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Application of Ion-exchange Resins in Photometry

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The application of ion-exchange resins in the spectroscopic method of studying complex compounds is discussed. The possible use of ion-exchange resins or poly(vinyl chloride) films impregnated with organic reagents in analytical practice with a photometric detector is examined. 82 references.

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I. INTRODUCTION

The new comprehensive programmes of environmental protection have generated new requirements for methods of analytical control of natural waters and waste waters. The foremost needs are for sensitivity, reproducibility, speed, reliability, and demonstrable precision of the relevant measurement, together with the development of analytical methods which can be automated and whose results can be processed on a computer.

One approach to this problem is to develop new analytical procedures (and to improve existing ones) in which a method of detection is combined with an enrichment method. The spectroscopy of ion-exchange resins, in which the wanted element is concentrated in the resin phase before being directly estimated, is a promising example of the newer analytical procedures.

In 1954 Fujimoto[1] studied the colour changes of ion-exchange resins produced by the sorption of various ions: his results have been applied in the development of qualitative and semiquantitative methods of elemental analysis. The first spectrophotometric study of resins was reported by Ryan[2] in 1960. However the full potential of the spectrophotometry of resins as a practical method of quantitative analysis was only demonstrated in 1976 (by a group of Japanese workers[3]).

This review will deal with studies of the spectroscopy of ion-exchange resins in coordination chemistry and in analytical chemistry.

We shall not be concerned with the extensive researches on hydration phenomena which have relied on the spectroscopic characteristics of ion-exchange resins. Molecular interactions during hydration have been studied by i.r. spectroscopy by Zundel over many years, and they are discussed in his monograph[4]. The nature of complex hydrates in ion-exchange resins and the state of the water in these materials, studied by NMR spectroscopy, were recently reviewed by Bystrov and coworkers[5], and further discussion of these phenomena would be superfluous.

II. STUDY OF COMPLEXES BY ION-EXCHANGE RESIN SPECTROSCOPY

Ion-exchange resins are widely used in studies of complex formation to determine the composition and stability of the complexes[6]. Because of the difficulty of determining the composition of complexes sorbed by resins, and of the difference between the forms of the complex in solution and in the resin phase respectively, it is necessary to study the spectral characteristics of the resin phase. Ryan[2,7,8] examined the complex forms of tetravalent and hexavalent actinides sorbed by anion exchange resins. Neptunium, plutonium, and uranium compounds were identified by comparing the absorption spectra of the resins with those of aqueous or non-aqueous solutions of the complexes, and with the spectra of the complexes in the crystalline state. Data on the solubility of the complexes in the various media were required.

In the case of tetravalent actinides sorbed by anion exchange resins from hydrochloric or nitirc acid solutions the anion entering the resin phase is MX_6^{2-}, where M = Pu, Np, Th, U, and X = Cl^-, NO_3^-. We should note that these compounds are sorbed in the presence of both the salts (sodium chloride, calcium nitrate) and the acids of the ligands. On the other hand in an aqueous phase these compounds can exist only at high concentrations of nitric or hydrochloric acid. For example, MCl_6^{2-} (where M = Np, Pu, U) exists in 12 M HCl, $Pu(NO_3)_6^{2-}$ in 13 M HNO_3, $Np(NO_3)_6^{2-}$ in 14 M HNO_3, and $U(NO_3)_6^{2-}$ in 15.7 M HNO_3.

The following mechanism was proposed[2] for the formation and sorption of the complex anions in the resin:

$$M^{+m} + n\,X^{-y} \rightleftarrows MX_n^{-ny+m},$$

$$MX_n^{-ny+m} + \frac{ny-m}{y}\,X^{-y}\,(\text{res}) \rightleftarrows MX_n^{-ny+m}\,(\text{res}) + \frac{ny-m}{y}\,X^{-y},$$

$$MX_n^{-ny+m} + (ny-m)\,H^+ \rightleftarrows H_{ny-m}MX_n.$$

The suggested reactions satisfactorily explain various phenomena observed during the sorption of metal anions by ion-exchange resins: the increased sorption in the presence of acids, the maximum in the curve of distribution coefficient against ligand concentration, and the possible sorption of intermediates formed during the reaction[2].

In the case of the formation of hexavalent actinide complexes in the resin phase the compounds $MO_2(NO_3)_4^{2-}$ and $MO_2(NO_3)_3^-$ are detected, whereas in an aqueous phase the concentration of actinide tetranitrates is very small, and in concentrated nitric acid only $MO_2(NO_3)_3^-$ is formed[7]. The relative concentration of these complex anions in the resin phase is found to be independent of the composition of the aqueous phase, but determined by the properties of the resin (total sorption capacity, extent of saturation by nitrate ions). Before this work it has been generally assumed that the ions entering the resin phase are those already present in solution. Only by using a spectrophotometric method could the difference between the compounds in the two phases be demonstrated. The identification of the actinide tetranitrates in the resin phase relied on the determination of the

charge of the sorbed compounds, on the synthesis of various complexes, and on comparative studies of the optical properties of complexes in the resin phase and in the crystalline state[7].

The sorption of uranyl ions has been studied for fluoride, chloride, bromide, and sulphate systems as well as for nitrate systems[9,10]. Spectrophotometric studies of cation and anion exchange resins after sorption of uranyl compounds gave extensive information on complex formation by the uranyl ion with these ligands, and identified the products of multi-step complex formation reactions (by utilising the selective sorption properties of the resin as a function of resin type and of the nature of the solvent).

The ions UO_2Cl^+ and UO_2Br^+ (identified by their characteristic absorption spectra in the region of stretching vibrations of the U–O bond) are sorbed by the resin from chloride and bromide systems at low concentrations of the halide ion. Fluoride cannot form a positively charged complex with the uranyl ion. Even at very low concentrations of F^- the equilibrium is displaced towards the formation of anionic fluorine complexes. Thus a study of the sorption of halogen complexes of uranyl on a cation exchanger established the following stability sequence of the anionic uranyl complexes with halide ions[9]:

$$F^- > Cl^- > Br^-.$$

The compounds $UO_2F_3^-$, $UO_2Cl_3^-$, $UO_2Cl_4^{2-}$, and $UO_2Br_4^{2-}$ were identified[9] from the visible and i.r. absorption spectra of anion exchange resins after sorption of complex uranyl ions. The coordination numbers and the symmetry of the intermediates were obtained by analysing the spectral characteristics. Thus the $[UO_2X(H_2O)_5]^+$ complexes have a coordination number of 6 and a D_{3h} point-group symmetry. Increasing the number of halogen groups ($UO_2X_3^-$, $UO_2X_4^{2-}$) lowers the coordination number to 4 (D_{4h} point-group symmetry).

Spectroscopic studies of resins used in the sorption of uranyl compounds in the presence of sulphate[10] confirmed the presence of consecutive reactions during the complex formation between uranyl and sulphate. The following compounds were identified: $UO_2HSO_4^+$, $UO_2(SO_4)_2^{2-}$, and $UO_2(SO_4)_3^{4-}$. It was shown that the ion $[UO_2(H_2O)_6]^{2+}$ is sorbed by a cation exchanger from a solution of uranyl sulphate in the absence of an excess of SO_4^{2-} ions. Increasing the concentration of sulphuric acid in the system causes the ion $UO_2HSO_4^+$ to be sorbed by the cation exchanger, whereas in neutral sulphate solutions this ion is not detected. The following compounds were also detected: $UO_2(SO_4)_2^{2-}$ (sorption from solutions containing uranyl sulphate with or without an excess of sulphuric acid) and $UO_2(SO_4)_3^{4-}$ (sorption from solutions containing an excess of lithium sulphate). The force constants f and the radii of UO_2^{2+} were calculated[10] from the U–O stretching vibration frequencies in the i.r. spectra (see Table 1). We note that the replacement of water molecules by SO_4^{2-} groups increases the radius of the UO_2^{2+} ion from 1.719 to 1.740 Å, indicating a change in the nature of the bond during the transition from the hydrated UO_2^{2+} ion to the $UO_2(SO_4)_3^{4-}$ anion.

Choppin and coworkers[11] studied the visible and i.r. absorption spectra of neodymium complexes with various ligands (SCN^-, Cl^-, NO_3^-, NO_2^-, CO_3^{2-}, OCN^-, CH_3COO^-, EDTA) and concluded that the spectra of the ion-exchange resins after sorption of these anionic neodymium complexes are almost indistinguishable from those of the concentrated aqueous solutions.

Most of the reported spectroscopic investigations of complexes sorbed by resins have been concerned with the ions of transition metals such as cobalt, nickel, copper, and iron[12–31]. This work is important not only because it adds to our understanding of the complex formation processes, but also because it highlights possible applications of ion-exchange resins as vehicles for the sample to be analysed by spectroscopic methods, since the formation of complexes by transition-metal ions in aqueous and in non-aqueous media is now well understood. By comparing results for ion-exchange resins containing the sorbed copper cations $[Cu(H_2O)_6]^{2+}$ and $[Cu(H_2O)_5Cl]^+$, and the anions $[CuCl_3(H_2O)]^-$ and $[CuCl_4]^{2-}$, the authors conclude[12,13] that ion-exchange resins are suitable matrices for the measurement of absorption and ESR spectra.

Table 1. Quantitative characteristics of uranyl compounds formed in a sulphate solution.

Compound	Resin	ν_3, cm^{-1}	f	$R_{UO_2^{2+}}$, Å
$UO_2(H_2O)_6^{2+}$	Dowex-50	958	7.625	1.719
$UO_2HSO_4^+$	Dowex-50	950	7.466	1.722
$UO_2(SO_4)_2^{2-}$	Dowex-1	910	6.880	1.738
$UO_2(SO_4)_3^{4-}$	Dowex-1	905	6.805	1.740

Marov and coworkers[14] studied the sorption of the copper cations $[Cu(H_2O)_6]^{2+}$ by a weakly basic anion exchanger containing primary, secondary, and tertiary amino groups, and they explained it in terms of complex formation between Cu(II) and the anion exchanger. This interpretation was confirmed by the ESR spectra. The following mechanism was proposed[14] (in the case of the primary groups) for the interaction between the copper cations and the anion exchanger:

$$4RNH_2 \ldots HOH + [Cu(H_2O)_6]^{2+} \rightarrow [Cu(RNH_2)_4(H_2O)_2]^{2+}.$$

These results are fully consistent with earlier ESR work[15] on the structure of a copper complex sorbed by a weakly basic anion exchanger.

Japanese workers[16] have reported the formation of anionic copper complexes during sorption by anion exchangers, and they have shown that the resins can be used in spectrophotometric studies. They examined the changes in the absorption spectra of the resins (broadening of the absorption peak, extending over the region $\lambda = 400–500$ nm) which occur as the concentration of copper ions in the system is increased. Whereas Heitner-Wirguin and Cohen[12] ascribe this phenomenon to changes in the structure of the sorbed anion (transition from $CuCl_4^{2-}$ to $CuCl_3^-$), these workers[16] assume dimerisation of the copper anions in the resin in contact with a more concentrated solution of copper chloride:

$$2CuCl_3^- + Cl^- \rightleftarrows \left[\begin{array}{cccc} & Cl & Cl & \\ & | & | & \\ Cl-Cu & - & Cl-Cu & -Cl \\ & | & | & \\ & Cl & Cl & \end{array}\right]^{3-}.$$

The formation of $Cu_2Cl_7^{3-}$ was confirmed[16] by applying the previously reported method[17–19] of determining the composition of the complex sorbed by a resin from the distribution coefficient. The quantity $\bar{n}_R$ (the mean

number of ligands in the metal complex within the resin phase) is determined from a plot of $\{\lg D + (\bar{n} - m/l)\lg[L]\}$ against $\lg[L]_R$, where D is the distribution coefficient of the metal M, $\bar{n}$ is the mean number of ligands in the complex, l is the charge on the anion of the ligand, and the subscript R refers to the resin phase. The basic equation for calculating $\bar{n}_R$ can be written

$$\frac{d\{\lg D + (\bar{n} - m/l)\lg[L]\}}{d\lg[L]_R} = \bar{n}_R - \frac{m}{l}.$$

The validity of this method of determining the number of ligands in the complex was tested with the well characterised iron(III)–chloride and cobalt(II)–chloride systems. The final conclusion was that the ion $CuCl_3^-$ is present in an anion exchange resin phase, but an increase in the concentration of copper ions in hydrochloric acid solution leads to the formation of $Cu_2Cl_7^{3-}$ ions.

Waki and coworkers[20] used this method to calculate the stability constants of polyphosphate copper complexes formed in an ammoniacal solution (pH > 10.5) by the reaction

$$Cu(NH_3)_4^{2+} + P_nO_{3n+1}^{(n+2)-} \rightleftarrows Cu(NH_3)_3P_nO_{3n+1}^{n-} + NH_3$$

The following stability sequence of the copper complexes with polyphosphates was established:

$$P_2 > P_3 > P_1 .$$

The difference in the absorption spectra of the resin phase was consistent with the assumed differences in structure.

Rutner[21] has analysed the reflectance spectra of anion exchange resins containing Co(II) and Fe(III) complexes sorbed from chloride solutions. The reflectance spectra of the cobalt complexes have minima at 695, 665, and 635 nm, corresponding to the absorption bands of the $CoCl_4^{2-}$ complex which is formed in the aqueous phase in the presence of 7.25 M HCl. The spectrum of the Fe(III) complex shows a single peak at 362 nm, corresponding to the absorption maximum of the $FeCl_4^-$ complex anion in aqueous solution.

The halogen complexes of cobalt and nickel were studied by Nortia[22], who also concluded that the compounds sorbed by the anion exchanger have the composition MX_4^{2-} (where $M^{2+} = Co^{2+}$, Ni^{2+}, and $X^- = Cl^-$, Br^-, and I^-). He examined[22] the reflectance spectra of the halogen complexes of cobalt and nickel in the resin phase, and he showed that ion-exchange resins can be used as solid solvents for measuring the magnetic moments of these complexes.

Coleman's study[23] of the chloride complexes of cobalt on ion exchangers was conducted at constant concentration of the metal in the resin, which was treated after sorption with gaseous HCl–H_2O mixtures of different component ratio. He showed that the configuration of the complex changes from octahedral to tetrahedral as the concentration of Cl^- increases. The identification of the $CoCl_4^{2-}$ ion in the anion exchanger from spectrophotometric measurements confirms earlier results[21,22].

The coordinational configuration of the cation of an element in the resin phase has attracted a great deal of interest[24-26]. Thus it was shown that Co, Ni, and Cu exist as hydrated ions in a sulphonated cation exchanger saturated with water. On drying the resin (by heating it to 100°C) the i. r. spectra show a decrease in the number of hydrated metal complexes and a corresponding increase in the intensity of the spectral bands arising from the interaction of the metal ions with the sulphonic acid groups of the resin. In contrast to the sulphonated resins, in the case of carboxylic acid resins the metal ions interact with the carboxylic acid groups even in the moist resin[25]. This is consistent with the known relative complexing powers of malonic acid (the monomer of the carboxylic acid resin used in the investigation) and of water.

A series of papers by Heitner-Wirguin and Ben-Zwi[27-31] discusses the Co(II)–X^- system, where $X^- = Cl^-$, NO_3^-, and SCN^-, and identifies the successive steps of the complex formation reaction ($Co(H_2O)_6^{2+}$, $Co(H_2O)_5X^+$, $Co(H_2O)X_3^-$, and CoX_4^{2-}). The cobalt–chloride system was studied in both aqueous and non-aqueous solutions: acetone and ethanol were used as solvents because they form a solvation shell similar to that formed by H_2O in aqueous solutions of the cobalt complex.

III. APPLICATION OF ION-EXCHANGE RESIN PHOTOMETRY IN ANALYTICAL PRACTICE

The changes in optical properties of resins during the sorption of ions were first exploited by a group of Japanese workers[32-34] in the 1950's. The colour changes during the reaction are an indication of the presence of various ions, and they can be used very successfully in qualitative spot tests. Furthermore the depth of colour, estimated visually against a reference scale of standard colours, offers a semiquantitative method of analysis of various ions. Therefore the work on spot tests with resins deserves to be mentioned as the earliest example of the application of resin photometry in analytical chemistry. Qualitative drop tests for various elements, leading to the formation of coloured complexes, chelate compounds, and dyes, are listed in Table 2.

A change in colour may be due also to the formation of a precipitate at the phase boundary[66-68], or to catalytic reactions[69]. Fujimoto[70] proposed the addition of an organic solvent (immiscible with water) after complex formation and sorption. In this case the colour change can be obseved without separating the phases.

Drop reactions on resins can be carried out by two fundamentally different methods[71]: 1) the formation of a coloured compound which is subsequently taken up by the resin phase, and 2) prior impregnation of the resin with the reagent, so that the reaction between the ion to be determined and the reagent occurs within the resin phase. Detailed information on experimental procedure and on the advantages of qualitative drop reactions on resins can be found in a review by Fujimoto[72] and in textbooks[73,74].

A sensitive new photometric method of determining various elements in natural waters, based on the direct measurement of light absorption in an ion-exchange resin containing sorbed ions, was proposed in 1976 by Yoshimura and coworkers[3]. The determination relies on the colour reactions of Cr(VI) with diphenylcarbazide, of Fe(II) with 1,10-phenanthroline, of Cu(II) with Zincon, and of Cd(II) with thiocyanate. These workers[3] only used standard analytical reactions, which they combined with measurements of light absorption by an ion-exchange resin. The sensitivity of this method is more than 10 times greater than that of the direct spectrophotometric method. Table 3 lists some comparative data on the sensitivity of photometric analysis in ion-exchange resins and in aqueous solutions[3]. The measurement error is 5–10%.

An improved method of determination of Cr(VI) by the reaction with diphenylcarbazide, using ion-exchange resin photometry, has been described[75]: up to 1 mg litre^{-1} of Cr can be determined in natural waters by using the recommended procedure.

Fujimoto's method of impregnating the resin with the reagent[71] consists in replacing the mobile counter-ions of the polymer network (containing chemically bound ions) by ions of the organic reagent. When the resin is placed in contact with the ions to be determined the latter penetrate into the resin phase where they form the corresponding coloured complexes.

Table 2. Drop reactions on resins.

Element	Reagent	Resin*	Limit of detection, μg	Dilution limit	Refs.
Al(III)	Alizarin	III	0.08	—	32
B	Curcumin	II	0.06	$1:5\cdot10^6$	33
Bi(III)	thiourea	V	0.1	$1:4\cdot10^5$	34
Bi(III)	Pyrocatechol Violet	IV	0.03	$1:13\cdot10^5$	35
$Br^-(Br_2)$	Schiff's reagent	VII	1.2	$1:10^4$	36
Co(II)	NH_4SCN	II	0.16	$1:13\cdot10^4$	1
Co(II)	nitroso-R-salt	I	0.003	$1:14\cdot10^6$	37
Cr(III), Cr(IV)	H_2O_2	I, II	0.3	$1:10^5$	38
Cu(II)	*p*-phenylenediamine and NH_4SCN	I	0.02	$1:2\cdot10^6$	39
Cu(I), Cu(II)	Bathocuproindisulphonic acid disodium salt	IV	0.001	$1:3\cdot10^7$	40
Cu(II)	Calcion	IV	0.003	$1:10^7$	40
Cu(II)	colour of copper ion, pH 5.0	VIII	0.1	$1:4\cdot10^5$	41
Fe(III)	Tiron	I	0.008	$1:5\cdot10^6$	43
Fe(III)	sulphosalicylic acid	I	0.004	$1:10^6$	43
Fe(III)	chromotropic acid	I	0.02	$1:2\cdot10^6$	45
Fe(II), Fe(III)	α,α′-dipyridyl	IV	0.0025	$1:16\cdot10^6$	44
Fe(III)	Ferroin	I	0.004	$1:12.5\cdot10^6$	45
Ga(III)	Alizarin S	I	0.03	$1:10^6$	46
Ge(IV)	hematoxylin	III	0.003	$1:2\cdot10^7$	47—49
Hg(II)	diphenylcarbazone	I	0.1	$1:10^4$	50
In(III)	Alizarin S	II	0.03	$1:13\cdot10^5$	51
Mg(II)	Xylidene Blue	I	0.007	$1:15\cdot10^5$	52
Mo(VI)	NH_4SCN and $SnCl_2$	I	0.024	$1:16\cdot10^5$	53
Mo(VI)	hydrazine dihydrochloride and Methylene Blue	IV	0.001	$1:6\cdot10^7$	54
Ni(II)	dimethylglyoxime and Br_2	I	0.011	$1:38\cdot10^5$	55
Ni(II)	rubeanic acid	IV	0.021	$1:19\cdot10^6$	56
NO_2^-	*m*-phenylenediamine	IV	0.015	$1:29\cdot10^5$	57
NO_3^-	*m*-phenylenediamine and Zn	IV	0.08	$1:5\cdot10^5$	57
S^{2-}	*p*-aminodimethylaniline	VII	0.05	$1:8\cdot10^5$	58
Th(IV)	Alizarin S	III	0.03	$1:10^6$	59
Ti(IV)	H_2O_2	IV	0.25	$1:16\cdot10^4$	60
Ti(IV)	Tiron	I	0.026	$1:11\cdot10^5$	61
Tl(I)	I^-	III	0.01	$1:13\cdot10^5$	62
V(V)	8-hydroxyquinoline	VIII	0.025	$1:16\cdot10^6$	63
V(V)	H_3PO_4 and Na_2WO_4	I	0.2	$1:2\cdot10^5$	63
V(V), Fe(III)	α,α′-dipyridyl	IV	0.1	$1:4\cdot10^5$	63
V(V)	diphenylamine	IV	0.04	$1:10^6$	53
Zr(IV)	Alizarin S	I	0.03	$1:13\cdot10^5$	64
Zr(IV)	Pyrocatechol Violet	IV	0.01	$1:4\cdot10^6$	65

*Symbols: I) strongly basic anion exchanger, 1%DVB; II) strongly basic anion exchanger, 8%DVB; III) strongly basic anion exchanger impregnated with reagent, 1%DVB; IV) strongly acidic cation exchanger, 1%DVB; V) strongly acidic cation exchanger, 2.5%DVB; VI) strongly acidic cation exchanger, 8%DVB; VII) strongly acidic cation exchanger impregnated with reagent, 8%DVB; VIII) carboxylic acid cation exchanger, 1%DVB.

Tanaka and coworkers[76,77] suggested the use of transparent polymer films based on poly(vinyl chloride) (PVC) to determine various metal ions. They examined[76] the possibility of determining copper, zinc, cadmium, nickel, mercury, and manganese by using PVC membranes impregnated with 1-(2-pyridylazo)-2-naphthol (PAN). Some analytical characteristics of PVC membranes[76] after contact with solutions of these ions are given in Table 4. The optical density was shown to be proportional to the concentration of the metal being determined in the range $10^{-5}-10^{-4}$ M. Because the absorption by the membrane itself is negligible in the region of absorption by the complexes (550–570 nm) it is legitimate to measure the absorption of the membrane with respect to that of air.

Table 3. Relative sensitivity of the photometric analysis of ion-exchange resins (c_1) and of solutions (c_2). (The quoted figures are the metal concentrations giving an optical density $A = 0.50$.)

Element	$10^6 c_1$, M	$10^5 c_2$, M
Cr(VI) *	0.6	1.8
Cr(VI) **	0.6	1.8
Fe(II)	2.9	3.9
Cu(II)	2.5	2.2
Co(II)	9.4	3.0

* In $0.05N$ H_2SO_4
** In $0.05N$ H_2SO_4 + 0.6 M NaCl

Table 4. Analytical characteristic of PVC membranes.

Ion	λ_{max}, nm
Cu^{2+}	565
Zn^{2+}	558
Cd^{2+}	558
Ni^{2+}	574
Hg^{2+}*	565
Mn^{2+}*	565

*Glycine + NaOH buffer solution; in the other cases NH_4Cl + NH_4OH (pH ~ 10).

A PVC membrane impregnated with bathophenanthroline has been used[77] for the rapid semiquantitative determination of iron in water. Because the reaction between Fe(II) and bathophenanthroline (Bphen) gives the charged complex $Fe(Bphen)_3^{2+}$, the PVC membrane was additionally impregnated with tributyl phosphate. It was shown that the colour developed by the membrane has an absorption peak at $\lambda = 540$ nm. The optimum concentration of hydrogen ions is in the range pH 3–6 (0.1 M acetate buffer). The optical density of the membrane depends on the time of contact between the phases: as Fig.1 shows, the optical density for a contact time of 20 min is significantly higher than for a contact time of 5 min. It is important to note that the optical density remains constant for a long period. The light absorption of the membrane is affected also by the nature of the anion present in solution. For a total anion concentration of 2×10^{-2} M the effect of the anion on the colour of a membrane in contact with a solution of Fe(II) increases in the sequence

$$Cl^- < Br^- < I^- < ClO_4^- < \text{alkylbenzoylsulphonate}.$$

Metal ions which form coloured complexes with Bphen (copper, cobalt, nickel, manganese) interfere with the determination of iron in solutions by a PVC membrane

impregnated with Bphen and tributyl phosphate. Alkali and alkaline earth metals, aluminium, and also the anions sulphate, phosphate, chloride, and nitrate have practically no effect on the determination of Fe(II).

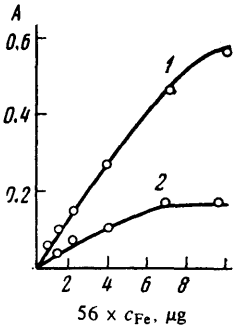


Figure 1. Calibration curves for the determination of iron: contact time 20 min (*1*) and 5 min (*2*).

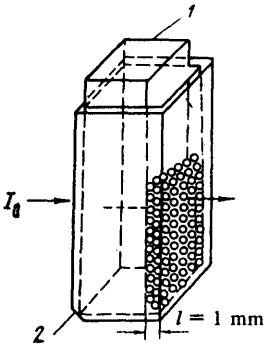


Figure 2. Conventional form of the cell for photometric analysis of the resin: *1*) quartz insert, *2*) drainage hole.

IV. METHODS OF PREPARATION OF SAMPLES FOR ANALYSIS

There are several methods of preparing the sample for photometric analysis (i.e. of preparing a light-absorbing layer uniformly packed with the ion-exchange resin). As in the photometric method of analysis of solutions, one uses quartz cells with parallel walls filled with resin grains[2,3,7,8,11,16,27]. Light absorption is measured 15–20 min after addition of the resin (the time needed to form a uniformly packed layer). In order to obtain the maximum packing density (and thus ensure reproducible results) it may be desirable to use a centrifuge[11,27].

Trace amounts of chromium in natural waters have been determined[75] in a cell with an outlet at the bottom: this allows the solution between the resin grains to be drained away, and helps the formation of a densely packed layer. A common form of the cell is shown in Fig.2. A quartz insert is used to decrease the thickness of the measured layer[8,16,75].

In the quantitative determination of elements[3] corrections must be applied for the light absorbed by the resin, the reagent, and the solution between the grains:

$$A' = A_{meas} - A_{sol} - A_{res} - A_{reag}.$$

Spectral measurements can be made with a mixture of the resin and colourless petroleum jelly, which is either added to the cell[24] or uniformly smeared on a glass plate[20]. Coleman[23] described a method of pressing the resin granules into disks, which are then used for sorption experiments and for light-absorption measurements. These disks are 0.2–0.6 mm thick.

A method of grinding the resin and pressing a mixture of the powdered resin with potassium bromide (or with petroleum jelly) has been used for i.r. spectral measurements[78-82]. Poly(vinyl chloride) membranes impregnated with an organic reagent were prepared [76,77] by dissolving PVC powder, a known weight of the reagent, and the required amount of plasticiser in tetrahydrofuran. After removing the solvent by evaporation the layer was placed between steel plates and pressed in a vacuum at 90°C. There is no information on the effect of lengthy storage on the analytical properties of the membrane.

V. POSSIBLE FUTURE DEVELOPMENTS OF ION-EXCHANGE RESINS IN PHOTOMETRY

The work discussed in this review suggests possible future developments of this area of analytical chemistry. First of all it should be possible to vary several parameters in order to achieve selectivity while increasing still further the sensitivity of the method, taking advantage of the concentration of the coloured complex which the resin offers. Furthermore the fund of knowledge available in the literature on the selectivity and sensitivity of reactions between metal ions and organic reagents still remains to be exploited.

Thus we envisage two main directions for further development, differing in the method used to produce the coloured complex in the resin.

1. The coloured resin is produced by allowing the metal ion to react with the anion of an organic reagent already present in the resin as an impregnant:

$$R{-}X^-_{(res)} + A^- \rightleftarrows R{-}A^-_{(res)} + X^-,$$
$$n\text{-}R{-}A^-_{(res)} + M^{n+} \rightleftarrows M(A{-}R)_{n(res)}.$$

2. The coloured resin is produced by sorption of the complex formed by an organic reagent with the metal ion in the aqueous phase:

$$M^{n+} + m\,HA \rightleftarrows MA_m^{-(m-n)} + m\,H^+,$$
$$R{-}X^-_{(res)} + MA_m^{-(m-n)} \rightleftarrows R_{(m-n)(res)}(MA_m) + (m-n)X^-.$$

Each approach has its own specific features and limitations. When further improvements in spectrophotometric apparatus and techniques are introduced, and the existing measurement problems are resolved, we can expect this combined method to be widely adopted in analytical practice for the determination of metal ions in natural waters and in waste waters.

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