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DEVELOPMENT IN THE SYNTHESIS AND APPLICATION OF ION EXCHANGE AND ELECTRON EXCHANGE RESINS

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INTRODUCTION

The introduction of cross-linked polymeric electrolytes – ion exchange resins – has provided an entirely new approach to many problems of purification and separation of chemically similar substances, i.e. to the central problems of analytical and preparative chemistry. The first problems to be solved in this way concerned desalting or deionisation of industrial solutions, e.g. in the sugar industry, the production of drinking water from sea water, or the substitution of undesirable ions by acceptable ones, e.g. calcium and silicate in boiler water by sodium and hydroxide.

Problems such as these make very simple demands of an ion exchanger. Selectivity for a particular ion is not required. On the contrary the polymer must be a general purpose absorber of a wide range of ions.

Much more sophisticated problems arise in separating individual substances from complex natural or industrial products. The introduction of polymeric ion exchangers in conjunction with chromatographic methods has brought about a real revolution in this field. It should be remembered that while chromatography is an exceptionally selective method of separation, it is lengthy and comparatively inefficient in terms of unit volume or cross-section of the apparatus (ion-exchange columns). Ion exchange and chromatography are therefore best used in analysis and in small scale synthesis. The extraction and purification of rare, highly dispersed, and radioactive elements, and the separation of stable isotopes are the fields of industrial inorganic chemistry in which the use of ion exchange and chromatography is expedient. As far as the polymeric materials are concerned, the chief problem here is to make selective absorbents which have at least a group specificity, and preferably an individual specificity for given elements.

In the organic chemical industry the most important applications of ion exchange and chromatography are related to the production of valuable small-tonnage products of complex nature – antibiotics, vitamins, hormones, alkaloids, active protein preparations (antigens, antibodies, enzymes, viruses, baceteriophages). In these cases, the advantages of the ion exchange method are used to the full; it is the most "gentle" of all preparative methods, and enables particularly sensitive and labile organic compounds to be purified and concentrated. Applications of ion exchange in organic chemical technology make special demands on the synthesis of ion-exchange resins. As in the previous case, high selectivity for individual ions is involved. In addition, the large dimensions of organic ions, containing various functional groups, pose additional problems in the synthesis of resins suitable for their separation and purification.

The use of polymeric resins as reagents in chemical reactions is a new field of application that has emerged recently. Cations and anion-exchange resins are used successfully as catalysts in reactions requiring acidic or basic catalysts. Special electron-exchange resins, i.e. polymers able to undergo reversible oxidation-reduction, are used as reagents for the oxidation or reduction of a given material; contamination of the product by extraneous matter, which occurs when the usual oxidising and reducing agents are used, is thus avoided. These are the most important aspects of the applications of ion-exchange and electron-exchange resins.

In the present review we shall deal with several new developments in the synthesis of polymeric materials that appear to offer prospects of industrial utilisation. But, since the polymers cannot be considered in isolation from the technological methods of purification and fractionation by sorption, we shall begin with a short review of new ion-exchange and chromatographic methods.

1. DEVELOPMENT OF ION-EXCHANGE AND CHROMATOGRAPHIC METHODS

Methods for the removal of all electrolytes (deionisation) have developed in two directions. Since deionisation with ion-exchange filters involves periodic regeneration (e.g. with alkali or acid), which accounts for the main cost of the process, two types of ion-exchange processes not requiring regeneration have been devised. The first of these is the widely known method of electrodialysis through ion-exchange membranes[1,2]. Cation- and anion-exchange membranes are selectively permeable to cations and anions respectively. At present, electrodialysis consumes fairly large quantities of electrical energy, the chief source of loss being the considerable resistance of the desalted water in the cells, which are 2–5 mm thick. The membranes themselves, some 0.5 mm thick, also have an appreciable resistance (about 20% of the total resistance of the apparatus). As a result, the energy consumed in desalting sea water to produce drinking water (e.g. decreasing the salt concentration from 2.5 to 0.025%) is about 5–8 kWh ton^{-1}.

The efficiency of a multicell electrodialysis system, i.e. the ratio of the power ideally required to remove the salts (as given by thermodynamics) to that actually required, is 10–15%. Consequently, there is great scope here for further improvement, both in construction of the apparatus and in perfection of the membranes – by making membranes that are simultaneously thinner and stronger. Ion-exchange membranes can be synthesised in two ways. The first involves binding powdered resins with various polymers, with subsequent curing ("vulcanisation") of the films thus obtained (heterogeneous membranes). The second method is the direct chemical synthesis of ion-exchange membranes from suitable polymer films (homogeneous membranes). Thus polyethylene film, with polystyrene grafted to it by irradiation, was the starting material for the synthesis of sulphonic acid cation-exchange membranes and others[3].

At the present time, electrodialysis through ion-exchange membranes has found wide application in the production of drinking water, for example on ships. It is also used successfully in the technology of antibiotics and other organic substances, for demineralising solutions, for exchanging cations or anions, and for varying pH without introducing alkali or acid. Ion-exchange membranes have interesting applications in chemical analysis, particularly in automatic plant control. With their aid, electrodes may be set up for continuous measurement of the concentration of any particular ion in a solution (e.g. sodium, ammonium, chloride, sulphate, etc. electrodes), through their concentration-dependent potential, in the same way that the hydrogen electrode is used to measure hydrogen ion concentration[4]. Such electrodes are stable, have a low inertia (equilibrium potential is established in fractions of a minute), and have a good electrical conductivity, which facilitates measurements of potential. There is no doubt that ion exchange membranes will be increasingly used in the future.

The second method of deionisation, especially applicable to solutions of non-electrolytes or weak electrolytes, and not requiring periodic regeneration of the ion exchanger, has been named "ion exclusion"[5,6]. This procedure is efficient for very heavily salted solutions of weakly dissociated substances, since the ion exchanger immediately absorbs the non-ionised component while the electrolyte is excluded and passes through the filter unabsorbed. The ion-exclusion method is based on the Donnan equilibrium. The ion-exchange filter, through which the solution to be demineralised passes, contains the same ion that is to be removed. For example, if demineralisation involves removal of NaCl, the filter is filled with the sodium form of a sulphonic acid cation exchanger; the degree of swelling of the resin is such that its particles contain 50% of water. Owing to the Donnan equilibrium, which is always set up when there is a cation free to diffuse (in this case Na^+) and a fixed anion (in this case the macro-anion of the resin), or vice versa, the concentration of NaCl in the liquid within the particles of ionite will be several times smaller than in the solution (sometimes, tens of times smaller).

According to the Donnan-equilibrium theory, the efficiency of the process, i.e. the ratio of the salt concentrations outside and inside the swollen ion exchanger, increases with decrease in salt concentration. The weakly dissociated component is distributed almost equally between the solution and the swollen resin. This results in an appreciable, though not very large, capacity of the ionite for a non-ionic component (e.g. for ethanol, the capacity in practice is about 0.5 mmole g^{-1}, whereas ion-exchange capacity is about 5 mg-equiv. g^{-1}).

The ion-exclusion process is carried out by passing an aqueous solution of the original mixture through the filter. The unionised component is held in the ion exchanger, while the salt is excluded from the particles and is removed from the filter. The non-ionic component is washed from the resin with water, and the cycle is repeated. With correct operation, both the salt solution and the non-ionised solution can be obtained without appreciable dilution. However, desalting is incomplete after a single cycle and the process generally needs to be repeated several times.

Ion exclusion has been successfully used to separate acetic from hydrochloric acid, boric acid from sodium chloride, amino acids from ammonium chloride, ethyl alcohol and ethylene glycol from sodium chloride, and so on[7]*. The usual swelling, strongly basic cation exchangers are suitable for the ion-exclusion process.

We shall now turn to processes for separating individual ions from complex mixtures. Chromatographic methods, using ion-exchange sorbents, are suitable for this purpose.

Of the three alternative methods of chromatography – frontal, elution, and displacement – the first is best suited to industrial applications, because it is extremely simple technologically and is economic in the use of the exchanger. In this method, the ion-exchange filter becomes saturated exclusively with the required ion, while the others pass through unabsorbed; it is essentially a one-stage process. Ion exchangers of high selectivity are required. Normal ion-exchange resins have exchange constants for different ions that do not differ much from unity and do not exceed 10, and, as a rule, ion exchangers of this kind are unsuitable for frontal separations. However, it has been found possible to synthesise ion exchangers having exchange constants for particular ions of the order of 10^5–10^6. With

* These cases do not appear to be mentioned in references 5–7 (Ed. of Translation).

such resins, frontal analysis can be carried out for analytical and preparative purposes. Success in this method depends entirely on the synthesis of suitable ion exchangers, a matter to which we shall return later.

We consider next developments in elution chromatography, in which the main difficulty has been diffusion of the zones and a consequent fall in concentration of the components in them. This drawback almost made elution chromatography valueless. It has been overcome by a procedure which sharpens the chromatographic zones. This procedure involves setting up a concentration gradient of eluent along the column; the result, as theory shows, is that the effective sorption isotherm of the components being separated becomes curved and the zones are sharpened. In order to create a concentration gradient of eluting electrolyte, the concentration of the solution supplied to the column is gradually varied by means of an automatic dispenser [8,9].

With small columns, it is sometimes possible to set up such a concentration gradient by applying an electric field and passing a current along the chromatographic column. Gradient-elution chromatography has been applied to the analysis of particularly complex multi-component mixtures. An example is the quantitative analysis of a mixture of twenty-five amino acids, carried out fully automatically [10].

Another example is the separation of radioactive elements, in particular the transuranium elements, on micro--columns (cross-section of 1 mm^2), using complexing acids as eluents (e.g. lactic, α-hydroxyisobutyric, etc.). In all cases mentioned, sharpening of the chromatographic zones was achieved by means of a pH gradient along the column. With micro-columns, an electric field may be used for this purpose [11]. The method can be used for preparative purposes, but only for particularly valuable substances, produced in comparatively small quantities (e.g. the purification of insulin).

Finally, we consider a recent development in chromatographic methods – a new version of displacement chromatography, in which this apparently discontinuous method has been converted to continuous operation, with all the technological advantages that this entails. Such a procedure is advantageous for the separation of ions very closely similar in properties, e.g. isotopes. Its efficacy has been demonstrated by the separation of the nitrogen isotopes [12]. A series of columns that can be connected together in different ways are filled with ion exchanger. A zone of the substances to be separated is then introduced into the first column and is moved forward by a solution of the displacing ion. Both the original ionic form of the resin and the displacing ion are selected in accordance with theory so that the boundaries of the mixed zone will remain sharply defined. The zone will then be stationary and its length will not change as it moves. During the process, the zone passes from one column to another. As a column is freed, the ion exchanger in it is rapidly regenerated and the column is again included in the process, which thus proceeds continuously; as the zone passes from one column to another, products are withdrawn from both ends of the zone, and more starting material is injected.

In our laboratory a detailed theory of continuous chromatography with withdrawal of products has been worked out [13] and a separation of the alkali metals, difficult to achieve by other methods, has been carried out. For the separation of the Li–Na pair, a zone 40 cm long was used to separate a mixture consisting of 50% Li and 50% Na. It moved at a rate of 0.004 cm sec^{-1} and an equilibrium distribution was established after a distance of 1.5 m. After this, withdrawal of products started. If products of 99.9% purity are withdrawn, the rate of withdrawal of each component is 25% of the total flow in the column. The only important requirement of the resin is rigidity, i.e. a small volume change on passing from one cycle to another. The sulphonic resin SBS-1 was found quite satisfactory. The method of continuous chromatography may prove very useful in the separation of closely similar substances.

2. NEW TRENDS IN THE SYNTHESIS OF ION-EXCHANGE MATERIALS FOR INORGANIC IONS

We shall consider three important ways of synthesising ion-exchange materials. Firstly, the synthesis of organic polymeric resins. Together with the traditional methods for making polymeric acids and bases of different strengths, a completely new route has emerged – the synthesis of exchangers containing groups able to form internal complexes (chelates) with particular ions. The application of this principle, which means that in the ion exchange process chemical donor-acceptor interaction between sorbent and sorbate is involved as well as electrostatic forces, results in enormous ion-exchange constants and high selectivity.

The second method, which is also being intensively elaborated, is based on inorganic polymers, formed mainly by the elements of the Fourth Group (e.g., zirconium or titanium). Various functional groups are easily attached to the polymer chain, consisting of atoms of zirconium and oxygen or titanium and oxygen. The possibility is thus presented of obtaining a large variety of ion-exchange materials able to complex with different ions, and making possible separation of elements by frontal analysis.

The third method is extremely important for producing exceptionally mildly acting exchangers, which can adsorb, reversibly and without deactivation, such complex organic substances as proteins and even viruses. The method uses cellulose and starch as the polymer framework to which ion-exchange groups are attached. We shall deal in turn with all three methods of synthesis, together with the practical applications of the resulting exchangers.

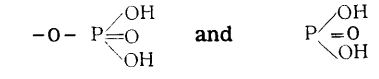
The ordinary universal-ion exchangers have now attained a high degree of reliability. The most flexible methods of synthesis have proved to be those based on styrene polymers, cross-linked with divinylbenzene or with other polyfunctional agents or copolymers of styrene with diolefines [1]. Sulphonation of such polymers gives strong sulphonic acid cation exchangers, while chloromethylation with formaldehyde and HCl gives chloromethylstyrene which combines with tertiary amines to give a strongly basic anion exchanger – a polymeric quaternary base. Chloromethylated polystyrene is a better starting material for the synthesis of resins containing various other functional groups [e.g. the mercapto (SH) group]. Weak cation exchangers – carbolyxic acid resins – are obtained by polymerisation and cross-linking of polymethacrylic acid. A series of anion-exchange resins of intermediate basic strength, containing secondary and tertiary amino groups, are obtained by polycondensation reactions.

These are the better known and generally used ion exchangers. They differ from each other in the dissociation constant of the functional groups, the capacity per millilitre, and the degree of cross-linking or swelling. Their selectivity, although variable, is, in the main, low, the ion-exchange constants not being very different from unity.

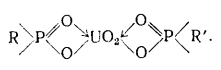
Current problems in the synthesis of selective exchangers call for the introduction of a whole range of different functional groups into polymers. What are the fundamental principles in this field ? The most important body of experience applicable to the development of new sorbents is that of analytical chemistry and the chemistry of complex compounds. In analytical chemistry one of the central principles is the utilisation of sparingly soluble compounds. The same principle applies equally to the development of selective resins. The majority of cations form highly dissociated salts with ordinary sulphonic acid cation exchangers. Ion exchange takes place with equilibrium constants K (i.e. with a change of free energy $\Delta G = -RT\ln K$) that depend on the valency of the ion, its radius, and extent of hydration. When the ion exchange constant is large (several powers of ten), i.e. when the free energy change $\Delta G = -RT\ln K$ is 3000–5000 cal mole^{-1}, sparingly soluble or undissociated compounds are formed between the ion and the resin.

Such compounds are obtained either when the anion-cation bond largely loses its heteropolar nature and becomes covalent or if a coordinate donor-acceptor bond is formed simultaneously with salt formation between the polymer and the cation, i.e. if a chelate compound is formed. Both phenomena can have the same result – a low dissociation constant for the salt – and it is not easy in practice to distinguish between them. Apparently the well-known effect of hydrogen sulphide on the heavy metals is an example of the first. The sulphides of iron, copper, nickel, mercury, etc. are practically undissociated homopolar compounds. The corresponding ion exchangers, containing the mercapto group (SH)[14–17], absorb and hold strongly all the metals of the "H_2S group" – iron, copper, mercury, cadmium, lead, zinc, etc. As in the vast majority of analytical chemical methods, group specificity is encountered here. Cases of absolute specificity for one element are extremely rare.

Fortunately, in problems of practical importance it is not necessary to separate all the elements of the Periodic Table. Usually we are concerned with mixtures of 2–5 components and here a combination of group methods has the desired result. The formation of an internal complex is illustrated by the case of salt formation with the phosphate group[18–20]. Thorium(IV), uranium as the uranyl ion, and iron(III) form weakly dissociated compounds with the phosphoric and phosphonic acid groups,



and



This results in exchange constants for uranium, relative to Ca^{2+}, Cu^{2+}, and Co^{2+}, of about 10^4–10^5. All the rare-earth elements except lanthanum are weakly sorbed on phosphoric and phosphonic acid resins. There are great possibilities here for selectivity and both these types of resin are likely to prove useful.

Before proceeding to a consideration of more complex cases, we shall return to the ordinary ion exchangers mentioned earlier. Of these, a carboxylic acid resin is undoubtedly able to form internal complexes[21–25] and this confers on it a greater selectivity than possessed by a sulphonic acid resin. For example, the exchange constants for Cu^{2+}, Ni^{2+}, and Co^{2+} reach 50–100, relative to Na and K, a fact which cannot be explained by the usual ion-exchange mechanism.

It is interesting that when polymethacrylic acid chain units are diluted with unionised units, i.e. when its capacity is reduced, all its selectivity for the transition metal ions disappears[26]. The reason is the increased distance between the carboxyl groups and consequent impossibility of forming chelates. At present there is little quantitative information about the stability constants of the complex salts formed by polymeric resins. The whole of this field is still in its early stages, but it is already clear that the effects of complex formation with polymeric resins are more pronounced than with low-molecular-weight substances. Here, the particular features of the polymeric framework, carrying the reacting functional groups, are manifested. The change from a dissociated salt to an undissociated one converts the macromolecular polyelectrolyte chains to an uncharged condition, whereupon they coil up in a random fashion; their dimensions become smaller, and the entropy correspondingly increases. In this way complex formation between an ion and the side groups of a linear polymer leads to a more favourable change of free energy than ordinary complex formation with a homologous low-molecular-weight substance. Consequently, the known stability constants of complexes are somewhat greater for polymeric resins, i.e. the polymer stabilises the complex. This is important for the evaluation of the effect of introducing specific complex-forming groups into a resin.

As a first approximation, we can use the stability constants measured for low-molecular-weight ligands, bearing in mind the correction due to the role of the polymer. In recent years a fairly large number of new resins have been synthesised, with various combinations of complexing groups. Most of these are assembled in Table 1, which also indicates their specificity. The most important resins, containing α-hydroxyquinoline group and the ethylenediaminetetraacetate group (EDTA), and most of the others, exhibit group specificity; the stability constants of various metals in the complex, and hence the ion exchange constants, which are their ratios, depend strongly on pH.

Table 2 shows the stability constants of EDTA complexes with various metals (at pH's where dissociation of carboxyl groups is complete).

The equilibrium constant K is given by

$$K = \frac{[MA^{(n-4)+}]}{[M^{n+}][A^{4-}]},$$

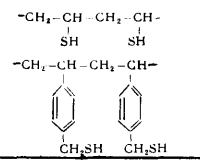
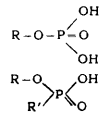
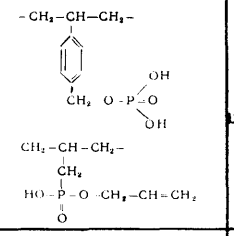
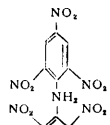
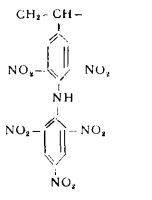
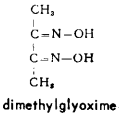
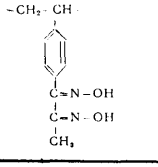
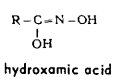
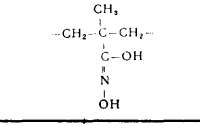
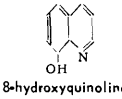
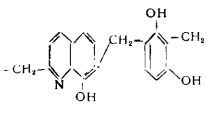
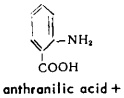
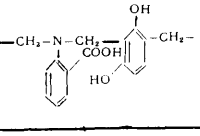
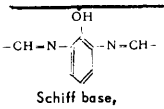
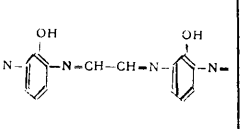
since the ions of metal and ligand combine in equimolar proportions regardless of the valency (n) of the metal. In practice, K is inversely proportional to $[H^n]$ if sorption is carried out at pH < 5, when COOH groups are weakly ionised.

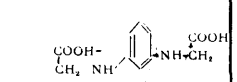
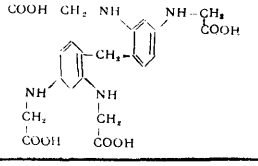
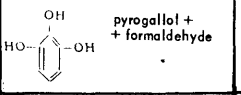
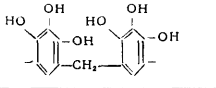
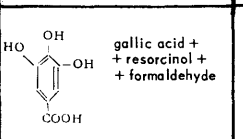
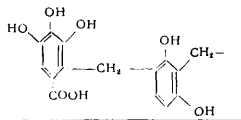
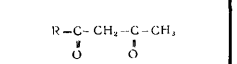
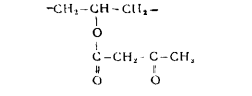
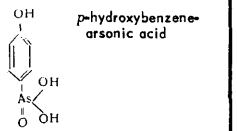
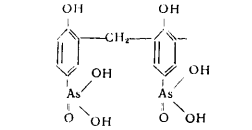
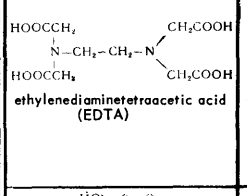
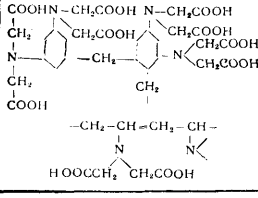
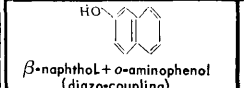
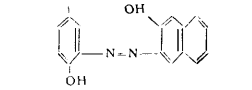
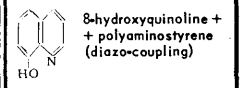
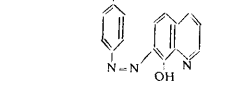
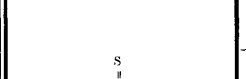
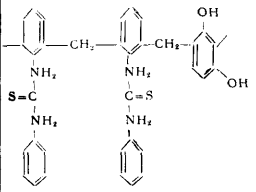
If we absorb a whole group of elements on a specific resin, e.g. the rare earths on a polymeric EDTA, we can elute differentially with solutions of different pH and obtain the individual substances in a pure state. In fact, all the ion-exchange methods now widely used in industry for isolating metals, without exception, make use of complex formation.

It will be recalled that in most industrial plants the extraction of uranium from its ores is accomplished by means of a strongly basic anion exchanger. This utilises the fact that uranium forms the anions $[UO_2(SO_4)_3]^{4-}$ and $[UO_2(CO_3)_3]^{4-}$ in sulphate or carbonate solutions. The same principle applies in the separation of gold as $AuCl_4^-$ from chloride solutions, on an anion exchanger.

The separation of the rare earths is carried out on a large scale on ordinary cation-exchange columns, but with

TABLE 1. Selective and complexing ion exchangers.

Functional group of low-mol.-wt. analogue	Chain structure	Sorption specificity	Reference
R–SH		Ag, Hg^{II} $Fe^{III}, Co,$ Ni, etc.	14–17
		Th, U^{IV} UO_2^{II}, Fe^{III}	18–20 27,28
 dipicrylamine		separation of K from Na, Ca, and Mg	29–31
 dimethylglyoxime		Ni	32
 hydroxamic acid		Fe^{III}	33
 8-hydroxyquinoline + + resorcinol + + formaldehyde		Cu, Ni, Co	34–37
 anthranilic acid + + resorcinol + + formaldehyde		Cu, Fe^{II}, Zn	36–38
 Schiff base, dinitrophenol + + glyoxal		UO_2^{II}	39

Functional group of low-mol.-wt. analogue	Chain structure	Sorption specificity	Reference
 *m*-bis(carboxymethylamino)-benzene + formaldehyde		Cu^{II}, Fe^{II}, Co^{II}	38
 pyrogallol + + formaldehyde		Hg, Pb, Br	40
 gallic acid + + resorcinol + + formaldehyde		Ca	34,35
 *β*-diketone		Cu, Ni, Co	41–43
 *p*-hydroxybenzene-arsonic acid		separation of Th^{IV} from Ca, Mg, and Zn	
 ethylenediaminetetraacetic acid (EDTA)	*m*-phenylenediamine + formaldehyde + + chloroacetic acid 	separation of Cu, Co, and Ni from Na, Ca, and Mg	45,46
 *β*-naphthol + *o*-aminophenol (diazo-coupling)		separation of Cu from Na, Ca, and Mg	34,35
 8-hydroxyquinoline + + polyaminostyrene (diazo-coupling)		Cu, Ni, Co	34,35
 *N,N'*-diphenylthiourea + + resorcinol + + formaldehyde		separation of Cu from Fe^{II}, and Co	

differential elution by complexing substances – citric acid, lactic acid, or EDTA. The difference is that in these traditional methods one makes use of complex formation in the solution while with selective ion exchangers, complex formation takes place on the surface of the exchanger. This has the obvious technological advantage that there is no loss of complexing agent in each elution cycle, which accounted for the main cost of the process and often rendered it uneconomic. Examination of Table 1 shows that complexing resins differ very greatly in their capabilities. A number of resins played an important historical role but are of little interest now, not having especially high ion-

TABLE 2. Stability constants of complexes formed by metal ions with EDTA (in ionic form).

Reaction $M^{n+} + A^{4-} \rightleftharpoons MA^{(n-4)+}$,

$$K = \frac{[MA^{(n-4)+}]}{[M^{n+}]\,[A^{4-}]}.$$

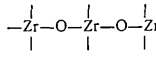
Metal	$\log_{10} K$	Metal	$\log_{10} K$	Metal	$\log_{10} K$
H	10.22	Mn (II)	12.79	Nd	16.61
Na	1.66	Hg (II)	21.80	Sm	17.14
Li	2.79	Fe (II)	14.33	Eu	17.35
Mg	8.69	V (II)	12.70	Gd	17.37
Ca	10.70	V (III)	25.9	Tb	17.93
Sr	8.63	VO	18.77	DY	18.30
Ba	7.76	Fe (III)	25.1	Ho	18.74
Zn	16.50	In	24.95	Er	18.85
Cd	16.46	Ga	20.27	Tm	19.32
Cu	18.80	Al	16.13	Yb	19.51
Ni	18.62	La	15.50	Lu	19
Co (II)	16.31	Ce	15.98	Sc	23.1
Pb	18.04	Pr	16.40	Th	23.2

-exchange constants. Others – for example, the phosphate, sulphydryl, and iminoacetate resins – are very promising.

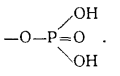
A shortcoming common to many ion exchangers is the strong complex formation with iron, generally regarded as a widespread impurity which must be removed in the separation of rare elements and elements present in low concentration. Another defect of all complex resins is their low chemical stability. Naturally, having spent capital on the synthesis of resins, one must be able to use them for at any rate several hundred cycles. This is frequently not possible, as they gradually lose their functional groups. This circumstance, and also the fact that methods for the synthesis of complexing resins and for their application have been insufficiently developed, explain why the use of such resins has not so far become widespread. However, it must be remembered that the first specimens have appeared only during the last 3–5 years and that the whole of this field is still in a state of flux.

The final choice of one selective resin or another is determined by concrete problems arising in the rare-elements industry. In this connection, several practically important problems, that can be solved by the use of selective complexing ion exchangers, may be mentioned. Among them are the separation of the rare earths on an ion exchanger, of the polymeric EDTA type, separation of the platinum metals, extraction of Ni, Co, Cu, Ag, Au, W, and Mo from diluted residues, possibly using a sulphydryl resin or the EDTA sorbent. Other interesting problems are the extraction of elementary iodine from mineral waters on a polymeric amine[47], and the extraction and purification of certain rare metals used in the semiconductor industry – germanium, gallium, indium, probably as complex anions on anion exchangers. Finally, the sorption of radioactive fission products of heavy nuclei is of great interest.

So far, we have discussed only organic polymeric materials. In recent years it has proved possible to prepare ion exchangers, among them some extremely selective ones, from inorganic polymers based on zirconium, titanium, and molybdenum. It is well known that in solution, zirconium forms chains of the type



Titanium forms similar chains. Polymerisation is particularly marked near the pH's at which the hydroxides are precipitated. If one adds to a solution of zirconium or titanium salt another salt (or acid) with the same or a different anion, at a favourable pH, a zirconyl polymer is precipitated, and the side bonds of the polymer are linked to one or other of the acid residues R. If the acid is polybasic, the anion R, which is firmly attached to the zirconium chain, retains the ability to attach itself to various cations, i.e. we have a cation exchanger. The first cation exchanger to be prepared in this way was zirconium phosphate[48,49]. The R groups attached to the zirconium chain were



The material obtained had the same characteristics as organic phosphate resins. But in contrast to the latter, the inorganic ion exchanger proved to be more stable to heat and to radiation.

The main feature of this material, as of other zirconium sorbents, is the extreme simplicity of preparation, in complete contrast to the complex synthesis of organic resins. In addition to the phosphate cation exchanger (whose capacity was about 1 mg-equiv. g^{-1} at pH 3 and 5 mg-equiv. g^{-1} at pH 11), British workers have prepared a mixed phosphate--citrate cation exchanger, which shows a selectivity towards the rare-earth elements[50]. A whole range of sorbents with zirconium chains carrying various selective functional groups[51] has found application in analysis. These sorbents gave separation factors for certain pairs of ions between 10^3 and 10^4, in one stage. Their properties are summarised in Table 3. Their synthesis is similar to that of the phosphate ion exchanger.

From titanium, phosphate and arsenate ion exchangers have so far been prepared. A new cation exchanger – ammonium phosphomolybdate[52] – is of particular interest for the separation of uranium fission products. Inorganic polymeric sorbents are widening the scope of synthesis of selective ion exchangers and merit detailed study.

TABLE 3. Properties of ion exchangers derived from zirconyl polymers.

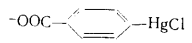
Ion-exchange group	Ions separated	Concentration ratio	Exchange capacity, mg-equiv. g^{-1}
—SH (sulphide)	Cu^{2+}/Ca^{2+}	10^{-3}—10^{-4}	
	UO_2^{2+}/Ca^{2+}	10^{-3}—10^{-4}	
	Fe^{3+}/Ca^{2+}	10^{-4}	1.5
$-H_2PO_4$ (phosphate)	Th^{4+}/Ca^{2+}	10^{-4}—10^{-5}	3
—OOC—CH_2 (citrate) HOOC—C—OH HOOC—CH_2	Ce^{3+}/Ca^{2+}	10^{-2}—10^{-3}	1.5
	La^{3+}/Ca^{2+}	10^{-2}—10^{-3}	
$-HC_2O_4$ (oxalate)	Co^{2+}/Ca^{2+}	10^{-3}—10^{-4}	0.75
	Sr^{2+}/Mg^{2+}	10^{-4}—10^{-5}	
$-H_2AsO_4$ (arsenate)	Co^{2+}/Ca^{2+}	10^{-3}	1.5
$-HCrO_4$ (chromate)	Sr^{2+}/Ca^{2+}	10^{-4}—10^{-5}	0.6
$-HCO_3$ (carbonate)	Ca^{2+}/Mg^{2+}	10^{-2}—10^{-3}	1.2
$-NO_2$ (zirconyl nitrite)	Co^{3+}/Ca^{2+}	10^{-4}	1.5

3. PROBLEMS IN THE PURIFICATION OF ORGANIC SUBSTANCES

The preparation of selective sorbents for absorbing organic substances from the gas or liquid phase deserves special consideration. The technical problems of purifying organic products, e.g. diolefines prior to polymerisation, are very acute at present and require development along new lines. The object is to remove hundredth and thousandth parts per cent of impurities that do not yield to separation or fractional distillation. This field is still in its early stages but its prospects are vast. We shall deal only with a few examples and possibilities. A very simple case is the sorption of different phenols on a sulphonic-phenolic resin in its H form. Here, the principle "like absorbs like" applies [53,54].

Anion exchangers in CN- or bisulphite form are selective sorbents for aldehydes and ketones [55,56]. Polymers containing boric acid groups selectively absorb polyhydric alcohols and carbohydrates [57-59].

Metals that complex with organic ligands were discussed as adsorbates earlier. However, they can equally well serve as adsorbents if it is required to absorb organic substances with characteristic functional groups. Thus, mercury atoms on a sorbent function as traps for mercapto compounds. The sorbents are made in two ways. (1) By the reaction between an alcohol-soluble phenol-formaldehyde resin and mercuric acetate in alcohol solution [60]. The mercury salt of the phenolic groups in the resin is precipitated. (2) Another method of making a "mercury sorbent" is to saturate a strongly basic anion exchanger with *p*-chloromercuribenzoate [61]:



The sorbent obtained is specific for substances containing the SH group; elution may be effected with a solution of H_2S.

Amines are sorbed on cation exchangers saturated with silver or copper ions, since the latter when sorbed on the resin lose none of their ability to complex with organic molecules [62]. It may be predicted that a cation exchanger saturated with cobalt, iron, or copper, and carefully dried, would specifically remove from hydrocarbons substances that can complex with cobalt, etc., such as alcohols, aldehydes, and ketones. Another interesting example is the specific sorption of acetylene on substances of a ketonic nature [63]. Poly(methyl vinyl ketone) might be a suitable sorbent for acetylene. The number of possibilities is immense.

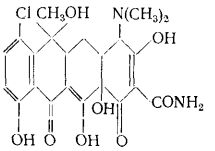
Another practically important question is the use of ion exchangers for purifying large complex organic ions – antibiotics, vitamins, alkaloids, etc. Work with such ions makes special demands on exchangers. Firstly, it seems that the polymer chains must be weakly cross-linked so that the network will be permeable to large ions. In other words, for sorbing large organic ions it is necessary to use strongly swelling exchangers. Thus, a whole range of SBS sulphonic cationites (butadiene-styrene sulphonic acid type) have been synthesised, having different degrees of swelling (swelling coefficients from 1.2 to 6–7). For the sorption of antibiotics mol. wt. 600–800, it is necessary to use a resin with a swelling coefficient of 2.5–3 (with certain antibiotics, the phenomenal quantity of up to 2 g per g of resin can be absorbed) [64,65].

For the sorption of such large ions as insulin (mol. wt. 12 000) a maximum-swelling resin is used (swelling coefficient 5–6). A capacity of 0.3–0.5 g per g of resin can thus be achieved [66].

For the sorption of inorganic ions, strongly cross-linked resins (swelling coefficient 1.2–1.3) are quite suitable. Hence, it is possible to use ion exchangers as molecular sieves, using a strongly cross-linked resin for desalting without loss of the organic ion, or separating a high-molecular-weight protein ion from low-molecular-weight amino--acids and peptides; this has often been done in our laboratory.

A second important factor is the steric impossibility of large ions occupying all the sites on closely spaced functional groups. Thus in an ordinary ion exchanger half or even more of the groups are substituted by ions of low--molecular-weight impurities, which are eluted with the desired product and contaminate it. This gives rise to a unique problem – the making of a strongly swelling exchanger with widely separated ion-exchange groups.

For sorbing streptomycin from a culture liquid, a special resin (KFUKh) was made on this principle. This is the product of simultaneous condensation of phenoxyacetic acid, chlorophenol, and formaldehyde [67]. In this resin, the phenoxyacetic acid units carry carboxyl groups while the chlorophenol units simply increase the distance between them. In the case of large complex ions problems of selectivity are also very acute. Thus, when antibiotics of the tetracycline group, e.g. aureomycin,



are sorbed on swelling sulphonic acid cation exchangers, the exchange constant relative to the Na^+ ion reaches the unusually high value of about 10^3. This indicates that in this case forces other than electrostatic are also acting. Apparently, hydrogen bonds are formed between the hydrogen of the amide group and the sulphonic acid group.

Even more characteristic effects are observed in the sorption of the penicillin anion on anion-exchange resins. It was noticed that the sorption and, more especially, the elution of penicillin were strongly dependent on the simultaneous presence of sulphate and phosphate anions. It was supposed that the additional bonding of the peptide groups of penicillin by means of hydrogen bonds with neighbouring adsorbed sulphate or phosphate created such large additional forces that the penicillin anions would not elute from the surface.

It proved possible to use this circumstance in sorbing penicillin on a sulphonic acid cation exchanger. Penicillin is sorbed on a high capacity resin (200–300 mg per g) as uncharged molecules, held by hydrogen bonds [68]. Elution proceeds well if 10% of acetone or 0.1% of urea are added to the solution of mineral acids; these break the hydrogen bonds formed by the peptide groups. From the infra-red spectra of a thin sulphonic acid cation-exchange membrane, it was shown that the peptide group of penicillin is involved in hydrogen bonding when it impregnates the membrane.

The sorption of an acid such as penicillin on what would seem to be an unnatural sorbent – a cation exchanger – permits the development of a selective method of purification. The purposeful creation (here one can use the term

"construction") of polymeric resins for the selective sorption of complex organic substances is a fairly literal application of the "lock and key" principle. Sorbent and sorbate must correspond to each other in their spatial configuration. The sorbent must contain suitably spaced groups having a given polarity or capable of forming hydrogen bonds with the sorbate. All this leads to a multitude of problems, which we shall not consider in detail.

In conclusion, we shall deal with the ion-exchange sorption of extremely complex substances – proteins and nucleic acids. Here there arises a special difficulty – the possibility of denaturing the material, of altering its macromolecular structure and thereby depriving it of its specific biological activity. The structures of many resins have unfavourable features which are harmful to the proteins being sorbed. Thus, sulphonic acid resins with closely spaced groups can form numerous hydrogen bonds with the peptide groups of a protein and assist the untwisting of its chains, thus destroying its natural spiral structure. In other cases the presence of the hydrophobic hydrocarbon portions in addition to the hydrophilic groups can have an unfavourable effect. For the sorption of these substances, ion exchangers based on cellulose and starch[69] are therefore of particular interest. Among these are the sulphonic acid cation exchangers prepared by the action of $ClCH_2SO_3H$ on cellulose powder, swollen in NaOH. A strongly basic anion exchanger, triethylaminoethylcellulose has been obtained as the bromide salt from diethylaminoethylcellulose and C_2H_5Br. An alternative method of obtaining quaternary bases is by the reaction of cellulose with triethanolamine and epichlorohydrin. Diethylaminoethylcellulose has been prepared from cellulose and 2-chlorotriethylamine. Treatment of an alkali cellulose with monochloroacetic acid gave a carboxylic acid ion exchanger, while treatment with $POCl_3$ gave a phosphate exchanger.

Cellulose ion exchangers, although they have a lower capacity (up to 0.5 mg-equiv. g^{-1}), have found wide application for the fractionation of biologically active proteins, nucleic acids, and viruses[70,71]. In contrast to the resins, this sorbent has proved to be exceptionally reversible and non-denaturing, apparently owing to the homogeneity and hydrophilic nature of its surface and the absence of hydrophobic groups. It is known, for instance, that sugars in enormous concentration not only do not denature proteins but actually improve their stability. The polymer framework of a cellulose sorbent has the same effect.

From the technological aspect, the application of ion exchangers to active protein preparation promises radical changes in the methods of production of serums, vaccines, antibodies, enzymes, and hormone proteins, i.e. the most important medical preparations.

4. POLYMERIC RESINS AS AIDS TO CHEMICAL REACTION

In recent years, a new application of ion exchangers has begun to develop – their use as catalysts in chemical reactions. This field undoubtedly has great possibilities. We have before us the example of nature, where all chemical reactions proceed in extremely mild conditions, with exceptional selectivity and high efficiency. They are all catalysed by enzymes, i.e. by macromolecular protein materials. Enzymic catalysis is undoubtedly associated with a certain combination of closely spaced functional groups, i.e. with the synergism of several groups. In synthetic resins, this principle has never yet been used.

All applications of ion exchangers as catalysts have so far been fairly primitive. Monofunctional polymers have been used to catalyse reactions requiring hydrogen or hydroxide ions. In other words, ion exchangers have been used as acid or basic catalysts. Their advantage is that solutions of acid or alkali, which have subsequently to be removed and which (particularly acids) cause corrosion difficulties with apparatus, need not be added to the reaction mixture. There are numerous examples of syntheses carried out under the influence of ion-exchange materials; some of these have been introduced in large-scale industry.

The simplest applications are in saponification and esterification. A certain element of specificity was found in these cases. Thus, high-molecular-weight esters (polyvinyl acetate) are more difficult to hydrolyse in the presence of ion exchangers, while low-molecular-weight esters react vigorously. Similarly, starch is not hydrolysed by polymeric ion exchangers, although it breaks down under the influence of ordinary mineral acids.

Other examples of specificity arise if some of the hydrogen ions in a sulphonic acid cation-exchange resin (sulphonated polystyrene) are replaced by organic cations – quaternary ammonium bases. Thus, if the quaternary base belongs to the aliphatic series (e.g. cetyltrimethylammonium), the ion exchanger is specifically active for the saponification of aliphatic esters, while if the cation contains aromatic groups (e.g. methyltribenzylammonium), the resin is specific for aromatic esters (methyl phenylacetate).

Nitriles can be hydrolysed in the presence of strongly basic anion-exchange resins, and disaccharides and peptides can be hydrolysed in the presence of sulphonic acid cation exchangers. Condensation reactions that can successfully be brought about by ion-exchange resins include not only esterification but acetal formation and aldol condensation (e.g. the synthesis of pentaerythritol). The latter is particularly successful on weakly basic anion exchangers. The condensation of acetone to mesityl oxide, and of nitroparaffins with aldehydes, can be brought about with strongly basic anion exchangers. All these reactions proceed in mild conditions, between room temperature and 100°. The dehydration of alcohols is another important reaction that occurs on sulphonic acid cation-exchange resins. The production of dioxane from ethylene glycol on sulphonated copolymers of styrene at 150° is an example.

The hydration of unsaturated hydrocarbons is equally successful on sulphonic acid resins. In particular, the Kucherov reaction (hydration of acetylene) can be catalysed by partially saturating a sulphonic acid resin with mercury ions. Additions to double bonds should also be mentioned, e.g. the synthesis of ethylene chlorohydrin, the cyanoethylation reaction (the addition of alcohols to acrylonitrile), etc.

An interesting example of catalysis, developed recently, is the formation of epoxides from olefines and peracids. This reaction can be carried out at 50°, with good yields, on a sulphonated polystyrene catalyst. It is interesting that attempts to accelerate the reaction with strong mineral acids were unsuccessful, because opening of the epoxide ring occurred. Thus, not only can acidic and basic ion exchangers sometimes replace strong acids and alkalis but they can also lead to new products. Some examples of catalysis on ion exchangers are summarised in Table 4.

In conclusion, we shall deal with electron-exchange polymers[72-75], i.e. resins that can undergo reversible oxidation and reduction. Such resins can oxidise organic substances and change the valency state of variable-valency

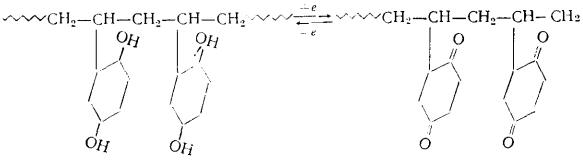
TABLE 4. Examples of catalysis by ion-exchange resins.

Reaction	Equation	Type of resin	t °C	Reference
Saponification of esters	$R_1-\overset{\overset{O}{\|\|}}{C}-O-R_2+H_2O \rightarrow R_1COOH+HOR_2$	sulphonic acid cation exchanger, strongly or weakly basic anion exchanger	35—50	77, 78
Saponification of nitriles	$R-CN+H_2O \rightarrow ROH+HCN$	strongly basic anion exchanger		79
Hydrolysis of carbohydrates	$R_1-O-R_2+H_2O \rightarrow R_1OH+HOR_2$	sulphonic acid cation exchanger		80
Hydrolysis of polypeptides	$R_1-CONH-R_2+H_2O \rightarrow R_1COOH+R_2NH_2$	ditto		81, 82
Esterification	$R_1-COOH+R_2OH \rightarrow R_1-COOR_2+H_2O$	sulphonated polystyrene		83, 84
Acetal formation	$2R_1OH+R_2CHO \rightarrow R_1-\underset{\underset{R_2}{\|}}{OCH}-OR_1+H_2O$		110	85, 86
Dehydration of alcohols	$2HO-(CH_2)_2-OH \rightarrow O\langle \overset{CH_2-CH_2}{CH_2-CH_2} \rangle O+2H_2O$	sulphonic acid resin	150	87
	$C_6H_{11}OH \rightarrow \langle \overset{CH=CH}{CH_2-CH_2} \rangle CH_2+H_2O$	ditto	150	
Condensation of ketones	$2CH_3COCH_3 \rightarrow (CH_3)_2C=CH-CO-CH_3+H_2O$	strongly basic anion exchanger		88
Aldol condensation	$2CH_3CHO \rightarrow CH_3-\underset{\underset{OH}{\|}}{CH}-CH_2-\overset{\overset{O}{\|\|}}{C}-H$	strongly basic anion exchanger (quaternary base)	0	89
	$CH_2O+C_2H_5NO_2 \rightarrow CH_3-\underset{\underset{NO_2}{\|}}{CH}-CH_2-OH$		25	90, 91
Additions to double bond	$(CH_3)_2C=CH_2+H_2O \rightarrow (CH_3)_2CH-CH_2OH$	sulphonic acid resin	50	90, 91
	$ROH+CH_2=CH-CN \rightarrow RO-CH_2-CH_2-CN$	strongly basic anion exchanger	40	
	$CH_2=CH_2+H_2O+Cl_2 \rightarrow ClCH_2-CH_2OH+HCl$			
Hydration of acetylene	$C_2H_2+H_2O \rightarrow CH_3-CHO$	Hg form of sulphonated polystyrene		93
Epoxide formation	$-\underset{\|}{C}=\underset{\|}{C}-+H_2O_2+CH_3COOH \rightarrow -\underset{\|}{C}-\underset{\|}{C}-+H_2O+CH_3COOH$	sulphonated polystyrene	40	94

ions by donating or removing electrons from them; transfer of hydrogen ions between resin and solution occurs at the same time. For example,

$$Fe^{3+} + R(red.) \rightleftharpoons Fe^{2+} + R(ox.) + H^+$$

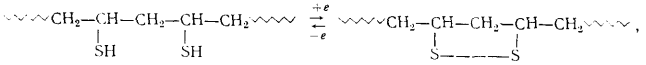
would be a typical reaction. Polyvinylhydroquinone (made by radical polymerisation of the monomer)



and vinylhydroquinone on styrene copolymers were synthesised for use as redox resins. The main difficulty was the insufficient swelling of these resins and the slow diffusion into them. It was overcome by the introduction of hydrophilic groups, for example, by sulphonation of some of the units.

The well-known conversion of hydroquinone to quinone serves as the oxidation-reduction reaction. As usual, the equilibrium of this reaction depends on pH. The polymer can be titrated with an oxidising agent to any redox potential. A supply of such a polymer, brought to a definite degree of oxidation and added to a solution containing variable-valency ions, acts as a redox buffer, i.e. it maintains in the solution a definite ratio between the oxidised and reduced forms. If one uses columns filled with an electron exchanger, one can carry out a complete oxidation or reduction of any form of an ion into another; the total electron exchange capacity reaches 5 mg-equiv. g^{-1}. Polymers, analogous to polyvinylquinone, containing anthraquinone and naphthoquinone, have been synthesised; others have been made by condensation of hydroquinone and its homologues with formaldehyde.

Another class of reversible oxidation-reduction exchangers is that represented by the polyvinylthiol resins:



and the analogous polystyrenethiol resins.

The chief advantage of electron-exchange resins in chemical synthesis is their insolubility and the possibility of carrying out a reaction without contamination by extraneous reagents. In many cases this is very important. For this reason other kinds of electron exchangers which lack this advantage, for example, ordinary cation exchangers saturated with metals of variable valency, do not seem very promising.

The chief drawback of modern electron-exchange resins is the same as that of cation exchangers – inadequate chemical stability, which forbids their use at temperatures that are at all high, and the use of strong oxidising agents for converting them to the oxidised form. For this reason there are not yet any important examples of the industrial application of electron exchangers. All the proposals concerning these materials, – for example, their use as catalysts for oxidations in systems containing an oxidising and a reducing agent at the same time – are very interesting but have not so far been put into practice.

Among the important applications, one should mention the absorption of oxygen dissolved in water on a hydroquinone-pyrogallol condensed resin, which is important in the fight against corrosion, and the preparation of hydrogen peroxide [95].

It is difficult to say at present whether chemical processes using redox resins will prove to be economically profitable. Much depends on the improvement of existing electron exchangers which, as has already been stated, are fairly complex and not very stable.

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THE ANALYTICAL CHEMISTRY OF THALLIUM

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INTRODUCTION

The ever increasing use of rare elements in various technical fields in recent years, and advances in metallurgy, have caused increasing interest in the analysis of such elements as thallium.

The existence of two comparatively stable states (univalent and trivalent) has resulted in a larger number of analytical methods for thallium than for indium and gallium, its analogues. These methods are based on the precipitation of univalent thallium (less often of trivalent thallium), on the oxidation of Tl^+ to Tl^{3+} and the reduction of Tl^{3+} to Tl^+. The Tl^+ and Tl^{3+} ions differ markedly in many of their properties. For example Tl^{3+} shows a pronounced tendency to form complexes, whereas Tl^+ shows practically none. The various complexes which recent studies have revealed, make possible more selective and sensitive analytical methods. A comparatively large number of methods of detection and determination of thallium have been published, but neither the handbook of Fresenius and Jander[1], nor Anderson's survey[2], completely cover the modern methods of analysis of this element.

This review systematises the analytical reactions of uni- and trivalent thallium published in recent years.

1. CLASSIFICATION OF METHODS FOR THE DETERMINATION OF THALLIUM

Detection. Thallium can be detected spectroscopically by a flame test, and by the characteristic formation of crystalline precipitates on addition of potassium iodide, chloroplatinate, chromate[3], thiosulphate[4], iodobismuthate[5], uric acid[6], and picrolonic acid[7], to solutions containing Tl^+, and by the appearance of a characteristic colour when trivalent thallium is treated with benzidine (or *o*-toluidine). The instantaneous oxidation of benzidine by Tl(III) produced from Tl(I) by reaction with Pt(IV), has been suggested as a spot test[8]. A photoluminescent detection of thallium has been described; this is based on the ability of hydrated Tl^+ to luminesce on introduction into the lattice of alkali-metal halides[9]. As little as 0.00012 μg Tl, at a limiting concentration of $1:10^7$, can be detected. The method has been applied to ores and minerals[10]. Reactions accompanied by fluorescence provide the basis for other methods of detection[11,12].

Methods for the determination of thallium. The most accurate methods for determining substantial quantities of thallium are gravimetric, principally involving precipitation as (1) the chromate, Tl_2CrO_4, (2) the iodide, TlI, (3) the thionalidate, $C_{12}H_{10}ONSTl$, (4) the mercaptobenzothiazolate, $C_7H_4NS_2Tl$, (5) the hydroxyquinolinate, $(C_9H_6ON)_3Tl$, (6) the hexamminecobalt(III) hexachlorothallate $[Co(NH_3)_6][TlCl_6]$, (7) the tetraphenylarsonium tetrachlorothallate $[(C_6H_5)_4As][TlCl_4]$, and (8) the diantipyrinylmethane tetrabromothallate, $C_{23}H_{24}O_2N_4.HTlBr_4$.

Of greater practical value are the titrimetric methods in which Tl(I) is oxidised by solutions of $KMnO_4$, $KBrO_3$, KIO_3, KIO_4, or the iodine, liberated when Tl(III) reacts with KI, is reduced with thiosulphate. Potentiometric methods are widely employed, using platinum spirals or discs as electrodes. Determinations of end-points amperometrically or conductimetrically find only slight application, though the former could be developed. A few papers describe coulometric methods based on the oxidation of Tl(I) with electrolytically generated substances such as free halogens or ferricyanide.

In industry thallium is frequently determined polarographically, after extraction from solution

The most important of the spectrophotometric and photometric methods involve precipitation of complex chlorides (or more seldom bromides), TlX_4^-, with large cations of various triphenylmethane dyes. The compounds formed are extracted with solvents such as benzene or toluene, and the optical density of the extracts measured; the dyes themselves remain in aqueous solution. The commonest dyes employed are methyl violet, rhodamine B, brilliant green, and certain other basic dyes.

Spectroscopic methods for determining thallium are most sensitive and widespread in analytical practice. Thallium can be detected by introducing a powder containing it into an oxy-acetylene flame: by the appearance of a green line at 5360.46 Å, 10^{-3}–5.10^{-4}% of thallium can be detected[13]. Spectroscopic methods have been described for determining thallium in zinc[14,15], in cadmium[16,17,18], in lead-zinc ores and the products of their processing[19], in lead[20,21], in soil[22], in pyrite[23], in zinc blende[24], and in ores and minerals[25]. The application of this method in forensic medicine is also described[26].