REVIEW

Some Aspects of Radiochemical Separation Methods*

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It is sometimes remarked that the academic analytical chemist is considered inferior to his purer brethren because he is able to find gainful employment outside the university. The knowledge that the result of one challenging theoretical problem may be of considerable social benefit adds a zest to the work of analytical chemists and particularly those in the area of radio-chemical saparations, for in this area the interplay between the pure scientist and technologist is seen at its best, as the programme of this conference shows. For this reason or some other the number of workers in the field is so large and the output so great that a full comprehensive review would be beyond our endurance and largely unnecessary since good reviews of the parts or the whole exist [1 — 8].

Consequently my remarks will be limited to some newer aspects of the two major methods of radiochemical separation; ion exchange and solvent extraction.

They are methods of general applicability, which may by used for solutions of high and low activity, for large and small amounts of material, in factory and laboratory and are of considerable academic interest. We now know a great deal about these processes and we will concentrate on some of the refinements of our knowledge that may lead to improved separations.

Inorganic ion-exchangers

Zirconium phosphate

The examination of possible ion-exchanging materials for the removal of strontium and caesium has encompassed such a bizarre range of substances that one is inevitably reminded of the alchemists searches for the Philosophers stone. Everything from brick dust to green algae has been tried, but of the few compounds of value the synthetic inorganic ion-exchangers are especially worthy of note, and of these zirconium phosphate and ammonium phosphomolybdate have probably proved most useful [3]. The former is able to withstand radiation and high temperatures, is stable over a fairly wide pH range (10 M-HCl — 8) and has a reasonable exchange capacity for the alkali metals, especially caesium (2 meq/g at pH 4). The exchange mechanism is based upon the —P—O—H groups in the compound and thus is similar to a strong acid organic ion-exchanger. However, problems remain; samples vary with the method of preparation, which leads to uncertainty in structural determinations and thermodynamic values. C. B. Amphlett et al. [9] and G. H. Nancollas [10] have shown the need for careful study of the thermo-

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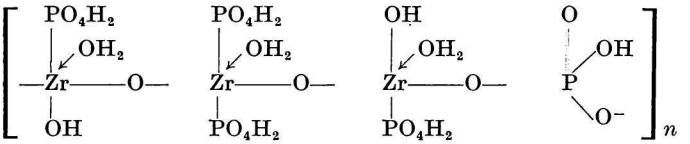
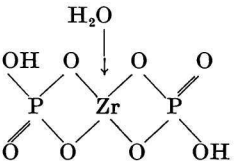
dynamic processes. When exchange is between rubidium and caesium or potassium and caesium adsorption isotherms are normal and rectilinear, but when the exchanging ions differ markedly in size, rubidium and hydrogen or caesium and hydrogen the curves are obtained with considerable distortion. When the phosphate is almost saturated with one or the other of the ions, reversal of selectivity may occur. The reason for this behaviour is not clear but the authors suggest that it is possibly a steric effect. The agreement in principle between these groups of workers show that all thermodynamic work is not wasted, but that values are only strictly applicable to the actual system investigated.

For several ion-exchangers the structure of the compound has been shown to be most important in determining exchange behaviour.

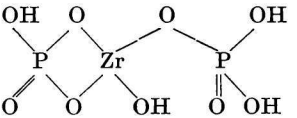
Two recent studies have helped to elucidate the structure of the phosphate which has previously thought to be a —Zr—O— lattice with acid phosphate groups attached to spare valency bonds [11] or a limited chain structure [12]:



G. H. Nancollas and V. Pekárek [13] have supported this structure for one of the five zirconium phosphates which they examined by crystallography, titrimetry and exchange equilibria. They believe that this is the structure of an amorphous phosphate of good M^+ capacity because of the number of primary hydrogen ions available. The structure:



is assigned to a crystalline material of relatively low exchange capacity commensurate with the presence of tertiary hydrogen ions. Intermediate structures are believed to result from ring breaking to give an extra replaceable hydrogen ion:



Forms that are semicrystalline or amorphous have this structure. It is clearly demonstrated that there is no correlation between crystallinity and exchange. Exchange is related to the number and acidity of available replaceable hydrogen ions. A similar conclusion is arrived at by G. Alberti et al. [14] who examined the effect on structure and exchange capacity of ten zirconium phosphates. They confirm the observation of V. Veselý and V. Pekárek [15] that heating leads to condensation of the phosphate to pyrophosphate and that exchange capacity is lost thereby. Consequently the after treatment of the prepared phosphates is of some consequence.

The idea of the adsorption being an exchange process has been challenged by V. Veselý and V. Pekárek [16], who have shown that for ammonium uranyl phosphate

the complex can be considered as a precipitation carrier, the equilibrium position being a function of the solubility products of the interacting phosphates.

Ferrocyanides

The complexities presented above prompted several workers to examine other inorganic compounds for their ion-exchange properties. One obvious group is the complex ferrocyanides $M^{I}_{2}[M^{II}Fe(CN)_6]$ or $M^{II}[M^{II}Fe(CN)_6]$ whose structure are well known and whose reaction with the alkali metals has been used analytically for nearly a century. In the way that C. P. Snow insists is typical of the development of science, work started independently in three centres, Řež [17—19], South Carolina [2] and Swansea [21]. Most of the divalent transition metal ions ferrocyanides have been examined. They are easy to make but are fine powders, which form slimes in solution so that generally they are not ideal for column work. The maximum take up corresponds to the theoretical for the reaction but under working conditions actual up take may be much less. It has been demonstrated that it is an ion-exchange process [18], and that it is not limited to univalent ions. The stability is good but not ideal. In our view the best of these is potassium cobaltous ferrocyanide [20] because it is readily obtainable in a fairly granular form, and it has already formed the basis of a method for determining caesium in urine, milk etc. [22]. The cadmium, zinc and copper are also potentially valuable, but all of the ferrocyanides present problems of crystallinity and removal of sorbed ions. It is possible that preparation by precipitation from homogeneous solution e. g. by hydrolysis of cyanohydrins might yield more suitable compounds. Another interesting example is the combination of ferrocyanide and molybdate, which exchanges caesium rapidly and selectively [23]. The knowledge of the structure of the parts enabled the structure of the whole to be duduced from X-ray powder photographs; the wide channels thus revealed accounting for the very rapid rate of exchange. Unfortunately the optimum range of stability is 0.8 — 1.0 and below and beyond 2 it breaks down.

Chromium polyphosphate glass

These types of inorganic ion-exchanger bore out the predictions about their performance made before the work commenced. The new one on which we have been working poses many theoretical problems, whilst possessing many admirable properties. It is a glass prepared very simply from chromic chloride and sodium tripolyphosphate. Its physical properties are summarised in Tab. 1. These allied to the ease of grinding the glass to any

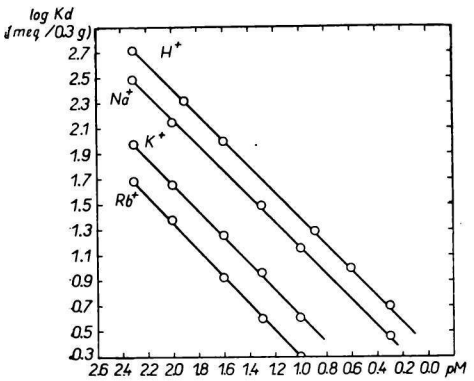


Fig. 1. Distribution coefficients for caesium ion (Kd) in the presence of different univalent ions (M).
Total vol. 10 ml; CsCl 0.5 . 10^{-3} M; Wt. of complex 0.3 g.
Slope for H^+, Na^+, K^+, Rb^+ = 1.

desired grain size fulfill the basic requirements of an inorganic ion-exchanger very well. The form dried at room temperature exchanges univalent ions by an ion-exchange process (Fig. 1) with preference for Cs^+, Rb^+, K^+, Na^+ and H^+; that dried at 150 °C loses its exchange capacity. The exchange is dependant upon pH and its capacity is greater than that for zirconium phosphate (at pH 4 4 meq/g compared with 2 and at pH 12 10 meq/g compared with 5.5).

Table 1

Physical properties of chromium polyphosphate glasses

a) Glass obtained at 25 °C	*b*) Glass *a1* dried at 150 °C
1. Non crystalline	*1.* Non crystalline
2. No breakdown of grain size in media in which it is insoluble	*2.* No breakdown of grain size in media in which it is insoluble
3. H_2O: Insoluble after 3 months	*3.* H_2O: Insoluble after 3 months
4. HCl 5 M: Insoluble after 5 days HCl 10 M: 10 ml dissolves 0.2 g in 24 hrs.	*4.* HCl 10 M: Insoluble after 8 days
5. HNO_3 5 M: Insoluble after 8 days 10 M: 10 ml dissolves 0.2 g in 4 days	*5.* HNO_3 10 M: Insoluble after 8 days
6. H_2SO_4 10 M: Insoluble after 1 month	*6.* H_2SO_4 10 M: Insoluble after 1 month
7. NaOH 0.05 M: Insoluble after 4 days 0.1 M: 10 ml dissolves 0.2 g in 2 days 0.5 M: readily soluble	*7.* NaOH 4 M: Insoluble after 5 days

The phosphate appears to be selective for univalent ions; at pH 3 250-fold excess of Ni(II), Co(II), Mn(II), Cd(II), Zn(II), Ca(II), Sr(II), Mg(II), Fe(II) and Cr(III) had no effect upon the distribution and uptake coefficient of caesium. This is in marked contrast with zirconium phosphate and the ferrocyanides. It should be a simple process then to separate the univalent cations from a mixture of multivalent cations and subsequently by elution with acid (>1 M) to separate the univalent ions from each other.

The mechanism is based upon hydrogen ion replacement but the structure is likely to be more complex than zirconium phosphate. Amorphous phosphate glasses are in fact conglomerations of various phosphates, whose proportions vary from glass to glass. J. R. Van Wazer [24] has shown that the distribution of fragments may be deduced from the rigid rod and flexible chain theories familar to polymer chemists. If these theories prove applicable to the chromium polyphosphate system it is possible that they could be employed to enable the optimum glass to be prepared.

We feel that we have several years hard research ahead to make the most of this potentially useful exchanger.

Solvent extraction

The practical value of solvent extraction has been fully recognised in the last decade; there have been tremendous advances since G. H. Morrison and H. Freiser published their book [25] in 1957. Almost every element can be extracted in some form including xenon [26]. The elegance of the method is often matched by the elegance of the explanation as for instance in recent paper by D. Dyrssen and D. J. Petrović [27] who are able to measure the activity coefficients of tripropyl phosphate relate these to those for tri-

butylphosphate and to observe the extent of dimerisation. A large amount of reliable data has been published much of it due to outstanding work in the various research laboratories attached to the Atomic Energy Authorities throughout the world. It may be possible to use this knowledge to better advantage than is often the case. J. W. O'Laughlin [28] has provided some useful examples of this, but the one which is taken here provides a good instance of international cross-fertilization.

Reverse-phase partition chromatography

In 1958 D. F. Peppard et al. [29] showed that di-(2-ethylhexyl)orthophosphoric acid (HDEHP) could be used to extract the lanthanides with an average separation factor between adjacent lanthanides of 2.24 ∓ 0.42. The quantitative measurement is the basis of what follows, had the results been quoted in the rough and ready way they often are it would have been difficult to make use of them in the way that T. B. Pierce [30 — 32] did. He absorbed HDEHP onto a suitable polymer and showed that the chromatographic behaviour of the reagent on the polymer was completely analogous with the solvent extraction by the reagent in toluene; the average chromatographic separation factor was 2.11 ∓ 0.57. By gradient elution with perchloric acid a good clean separation of the lanthanides is possible.

Reverse-phase partition chromatography is becoming more widely used for performing multiple separations and for predicting the behaviour of uninvestigated liquid-liquid extraction procedures! Care is needed to ensure that the system is truly reversible under the conditions of use. We have had a student experiment based on reverse phase thin layer chromatography with 1-(2-pyridylazo)-2-naphthol (PAN) as the ligand. Results depend greatly upon operator, conditions of solvent removal and it is possible that PAN does not react rapidly enough for equilibrium to be reached.

Counter-current distribution

One of the disadvantages of the reverse phase technique is that only small amounts can be handled. It is worth using the values of the separation factors to see if counter-current

Table 2

Countercurrent distribution of lanthanides

D	HCl/HDEHP; 200 transfers			
	X	r_{max}	r_i	contamination %
100	0.990	198	196.5	33
45.5	0.978	195.6		
10	0.91	182		
4.5	0.82	163	174	2.5
2.2	0.69	138		
1	0.5	100	120	0.25
0.022	0.0215	4.3	2.5	34
0.010	0.0099	1.98		

Average separation factor 2.2; $r_{max} = nX$

distribution would be a valuable procedure. The results for selected distribution ratios and 200 transfers are readily calculated [33] and are shown in Tab. 2. It is seen that over the range $D = 0.1 — 10$ a reasonable separation is possible. With the lanthanides it would be possible to adjust the pH so that D for the middle elements $\simeq 1$ and carry out, say, 10 transfers. If the fractions are collected into three lots of low, medium and high distribution ratios, the pH of each fraction is adjusted so that the average distribution ratio of each is approximately 1 and then each fraction is put through 200 tranfers, the process and the results are analogous to gradient elution chromatography. It may be objected that this is a relatively slow business, which is true but it may be countered that it is still a simple procedure and capable of handling large amounts. One of the few instances of the method being used for inorganic separations is the separation of kilogram amounts of gadolinium oxide in >95 % purity from rare-earth oxides [34]. Recently R. B. Brooks [35] has applied the method to the separation of trace elements in geological materials. He used an HCl—methylisobutyl ketone system to separate various elements with some success, and an 8-hydroxyquinoline—chloroform system for concentrating trace elements from large volumes of sea water, reporting enrichment factors of 400 000. It is probable that better systems could be devised, and that counter-current distributions could play a large part in inorganic solvent extraction now that a relatively large amount of reliable data is available to enable optimum conditions to be chosen.

Solvent effects

The role of the solvent has always been mentioned in discussions about solvent extraction, but the variation of K_{DX}/K_{DR}^n in the extraction equation

$$D = K^* \frac{K_{DX}}{K_{DR}^n} \cdot \frac{[HR]_{org}^n}{[H^+]^n}$$

as a function of solvent has received very little attention. (K_{DX} = partition coefficient of the neutral extractable chelate, K_{DR} = the partition coefficient of the neutral reagent HR, K^* is a constant and n is the number of moles of reagent per mole of chelate.) Yet variation of this factor from solvent to solvent could affect the minimum pH for effective extraction and would make the choice of solvent most important. It might be postulated that the polarity of a metal ion in a chelate would show up markedly in K_{DX}. H. A. Mottola and H. Freiser [36] have measured the partition coefficients of 8-hydroxyquinoline, 2-methyl-8-hydroxyquinoline and 4-methyl-8-hydroxyquinoline and their copper chelates between water and a variety of solvents; and attempted to correlate the results with the dielectric constant of the solvent and the solubility parameter in a most interesting way. They also give a measure of K_{DX}/K_{DR}^n as the difference in $pH_{\frac{1}{2}}$ with respect to chloroform and plot this in increasing order of K_{DR}. There are two odd things about this approach; $\Delta\, pH_{\frac{1}{2}}$ is not plotted as an actual function of K_{DR} and K_{DR} is greatest in the chloroform system. The range of $\Delta\, pH_{\frac{1}{2}}$ is about 1. It would seem more logical to plot log K_{DX} vs. log K_{DR} for each system. This yields the following slopes and 95 % confidence limits, as determined by the method of least squares; 8-hydroxyquinoline (0.79 ∓ 0.64), 2-methyl-8-hydroxyquinoline (0.91 ∓ 0.98), 4-methyl-8-hydroxyquinoline (1.11 ∓ 1.90). Each of these sets of data contain small ranges of results (log K_{DX} 1.98 — 3.48; 2.89 — — 4.48 and 2.80 — 4.56 respectively). But because the reagents are so similar it doesn't seem unreasonable to combine the results whence a line of slope 0.88 ∓ 0.38 is obtained.

This value may be compares with a slope of 2.4 found in the preliminary investigation of the 2-(2-pyridylazo)-1-naphthol—zinc system between a number of solvents carried out at Swansea.

It is readily deduced that if the slope is k under identical conditions of pH and reagent concentration and if

$$D_1 = K^* \frac{K_{DX1}}{K^n_{DR1}} \text{ and } D_2 = K^* \frac{K_{DX2}}{K^n_{DR2}};$$

$$\log D_1 - \log D_2 = (k - n)(\log K_{DR1} - \log K_{DR2}) =$$

$$= \left(1 - \frac{n}{k}\right)(\log K_{DX1} - \log K_{DX2}).$$

If the value of $k = 0.88$ is significant there will be some slight advantage in using a solvent in which the K_{DR} is low. However the conclusion to be drawn from these results if that broadly speaking it is sensible to choose the solvent on grounds of convenience and economy because there is probably not a great deal to be gained in the extraction by choice of solvent. It is useful to know that for applications, such as counter-current distribution, where a solvent less dense than water is likely to be used values obtained in carbon tetrachloride systems may be used.

It is of course true that these conclusions are reached by roughly treating a few results. The precision of the individual values is good enough to show that this is a crude process and that the correlation can never be good. It would seem however that trends might be better detected by treating families of substituted reagents as one and by using smaller ligands and larger metal ions so that effects of polarity might be shown more clearly.

In this survey only a few points have been picked out. Interesting and relevant areas such as sub-stoichiometry and the problem of selectivity will be dealt with elsewhere in the conference. The practical applications also dealt with in other papers have been indicated rather than emphasised, even though they provide the basis of our existance. Systems based on molten salts have not been discussed because of the paucity of published data. Simplications have been made, there is still much to be elucidated, but the major fact remains that there is a large degree of understanding of the processes of the major methods of radiochemical separations and that large amounts of data are being published. The future lies in combining the two in an intelligent way to predict the optimum approach when faced with new problems.

NIEKTORÉ ASPEKTY RÁDIOCHEMICKÝCH SEPARAČNÝCH METÓD

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Prvá časť práce je venovaná použitiu anorganických vymieňačov iónov: fosforečnanu zirkoničitého, ferokyanidov a chromofosforečných skiel, ktoré majú význam predovšetkým na izoláciu cézia z produktov štiepenia. Výsledky zistení v laboratóriu autora sa porovnávajú s údajmi v literatúre.

Druhá časť práce sa zapodieva extrakciou chelátov. Tu sa rozoberá extrakčná chromatografia, Craigova metóda a vplyv rozpúšťadla na extrakciu.

НЕКОТОРЫЕ ВОПРОСЫ РАЗДЕЛИТЕЛЬНЫХ РАДИОХИМИЧЕСКИХ МЕТОДОВ

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Первая часть работы посвящена применению неорганических ионитов: фосфорнокислого циркония, ферроцианидов и хромофосфорнокислых стекол, которые применяются главным образом для выделения цезия из продуктов деления. Результаты, полученные в лаборатории автора, сравниваются с литературными данными.

Во второй части работы описывается экстракция хелатов. Здесь обсуждается экстракционная хроматография, метод Крайга и влияние растворителя на экстракцию.

Preložila T. Dillingerová

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