation (at concentrations up to one third of an effective monolayer), linear macromolecules with a narrow molecular-mass distribution are formed; with increase in the degree of conversion there is an increase in the contribution of processes of chain transfer to the polymer, leading to branching of the macromolecules and marked broadening of the molecular-mass distribution.[85] This may lead to additional non-uniformity of the characteristics of the grafted layer.

The conformation of the grafted chains is determined by their chemical character, in particular their affinity for the surface hydroxyl groups of the carrier. Infrared spectroscopy has established that a large number of hydrogen bonds are formed between polymethyl methacrylate and an aerosil surface.[78,86] With a small quantity of deposited polymer, its molecules have a branched conformation, whereas at high concentrations they form a non-planar coil. Similar effects are observed in the polymerisation of vinylpyridines on an aerosil surface or of acrylic acid on an aminopropylaerosil.[79,88] The formation of hydrogen bonds between the functional groups of the polymer and the carrier leads to uniform covering of the surface and increases the strength of attachment of the polymer and the degree of shielding of the surface. It should be noted, however, that in systems with a strong adsorption interaction there is a sharp decrease in the rate of polymerisation.[79,88]

An increase in the strength of the bonding of the polymers to the carrier surface is achieved by copolymerising vinyl monomers with unsaturated organosilicon compounds containing reactive chorosilyl or ethoxysilyl groups, for example $(C_2H_5O)_3SiCH=CH_2$[99,105] and $(C_2H_5O)_2Si(CH_3)CH_2OCOC(CH_3)=CH_2$.[94] In Ref.99 it is stated that the grafted polymer obtained in this way cannot be separated from the carrier even by treating with HF; this is attributed to the many-point grafting of the polymer and the marked shielding of the carrier surface.

The last method of synthesis gives sorbents whose structures are identical to those of the specimens obtained by modifying the carrier surface with prepared polymers containing active organosilicon groups[117,125] (see above). A third method of obtaining sorbents of this kind involves the two-dimensional cross-linking of grafted monomeric organosilicon compounds. An example is provided by the cross-linking of grafted primary amines with diepoxides:[110]



After treatment in this way, the time of stable operation of the sorbent increases from several days to several months.

The data in the present section show that, on the average, mineral carriers modified by polymers have a higher stability to hydrolysis than sorbents with a brush structure. In a number of cases they can be synthesised without using organosilicon compounds. They are characterised by an increase in the exchange capacity to 2.5 mg-equiv g^{-1}. The capacity of ion exchangers based on organic polymers is generally much higher, but this difference is counterbalanced slightly by the large bulk density of the sorbents based on mineral carriers. Thus the exchange capacity of a sulphonic acid cation exchanger based on silica is 2.2 mg-equiv g^{-1}, which corresponds to 1 mg-equiv cm^{-3}; for Dowex 508 the corresponding quantities are 5 mg-equiv g^{-1} and 1.7 mg-equiv cm^{-3}.[108,109]

The disadvantages of the methods described, particularly those involving polymerisation on the surface, include the difficulty of controlling the course of the reaction and the unpredictable change in the structural characteristics of the sorbents; in many cases the specific surface decreases by a factor of 2.5–10, with almost the same decrease in the specific pore volume.[108,109] The mass-exchange characteristics of sorbents with thick polymeric modifier layers are close to those of organic ion exchangers, and are much inferior to those of sorbents with a brush structure; in the general case, this lowers the efficiency of chromatographic columns (see for example Ref.132). Nevertheless, the use of these sorbents is often justified even in HPLC, when the efficiency of separation is limited by another parameter of the process, for example the diffusion of the compounds being analysed in the chromatography of proteins.

4. Hydrolytic polycondensation of organosilcon compounds

The essential feature of the method being considered is the hydrolysis of trichloro- or trialkoxysilanes X_3SiR to give polysiloxanes. Since this gives a three-dimensional structure of $-Si-O-Si-O-$ bonds, these materials, despite the fact that they do not contain silicon dioxide, are in many respects analogous to modified silica specimens. If the hydrocarbon group R does not contain ionogenic functional groups, these are introduced into the prepared polysiloxane.

Ion exchangers are formed directly by the hydrolytic polycondensation of $Cl_3SiCH_2C_6H_4SO_3H$,[133] $Cl_3SiC_6H_4C_6H_4PCl_2$ (after oxidising the phosphonite group to phosphonate),[134], $Cl_3SiC_6H_4POCl_2$,[135] 1,1-dichloro-1-silalactones,[31,136] $Cl_3Si(CH_2)_nCOCl$ (n = 3,10),[31] $(C_2H_5O)_3Si(CH_2)_3NHCH_2CH_2NH_2$,[137] $[(C_2H_5O)_3Si(CH_2)_3]_2NCH_3$,[138] and $[(CH_3O)_3Si(CH_2)_3]_4N^+Cl^-$.[138] The exchange capacities of these sorbents are 2–6 mg-equiv g^{-1}. Convenient intermediate materials for synthesising ion exchangers are provided by the hydrolysis products of $X_3Si(CH_2)_nC_6H_5$ (X = Cl, C_2H_5O; n = 0–2),[139–142] Cl_3SiCH_2Cl,[143] $(C_2H_5O)_3SiCH_2SH$,[144] and $(CH_3O)_3Si(CH_2)_3SH$.[142]

Of all modified mineral carriers, ion exchangers based on polysiloxanes have the highest exchange capacity, only slightly lower than that of organic ion exchangers. This advantage, however, does not compensate the disadvantages associated with the fact that they do not contain a rigid silicon dioxide matrix. Polysiloxanes are less stable, and, like organic ion exchangers, undergo considerable swelling in various solvents, so that they are unsuitable for use in HPLC. The ionogenic groups of these ion exchangers differ considerably in their accessibility; the inner groups are inaccessible to large organic molecules, and this restricts the possibilities for the application of ion-exchange polysiloxanes in sorption and catalysis. Moreover, considerable difficulties are encountered in the preparation of polysiloxanes with required values of the specific surface, specific volume, and pore dimensions, whereas in other known methods of synthesis these parameters are easily varied by selecting an appropriate carrier.

The mechanical and mass-exchange characteristics of polysiloxanes can be improved by carrying out the simultaneous polycondensation of functional organosilicon compounds with tetraethoxysilane or polyethoxysiloxanes,[141,142,145,146] but the exchange capacity is lowered, and the synthesis is more complicated.

Hydrolytic polycondensation may provide a useful method for the synthesis of film ion exchangers.

III. Industrial ion exchangers based on modified mineral carriers

A number of firms in other countries now produce ion exchangers based on silica, chiefly for use in chromatography. The principal sorbents and the firms producing them are listed below (in most cases, in the sorbent names, the numbers denoting the particle size of the sorbent or the average pore diameter are omitted).

Sorbents for the HPLC of organic compounds

Weakly basic ion exchangers: Nucleosil NH_2, Nucleosil $N(CH_3)_2$, Polygosil NH_2, Polygosil $N(CH_3)_2$ (Macherey-Nagel, FRG–Switzerland); Zorbax NH_2 (Du Pont, USA); Bondapak NH_2 (Waters, USA); Aminopropyl-Daltosil 100, DEAE-Daltosil 100 (Serva, USA); DEAE 2SW Spherogel TSK-IEX (Beckman, USA); Lichrosphere 100 NH_2 (Merck, FRG); Vydac 601 SC (Separations Group, USA); Silasorb DEA (Lachema, Czechoslovakia).

Strongly basic anion exchangers. Nucleosil SB (Macherey-Nagel, FRG–Switzerland); Partisil 10 SAX (Whatman, UK); SAX Ultrasil (Beckman, USA); TEAB-Daltosil 100, TEAP-Si 100 (Serva, USA); Zorbax SAX, Zipax SAX (Du Pont, USA); Supelcosil LC-SAX (Supelco SA, Switzerland); Vydac 301 SC, Vydac 301 TPB (Separations Group, USA); Silasorb S (Lachema, Czechoslovakia).

Weakly acidic cation exchangers. Carboxymethyl-Daltosil 100, Carboxymethyl-Si60 (Serva, USA); CM 2SW Spherogel TSK-IEX (Beckman, USA).

Strongly acidic cation exchangers. Partisil SCX (Whatman, UK); Zorbax SCX, Zipax SCX (Du Pont, USA); Nucleosil SA (Macherey-Nagel, FRG–Switzerland); SCX Ultrasil (Beckman, USA); Vydac 401 SC, Vydac 401 TPB (Separations Group, USA); Supelcosil LC-SCX (Supelco SA, Switzerland); Sulfopropyl-Daltosil 100, Sulfopropyl-Si100 (Serva, USA).

Sorbents for the chromatography of biopolymers

Weakly basic anion exchangers: Ultropac TSK 545 DEAE (LKB, Sweden); SynChropak AX, SynChropak CATSEC, SynChroprep AX, SynChropak ASC (SynChrom, USA); Zetaprep DEAE (Molecular Separations Division, USA); Aminopropyl-Si100, DEAE-Si100 (Serva, USA); Nucleogen-DEAE (Macherey-Nagel, FRG–Switzerland); Spherogel TSK IEX 530 DEAE (Beckman, USA); TSK Gel IEX-545 DEAE SIL (Toyo Soda, Japan); Zorbax Bio-Series WAX-300 (Du Pont, USA); Shimadzu Shim-pack WAX1(2) (Shimadzu, Japan).

Strongly basic anion exchangers. SynChropak Q, SynChroprep Q, SynChropak QSC (SynChrom, USA); Zetaprep QAE (Molecular Separations Division, USA); Sep-Pak Accell QMA (Waters, USA); Zorbax Bio-Series SAX-300 (Du Pont, USA).

Weakly acidic cation exchangers. Ultropak TSK 535 CM (LKB, Sweden); SynChropak CM, SynChroprep CM, SynChropak CSC (SynChrom, USA); Zetaprep CM (Molecular Separations Division, USA); Carboxymethyl-Si300, Carboxypentyl-Si500 (Serva, USA); Sep-Pak Accell CM (Waters, USA); Spherogel TSK IEX 540 CM (Beckman, USA); Zorbax Bio-Series WCX-300 (Du Pont, USA); Shimadzu Shim-pack WCX-1 (Shimadzu, Japan).

Strongly acidic cation exchangers: Nucleosil SA Catecholamine (Macherey-Nagel, FRG–Switzerland); Zorbax Bio-Series SCX-300 (Du Pont, USA).

Sorbents for ion chromatography

Strongly basic anion exchangers: Partisil SAX (Whatman, UK); Vydac 302 SC (Separations Group, USA); Wescan Anion (Wescan Instruments, USA); Zipax SAX (Du Pont, USA); Supelcosil LC-IC (Supelco SA, Switzerland); Nucleosil Anion (Macherey-Nagel, FRG–Switzerland); R Sil An (Alltex Association, USA); TSK Gel IC-Anion SW (Toyo Soda, Japan).

Strongly acidic cation exchangers: Partisil SCX (Whatman, UK); Vydac CX (Separations Group, USA); Zipax SCX (Du Pont, USA).

Unfortunately, detailed information on the structures of most of these sorbents is not available either in the firms' literature or in the original papers; the methods of synthesis are not known, and in some cases it is not possible to say anything about the composition of the functional groups on the surface. It may be noted that the carrier most frequently employed is porous silica with an average pore diameter of 6–30 nm; sorbents for separating biopolymers have a large pore diameter, reaching 100 nm. In a number of cases (the sorbents Zipax, Vydac SC, Corasil, SynChropak ASC), the carriers are particles with a non-porous glass core and a porous external layer of silica with a thickness of about 1 μm.

Most of these sorbents consist of silica with chemically grafted monomeric organosilicon compounds. The weakly basic anion exchangers contain the groups $-NH_2$, $-N(CH_3)_2$, $-N(C_2H_5)_2$ (DEAE sorbents). The strongly basic anion exchangers contain different grafted tetra-alkylammonium salts. The weakly acid cation exchangers contain $-CH_2COOH$ groups (sorbents of the Carboxymethyl, CM series). In strongly acidic cation exchangers, attached aryl and alkyl sulphonic acids are used to equal extents. The synthesis of sorbents for the chromatography of biopolymers (in particular the sorbents of the DEAE and CM series) is often carried out with preliminary modification of the surface by a γ-glycidoxypropyltrialkoxysilane followed by the introduction of the required functional group.

Sorbents with polymers attached to the surface have appeared in recent years. Thus sorbents of the SynChropak series are obtained by modifying the surface with polyethyleneimine; the cation exchanger Zipax SCX contains a sulphonated layer of a fluorocarbon polymer on its surface.

The range of mineral carriers used is being extended. In particular, sorbents of the Zorbax Bio-Series are based on zirconated silica gel.

In the near future there should be an increase in the proportion of sorbents with deposited polymers and also sorbents based on mineral carriers with an increased stability to hydrolysis in alkaline media.

IV. Applications of ion exchangers based on modified mineral carriers

1. The concentration and separation of inorganic anions

One of the principal fields of application of ion exchangers based on organic polymers is the extraction from solution and separation of inorganic ions (see for example Ref.147). In recent years, however, the sorption of transition metal ions has been carried out increasingly using complexing sorbents,[148] which ensure high stability and selectivity of the binding of the metal ions. On this basis, research workers studying the synthesis of sorbents for metal ions immediately began to graft complex-forming groups on to the surface of silica, so that the number of publications on the applications of ion exchangers based on silica on this field is comparatively small (p.321 of Ref.9, and Refs.53–56, 64, and 149–165).

The most interesting results have been obtained on the sorption of noble metal ions. In strongly acidic media (2–4 M HCl), the quantitative sorption of rhodium(III) and iridium(IV) by aminosilica is observed,[157,162] and this makes it possible to separate these elements from other noble metals and a 10^4-fold excess of non-ferrous metals and iron(III). Anion exchangers based on silica can be used to separate gold from a large excess of non-ferrous metals[64,159] and silver from platinum and palladium.[153] Palladium(II), platinum(IV), osmium(VI, VIII), and ruthenium(IV) are sorbed by anion exchangers based on silica in the weakly acidic range;[157,160–162,164,165] the mechanism of sorption has not yet been established.

Sulphonic acid[151,154,155] and phosphonic acid[53–56] cation exchangers based on silica show an increased affinity for multiply-charged metal ions, in particular aluminium(III), scandium(III), zirconium(IV), and thorium(IV), so that these metals can be separated selectively from materials with complex compositions, for example alloy steels.

Silica with grafted ethylenediamine has proved effective for the anion-exchange binding of $Cr_2O_7^{2-}$, MnO_4^-, WO_4^{2-}, MoO_4^{2-}, AsO_4^{3-}, SeO_4^{2-}, and uranium(VI) as carbonate complexes (p.321 of Ref.9, and Refs.149, 150, and 152), so that it can be used to extract these anions from sea water.

In all the works cited it is pointed out that the main advantage of silica sorbents is the high rate of attainment of sorption equilibrium which makes it possible to work at high rates of flow of the solution being analysed through the column containing the sorbent (up to 100 ml min^{-1} cm^{-2}); this is particularly important in the extraction of ions from large volumes of dilute solutions. In most cases, quantitative desorption of the ions from the surface is achieved using small volumes of eluant, so that the concentration coefficient in a single "sorption–desorption" cycle is 10^2–10^3, which is appreciably greater than that for the organic-polymer analogues. The higher selectivity of sorbents based on silica is also noteworthy. The advantages of modified silicas include the possibility of determining sorbed ions on the surface by a wide range of physical methods: X-ray fluorescence,[9,37,38,149,150–152,156,157,162] luminescence,[151,158] and spectral methods.[151,166] This makes it possible to lower the detection limits of elements and to reduce the time taken for analysis.

2. High-pressure in chromatography

For a long time, high-performance liquid chromatogray did not find application in inorganic analysis, and the few published papers dealt chiefly with the separation of complexes of metals with organic ligands using reversed-phase methods (see the published reviews[167,168]). A powerful stimulus to work in this field was provided by the classical study of Small, Stevens, and Bauman,[169] who proposed the use of ion-exchange stationary phases combined with a conductometric detector. Subsequent studies (see the published monographs[170,171] and review[172]) fundamentaly altered existing views on many traditionaly difficult problems in inorganic analysis. Thus when ion chromatography is used, the time taken to analyse mixtures of the anions Cl^-, Br^-, I^-, NO_2^-, NO_3^-, and SO_4^{2-} and mixtures of the cations Li^+, Na^+, K^+, Rb^+, and Cs^+ or all the lanthanide elements at concentrations of 0.1–1 μg ml^{-1} is 5–20 min.

The most popular materials used in ion chromatogray are strongly basic anion exchangers (for the separation of anions) and sulphonic acid cation exchangers (for separating cations); the structure and

characteristics of the sorbents are varied over a wide range, depending on the eluant and the detection system.

When a conductometric detector is used, the eluant should have a low conductivity; the low concentration of the eluant makes it necessary to use specially synthesised sorbents with a low capacity (0.01–0.1 mmol g^{-1}), in which the ion exchange groups are concentrated chiefly on the outer surface of the granule.[170] In the analysis of anions by the so-called two-column version of ion chromatography with conductometric detection, weakly alkaline carbonate–bicarbonate solutions are used as eluants; under these conditions, silica sorbents are unstable, and it is necessary to use ion exchangers based on zirconated silica specimens or organic polymers.

When other methods of detection are used, for example spectrophotometric,[73–75,77,173–177] refractometric,[178–180] potentiometric (at a copper electrode),[181] emission (using an inductively bound plasma),[182] and atomic absorption[183] methods, the stability and capacity requirements to be satisfied by the sorbents are not so severe, so that it is possible to use the same ion exchangers as in the HPLC of organic compounds. In the ion chromatography of ions, extensive use is made of dynamically modified sorbents obtained by the adsorption of long-chain quaternary ammonium salts on silica[73] or reversed-phase sorbents.[74,75,77,173,174,184,185] An attractive feature is the possibility of easily varying the sorptive capacity of the ion exchangers, and the use of aqueous eluants ensures the high stability of these phases modified by adsorption.

The problems of the ion-chromatographic analysis of mixtures of alkali metal cations and various mixtures of the anions of inorganic acids have now been fully solved. Specific examples of the use of ion exchangers based on silica for these purposes can be found in the literature of the firms producing these materials, and in published monographs[170,171] and original papers.[73–75,77,132,173–180,184]

The efforts of research workers are now concentrated on the problems of analysing the alkaline earth and transition metals.[181,183,186–196] A number of complexing sorbents have been proposed for this purpose, in particular silica specimens with grafted 8-quinolinol,[195,196] crown ethers,[193] and related compounds,[194] but data in other papers indicate that the use of traditional cation exchangers makes it possible to achieve equal selectivity and efficiency of separation. The selectivity and retention are controlled by adding to the eluant complexing reagents such as hydroxyisobutyric,[190,191] citric,[181,189] and tartaric acids,[181,187,188] and ethylenediamine.[181] The ions are detected spectrophotometrically; for this purpose they are converted at the outlet from the analytical column into complexes with highly sensitive reagents such as PAR[183,187,188,191] or Arzenazo I.[190] It is possible in principle to use eluants to which the photometric reagent, for example Arsenazo III,[186] has been added beforehand; in this case the ion-exchange separation of the complexes of the metal ions with this reagent takes place. An interesting example is the use of EDTA solution as eluant; the metal ions being determined are converted into negatively charged complexes with EDTA, which are separated on a strongly basic anion exchanger followed by conductometric or spectrophotometric detection; an important feature is that the accompanying anions can be determined simultaneously.[192]

3. The chromatography of organic compounds

In the high-performance liquid chromatography of organic compounds, sorbents based on silica with grafted monomeric organosilicon compounds are mainly used. The most widely used substrates are organc acids, amines, and aminoacids. The dependence of the retention of the compounds being separated on the nature of the grafted ion-exchange group, the structure of the compounds being separated, and the composition of the eluant has been studied in detail. Thus the order of the elution of carboxylic acids coincides with the order of increase in their acidic dissociation constants.[108,197,198] The dependence of the retention of organic acids by a weakly basic anion exchanger on the acidity of the eluant is given by a curve with a maximum;[197] the retention on the ion exchangers is inversely proportional to the ionic strength of the eluant.[46,199]

The most extensive use of the HPLC of ionogenic organic compounds is in medicine and for the control of environmental pollution. A large number of studies[46,200–204] have been devoted to the determination of catecholamines—dopamine, noradrenalin, adrenalin, and dihydroxyphenylalanine—using a strongly acidic cation exchanger. Considerable attention is being paid to the determination, in blood and other biological materials, of various medicines and drugs—caffeine, aspirin,[45] morphine, cocaine, quinine,[199] codeine, heroin,[205] nicotine,[46] and penicillamine.[206] Data have been published on the use of ion exchangers based on silica to separate aminoacids,[204,207] carboxylic acids,[45,108,197,198,202,208–211] alkyl sulphonates,[212] aliphatic and aromatic amines,[202,213] pyridinium aldoximes,[214] and other pyridine derivatives.[46] In recent years, organic acids and other compounds have often been determined by ion chromatography with conductometric detection.[208,209,211,212]

An interesting feature is the use of strongly basic and weakly basic anion exchangers based on silica in the exclusion chromatography of cationic polymers, for example polyethyleneimines and polyvinylpyridines.[110,215,216] The use of fixed groups with the same charge on the carrier surface completely suppresses the desorption of the polymers.

4. The chromatography of biopolymers

Judging from the number of publications, the main field of application of ion exchangers based on mineral carriers is the chromatography of biopolymers. This is not surprising, since the role of biotechnology is steadily increasing, and the only acceptable method for analysing, separating, and purifying the complex mixtures in these processes is liquid chromatography, in particular ion-exchange chromatography, which is the most universal method for compounds of this class. Previously, the analysis and separation of biopolymers was carried out almost exclusively using sorbents based on polymers and soft gels, which show appreciable non-specific sorption. The high degree of swelling and low mechanical strength of wide-pore sorbents based on organic matrices, however, made them unsuitable for HPLC, so that attention was transferred to mineral sorbents. An advantage of these sorbents is that they are unaffected by biological action and withstand various forms of sterilisation.

Various aspects of the application of ion exchangers based on silica in the chromatography of biopolymers have been described in detail in various monographs[6,7,11] and reviews.[12,217–220] In the present review, therefore, only some of the most important features will be examined, and references will be given to various specific applications.

One of the basic requirements to be satisfied by sorbents for the chromatography of biopolymers is that the pore size of the sorbent should correspond to the dimensions of the molecules of the compounds being separated. Here it is necessary to take account of the fact that increase in the pore diameter of the sorbent leads to a decrease in its surface area and hence in the sorptive capacity and efficiency of the sorbent. A large number of studies have therefore been devoted to the optimisation of the porous structure of the sorbent to solve various specific problems (see for example Refs.52, 115, 121, 221, and 222).

A characteristic feature of proteins is their strong non-specific interaction with the surface of silica, which leads to their irreversible sorption and often to the loss of the biological activity of the compounds being separated.[223] It is therefore necessary to effectively shield the silica surface from reaction with proteins; this is achieved by modifying the surface beforehand by dipolar groups[27,52,70,224] or polyethyleneimine.[112–116,121,225] Moreover, protein molecules are capable of many-point ion-exchange bonding to the sorbent, so that to decrease the retention, sorbents with a low surface concentration of ion-exchange groups are used.[34,65–68,70,112]

The ion-exchange separation of biopolymers is most frequently carried out in a weakly alkaline medium, that is in the range of hydrolytic instability of silica sorbents. The chromatography of biopolymers is therefore often carried out using sorbents with adsorbed or grafted polymers[12,112–116,119–121,124,225–229] or sorbents based on zirconated silica specimens.[22,27,230]

The ion-exchange retention of proteins, viruses, and other biological adsorbates depends on many parameters, in particular the composition, acidity, and ionic strength of the eluant. Detailed experimental studies of these topics have been described.[226,227,230–233] The selection of the best conditions is assisted by data on the adsorption isotherms for proteins on ion exchangers[234] and the results of theoretical studies.[235,236] Thus a correlation has been established[235] between the retention of a protein and the number of charges involved in the adsorption–desorption process.

Ion exchangers based on silica are used in the chromatographic analysis of mixtures of basic proteins, α-chymotrypsin, cytochrome C, and lysozyme,[27,70,116,124,229,231,237] nucleosides,[45] nucleoside phosphates,[34,238] nucleic bases,[239] oligonucleotides,[66,67,69,113,221, 224,225,240–243] ribonucleic acid,[113,221,244] and DNA restriction fragments,[67,68,221,245–247] and to separate growth factors.[233,248,249]

Ion exchangers based on minerals are being more widely used for the preparative separation of biological compounds,[219,220,250,251] in particular interferon,[252] and also for their purification by chromatofocussing.[228,253]

5. Catalysis

Ion exchangers based on organic polymers, primarily sulphonic acid cation exchangers, are widely used in catalysis[147,254] in hydrolysis, hydration, esterification, alkylation, condensation, etc. The range of reactions catalysed is determined in practice only by the chemical nature of the ionogenic group, so that the replacement of an organic polymer by an inorganic matrix should not influence the catalytic properties. At the same time, it should be expected that ion exchangers based on mineral carriers will make it possible to carry out processes requiring a higher temperature or accompanied by strong exothermic effects leading to local superheating with consequent degradation of the catalyst.

The mesoporous structure of the carrier ensures that all the reaction centres are accessible, so that the specific activity (calculated for one centre) of ion exchangers based on mineral carriers should be much greater than that of organic polymer resins. In spite of the greater exchange capacity of organic ion exchangers, their activity calculated for unit mass or unit volume may be lower. This effect should be greatest for reactions involving large organic molecules.

The limit of the thermal stability of sulphonic acid cation exchangers based on silica and obtained by polycondensation is more than 100 K higher than that of the organic-polymer analogue Amberlite 15.[142] In the hydrothermal treatment of sulphonic acid cation exchangers, the greatest stability is shown by catalysts in which the silicon atom is joined to an aliphatic carbon atom.

Sulphonic acid cation exchangers based on silica have been used to catalyse the alkylation of alcohols by isobutylene to obtain alkyl t-butyl ethers (in particular methyl t-butyl ether)[255,256] and of phenol by dec-1-ene,[257] the dehydration of alcohols,[142] esterification,[142] and the gas-phase nitration of benzene by nitrogen dioxide.[142] Comparison of the activity of sulphonic acid cation exchangers based on silica with that of analogous cation exchangers based on organic polymers (KU-2, Amberlite 15, Lewatit SPC 108/H) showed that the former in many cases have a higher specific activity, calculated both for one centre and for unit mass or volume, in spite of the lower concentration of sulphonic acid groups.

Strongly basic silica anion exchangers with grafted optically active aminoalcohols and alkaloids are used to catalyse Michael asymmetric addition.[258,259] It was unexpectedly found that by varying the length of the chain joining the active centre to the carrier, and the accessibility of the silanol groups of the surface, it is possible to reverse the enantio-selectivity of the addition. This indicates that the carrier plays an active part in the formation of the intermediate substrate–catalyst complex.

A second method of using ion exchangers based on silica in catalysis is by the attachment of transition metal complexes. The heterogeneous metal-complex catalysts obtained in this way combine the high activity and selectivity of homogeneous metal-complex catalysts with the technology of traditional heterogeneous catalysts.[4,5] The metal complexes are usually attached by the coordination of ligands grafted to the carrier, but in a number of cases ion-exchange attachment is preferred. Examples include the attachment of chloro-complexes of platinum(II) and platinum(IV) to anion exchangers with grafted quaternary ammonium and phosphonium groups to obtain catalysts for the industrially important reaction of hydrosilylation of unsaturated compounds.[33,62] The ion-exchange attachment of platinum gives more stable catalysts than attachment by coordination (bonding through the phosphine group), and the catalyst can be used repeatedly without loss of activity. The selectivity of the formation of the β-isomer in the hydrosilylation reaches 100%. Unlike catalysts with a polymeric matrix, the silica carrier ensures the activity of all the platinum atoms.

Modified silica specimens can also be used to catalyse inter-phase transfer, as shown for the alkylation of phenol,[35] the synthesis of esters,[260] and halide exchange.[61,261] The catalytic properties of strongly basic phosphonium ion exchangers based on silica differ considerably from those of their polymer-based analogues and hexadecyltributylphosphonium bromide.[35,261]

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