# SEPARATIONS PROCESSES IN ANALYTICAL CHEMISTRY

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## INTRODUCTION

Industrial hygiene chemistry is an extremely demanding branch of analytical chemistry. Whereas many areas of applied chemical analysis are self-limiting, e.g., gas, mineral or metallurgical analyses, the field of industrial hygiene chemistry covers the tremendous breadth of the thousands of chemical substances encountered in man's working environment. This complexity is compounded further by the need to separate, characterize and determine quantitatively trace quantities of these organic and inorganic substances in the presence of overwhelming quantities of bulk materials containing chemical interferences. The successful application of *all* modern physical and chemical methods of analysis to the detection and determination of these individual chemical entities requires in many instances, the preliminary separation and concentration of an analytically desired constituent from the bulk diluents and interfering elements present in biological tissues and fluids, complex mixtures of aerosols or industrial process materials and finished products. The daily solution of these problems requires a full understanding of the basic principles of the separation processes which must be applied to these sample systems to obtain the accurate analytical data needed for the valid and complete assessment of environmental conditions and their effects on the health of the worker.

This chapter provides a basic theoretical treatment of two of the most powerful techniques used in inorganic separations; i.e., solvent extraction and ion exchange chromatography. These methods have provided the foundation of numerous analytical procedures used in the industrial hygiene laboratory. The solvent extraction technique has been used widely for rapid, cleancut separations of trace level quantities of analytically desired elements and compounds (dithizonates, dithiocarbamates and 8-quinolinates of the heavy metals, phenolic compounds and ferric chloride, as examples) from biological and environmental sample materials. Ion exchange chromatography has proved to be extremely valuable in separating fractional part per million concentrations of interfering chemical elements from one another to increase the specificity, accuracy and sensitivity of their final method of estimation in diverse industrial hygiene samples.

## CLASSIFICATION OF SEPARATION PROCESSES

Although great strides have been made in the development of highly selective analytical methods, the analytical chemist is called upon to deal with samples that are increasingly complex. As a result, inclusion of separation steps might be necessary even with highly discriminatory instrumental methods such as neutron activation or atomic absorption analysis. Furthermore, separation of a component of interest from the sample medium may also serve to concentrate it, which would effectively increase the sensitivity of the analytical method ultimately employed.

One of the most powerful approaches to separations involves using pairs of phases in which the component of interest transfers from one to the other in a manner that differentiates it from interferences. It is useful to classify phase separation processes according to (a) the state of the phase pair involved (solid, liquid or gas), (b) whether the phase is in bulk or spread thin as on a surface and (c) the means of contacting the phase pair: (i) batch, (ii) multistage (iii) countercurrent.

Bulk and "thin" phases can be distinguished in that by the latter is meant a spreading of the phase involved over a relatively large surface area. Thus, both distillation and gas-liquid chromatography (GLC) are separations involving gas-liquid phase pairs but in the latter, the liquid phase is spread out as a thin layer on a largely inert solid supporting material. Similarly, solvent extraction and liquid partition chromatography (either paper or column) involve a liquid-liquid phase pair but in the latter, one of the liquid phases is present as a supported thin layer. In these two examples cited, the mode of contacting the phases can also be different. In a simple distillation process, a batch of the mixture is placed in the boiler and the distillate contains the more volatile components. In contrast, with GLC, the gas mixture moves countercurrently to the immobilized liquid layer ensuring that the increasingly depleted mobile gas phase encounters a fresh clean portion of the immobilized liquid phase. In countercurrent processes, a large number of equilibration (or approximate equilibration) steps occur. It is possible to carry out separations involving bulk phase pairs with countercurrent contacting. Thus, fractional distillation, in which a packed distillation column and reflux head are used, involves countercurrent contacting.

This chapter is devoted to the description of the principles and practices of two-phase separation processes, solvent extraction and ion exchange, which are important in dealing with complex aqueous mixtures. Elsewhere in this syllabus (Chapter 21) several forms of chromatography are also covered.

# SOLVENT EXTRACTION

## General Principles and Terminology

Solvent extraction is a process in which a solute of interest transfers from one solvent into a second which is essentially immiscible with the first. Because the extent of such transfer for various solutes can be varied individually from negligible to essentially total extraction, through control of the experimental conditions this process provides the basis for many excellent separations.

Fundamentally, all solvent extraction procedures can be described in terms of three aspects, or steps:

*First,* the distribution of the solute, called the extractable complex or species, between the two immiscible solvents. This step can be described quantitatively by Nernst's Distribution Law which states: The ratio of the concentrations of a solute distributing between two essentially immiscible solvents at constant temperatures is a constant, provided that the solute is not involved in chemical interactions in either solvent phase, or

$$K_{D_A} = \frac{[A]_o}{[A]} \qquad (1)$$

where A is a solute distributing between an organic solvent in which the molar concentration of A is expressed as $[A]_o$ and an aqueous phase as A without subscript. The constant $K_D$ is called the *distribution constant.*

*Second,* chemical transformations to produce an extractable species are of primary importance in solvent extraction processes inasmuch as most of the substances of interest, particularly metal ions, are not usually encountered in a form that can be extracted into an organic solvent. This second aspect of extraction concerns the chemical interactions in the aqueous phase or formation of the extractable complex.

*Third,* chemical interactions in the organic phase may be necessary, such as self-association or mixed ligand complex formation. Such chemical interactions do not negate the validity of the Nernst distribution law, but obviously the extraction cannot be described quantitatively by such a simple equation. For this purpose it is necessary to know how each of the contributing reactions affects the extent of extraction and this is discussed in the following sections.

The extent of extraction may be described in terms of the *distribution ratio* as follows:

$$D_A = \frac{C_{A(o)}}{C_A} \qquad (2)$$

where D is the distribution ratio, $C_{A(o)}$ and $C_A$ correspond to the total analytical concentration of component A in whatever form it is present in the organic $_{(o)}$ and aqueous (A) phase, respectively. If the substance does not enter any chemical reactions in either phase, then $D_A$ reduces to $K_{D_A}$. (K = distribution constant)

Another important way of expressing extent of extraction is by the *Fraction Extracted*

$$F_A = \frac{C_{A(o)} V_o}{C_{A(o)} V_0 + C_A V} = \frac{D_A R_V}{D_A R_V + 1} \qquad (3)$$

where F = fraction extracted, $V_o$ and V are the respective volumes of the organic $_{(o)}$ and aqueous phases, $R_V$ is the phase volume ratio, $V_0/V$ (others as in equation 2). The *percentage extraction* is simply 100F.

Equation (3) demonstrates the possibility of increasing the extent of extraction with a given D value by increasing the phase volume ratio. If instead of a single batch extraction, a second or third extraction is carried out on the same aqueous solution by successive portions of organic solvent such that $R_V$ remains the same, the additional fractions extracted are F(1-F) and F(1-F)$^2$, respectively. The fractions remaining in the aqueous phase following *n* successive extractions is $(1-F)^{n-1}$.

*Separation Factor:*

If two substances A and B are present in a solution in an initial concentration ratio, $C_A/C_B$, then upon extraction their concentration ratio in the organic phase would be $C_A F_A/C F_B$, where $F_A$ and $F_B$ are the corresponding fractions extracted. The ratio $F_A/F_B$, which is the factor by which the initial concentration ratio is changed by the separation, is a measure of separation. A corollary measure of separation which represents the change in the ratio of concentrations remaining in the aqueous phase is $(1-F_A)/(1-F_B)$.

Two substances whose distribution ratios differ by a constant factor will be separated most efficiently if the product, $D_A D_B$, is unity. As an illustration of this principle, consider the case of a pair of substances whose distribution ratios are $10^3$ and $10^1$ respectively. If these substances were present in equal quantity, then a single extraction would remove 99.9% of the first and 90% of the second. A much more efficient extraction would be obtainable if, using the same factor of 100 between the distribution ratios, the two distribution ratios were $10^{+1}$ and $10^{-1}$. In this case respective fractions extracted would be 90% and 10%.

## Classification of Extraction Systems

The following classification refers essentially to inorganic systems, particularly those involving metal ions. There are, of course, many organic compounds which are extracted without any significant chemical reaction such as alcohols, ethers and carboxyl compounds. Systematic changes in the extraction of such compounds by various solvents can be related to molecular weight, hydrogen bonding and less specific interactions.

Chemical reactions are at the very heart of metal ion extractions. Most metal salts are soluble in water, but not in organic solvents, particularly of the hydrocarbon and chlorinated hydrocarbon types. This results not only from the high dielectric constant of water but, more importantly, from its ability to coordinate with the ions, especially the metal ion, so that the hydrated salt more nearly resembles the solvent. To form an extractable metal complex it is necessary to replace the coordinated water from around the metal ion by groups, or ligands, that will form an uncharged species that will be compatible with a low dielectric constant organic solvent.

Formation of an extractable metal species can be accomplished in a great variety of ways which makes a classification of extractions based on this very useful, particularly as a guide to the under-

standing of the thousands of different extractions systems now in use.

The formation of an uncharged species that is extractable by the relatively non-polar organic solvent can involve

1. Simple (monodentate) coordination alone, as with $GeCl_4$;

2. Heteropoly acids, a class of coordination complexes in which the central ion is complex rather than monatomic, as with phosphomolybdic acid, $H_3PO_4 \cdot 12MoO_3$,

3. Chelation (polydentate coordination) alone, as with Al (8-quinolinolate)$_3$,

4. Ion-association alone, as with $Cs^+$, $(C_6H_5)_4B^-$ or

5. Combinations of the above, such as:

   a. Simple coordination and ion-association — e.g., ("Onium"$^+$), $FeCl_4^-$, ["Onium" stands for one of the following cation types, hydrated hydronium ion, $(H_3O)_3O^+$, a rather labile cation requiring stabilization by solvation with an oxygen-containing solvent, a substituted ammonium ion, $R_nNH^+_{(4-n)}$ where R is an alkyl or aralkyl group and N may vary from 1 to 3, a sub-

stituted phosphonium ion $R_4P^+$, stibonium ion $R_4Sb^+$, sulfonium ion and other ions of this sort, including the important category of cationic dyes such as Rhodamine B].

   b. Chelation and ion-association with either positively or negatively charged metal chelates — e.g., Cu(2, 9-dimethyl-1,10-phenanthroline)$_2^+$.$ClO_4^-$ or 3 (n-$C_4H_9NH_3^+$) Co (Nitroso R Salt)$_3^{-3}$ — and, finally,

   c. Simple coordination and chelation — e.g., Zn(oxinate)$_2$ · pyridine. This category is of significance for chelates that are coordinatively unsaturated — i.e., those with a monoprotic bidentate reagent in which the coordination number of the metal is greater than twice its valence.

An examination of the foregoing material and of Table 18-1 serves to underline the close relationship between inorganic and analytical chemistry employed in the principles and practice of metal extraction systems. A thorough understanding of analytical solvent extraction of metals requires a deep appreciation of many branches of coordination chemistry.

Table 18-1   Metal Extraction Systems
PRIMARY SYSTEMS

I. Simple (Monodentate) Coordination Systems

   1. Certain halide systems — e.g., $HgCl_2$, $GeCl_4$

   2. Certain nitrate systems — e.g., $(UO_2^{2+})$ (TBP)$_2$ (NO$_3^-$)$_2$

II. Heteropoly Acid Systems — e.g., $H_3PO_4 \cdot 12MoO_3$

III. Chelate Systems

   A. Bidentate chelating agents                         Reactive Grouping

      a) 4-Membered ring systems

          1. Disubstituted dithiocarbamates — e.g., $Na^+$, $(C_2H_5)_2$ NCSS$^-$ or $(C_6H_5CH_2)_2$ NCSS$^-$ Xanthates — e.g., $Na^+$, $C_2H_5$ OCSS$^-$         $S=C-S^-$

          2. Dithiophosphoric acids — e.g., diethyldithiophosphoric acid         $S-P-S^-$

          3. Arsinic and arsonic acids — e.g., benzenarsonic acid         $^-O-As-O^-$
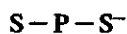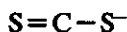
      b) 5-Membered ring systems

          1. N-Acyl hydroxylamines — e.g., N-benzoylphenylhydroxylamine (BPHA) or benzohydroxamic acid         $O=C-N-O^-$

          2. N-nitroso-N-arylhydroxylamines — e.g., Cupferron, (N-nitrosophenyl-hydroxylamine) or neocupferron, (N-nitrosonaphthylhydroxylamine)         $O=N-N-O^-$

          3. α-Dioximes — e.g., Dimethylgloxine, cyclohexane-dionedioxime (Nioxime)         $N=C-C=N^-$

          4. Diaryldithiocarbazones — e.g., Dithizone, (diphenyldithiocarbazone)         $N-N=C-S^-$

          5. 8-Quinolinols — e.g., Oxine, (8-quinolinol), Methyloxine, (2-methyl-S-quinolinol)         $N=C-C-O^-$
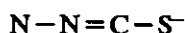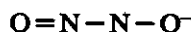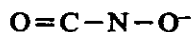
6. Quinoline-S-thiols, dithioxamides — e.g., thio-oxine, (quinoline-8-thiol) N, N'didodecyldithiooxamide     $N = C - C - S^-$

7. Quinoline-S-selenol     $N = C - C - Se^-$

8. O-Dihydroxybenzenes — e.g., catechol, phenylfluorone, rhodizonic acid     $^-O - C = C - O^-$

9. o-Dimercaptobenzenes — e.g., toluene-3, 4-dithiol     $^-S - C = C - S^-$

10. Thionalid (thioglycolic-$\beta$-aminophthalide)     $O - C - C - S^-$

  c) 6-Membered ring systems

    1. $\beta$-Diketones — e.g., Acetylacetone, TTA (thenoyltrifluoroacctone) dibenzoylethane, Morin, quercetin, quinalizarin     $O = C - C = C - O^-$

    2. o-Nitrosophenols — e.g., 1-nitroso-2-naphthol     $O = N - C = C - O^-$

    3. o-Hydroxyloximes — e.g., salicyladoxime     $N = C - C = C - O^-$

  d) Larger ring systems

    1. Mono or dialkyl-phosphoric or -phosphonic acids     $O = P - OHO = P - O^-$

B. Polydentate chelating systems

  1. Pyridylazonaphthol (PAN) and pyridylazoresorcinol (PAR)     $N = C - N = N - C = C - O^-$

  2. o, o' Dihydroxyazobenzenes — e.g., 2, 2'-dihydroxy-5'-isopropy 1-4-methyl-4-nitroazobenzene     $O - C = C - N = N - C = C - O^-$

  3. N, N'-(Disalicylidene) ethylenediimine (also S analog)     $^-O - C = C - N = C - C = N - C = C - O^-$

  4. Glyoxal bis(2-hydroxyanil) (also S analog)     $^-O - C = C - N = C - C = N - C = C - O^-$

IV. Simple Ion Association Systems

  A. Metal in cation

    1. Inorganic anions — e.g., $Cs^+$, $I_3^-$ or $PF_6^-$

    2. Tetraphenylboride anion

    3. Dipicrylamine anion

    4. Alkylphenolate anion

    5. Carboxylate and perfluorocarboxylate anions

# MIXED SYSTEMS

V. Ion Association and Simple Coordination Systems

  A. Metal in cation

    1. Oxygen solvents — e.g., alcohols, ketones, esters, ethers — e.g., $[(UO_2)(ROH)_6]^{+2}$, $2NO_3^-$

    2. Neutral phosphorus compounds, phosphates, phosphonates, phosphinates, phosphine oxides, and sulfides

  B. Metal in anion (paired with "onium" ion)

    1. Halides — e.g., $FeCl_4^-$

    2. Thiocyanates — e.g., $Co(CNS)_4^{-2}$

    3. Oxyanions — e.g., $MnO_4^-$

VI. Ion Association and Chelation Systems

  A. Cationic chelates

    1. Phenanthrolines and polypyridyls — e.g., Cu(I) (2, 9-dimethylphenanthroline)$_2^+$

    2. Tetraalkyl methylenediphosphonates — e.g., $(RO)_2P - CH_2 - P(OR)_2$

B. Anionic chelates
    1. Sulfonated chelating agents
        a. 1-Nitroso-2-naphthol — e.g., Co (III) (nitroso R salt)$_2^{-2}$
        b. 8-Quinolinol — e.g., Fe(III) (7-iodo 8-quinolinol-5 sulfonate)$_2^{-2}$

VII. Chelation and Simple Coordination Systems — e.g., Th(TTA)$_4$ · TBP, Ca (TTA)$_2$ · (TOPO)$_2$

## GENERAL EXPERIMENTAL TECHNIQUES

### Methods of Extraction:

(1) Batch Extraction

When experimental conditions can be adjusted so that the fraction extracted is 0.99 or higher ($DR_V > 100$) then a single or batch extraction suffices to transfer the bulk of the desired sub-stance to the organic phase. Most situations in analytical extraction fall into this category. The usual apparatus for a batch extraction is a separatory funnel such as the Squibb pear-shaped type. (For additional special types of funnels see reference (1).)

Even when the $DR_V$ of the desired substance is as low as 10, carrying out batch extraction twice will transfer 99% of the material to the organic phase.

If one chooses as a desirable criterion of separation of a pair of substances that one be at least 99% extracted and the other no more than 1%, then it can be seen that $D_1R_V > 100$ and $D_2R_V < 0.01$.

(2) Continuous Extraction

For substances whose $DR_V$ values are relatively small, even multiple batch extraction cannot conveniently or economically (too much organic solvent required) be used. Continuous extraction using volatile solvents can be carried out in an apparatus in which the solvent distilled from an extract collection flask is condensed, contacted with the aqueous phase and returned continuously to the extract collection flask. Continuous extraction apparatus for solvents that may be either heavier or lighter than water is shown in Figures 18-1 and 18-2.

(3) Countercurrent Distribution (CCD)

A special multiple-contact extraction is needed to bring about separation of two substances whose D values are very similar even under optimum conditions. In principle, countercurrent distribution could be carried out in a series of separatory funnels, each containing an identical lower phase. The mixture is introduced into the first portion of upper phase in the first funnel. After equilibration, the upper phase is transferred to the second funnel and a new portion of upper phase (devoid of sample) is introduced into the first funnel. After both funnels are equilibrated the upper phase of each is moved on to the next funnel and a fresh portion of upper phase is again added to the first funnel. This process is repeated as many times as necessary collecting the upper phases as "elution fractions."

With automated CCD equipment several hundred transfers can be accomplished conveniently which permit the separation of two solutes whose $D_1/D_2$ is less than two.

The relation of the distribution ratio, D, of a solute in a CCD process to the concentration in the various separatory funnels or stages can be shown to be given by the binomial expansion:

$$[F + (1-F)]^n = 1 \qquad (4)$$

where F, the fraction extracted, is $DR_V/1 + DR_V$, as shown in (3), and $n$ is the number of stages in the CCD process.



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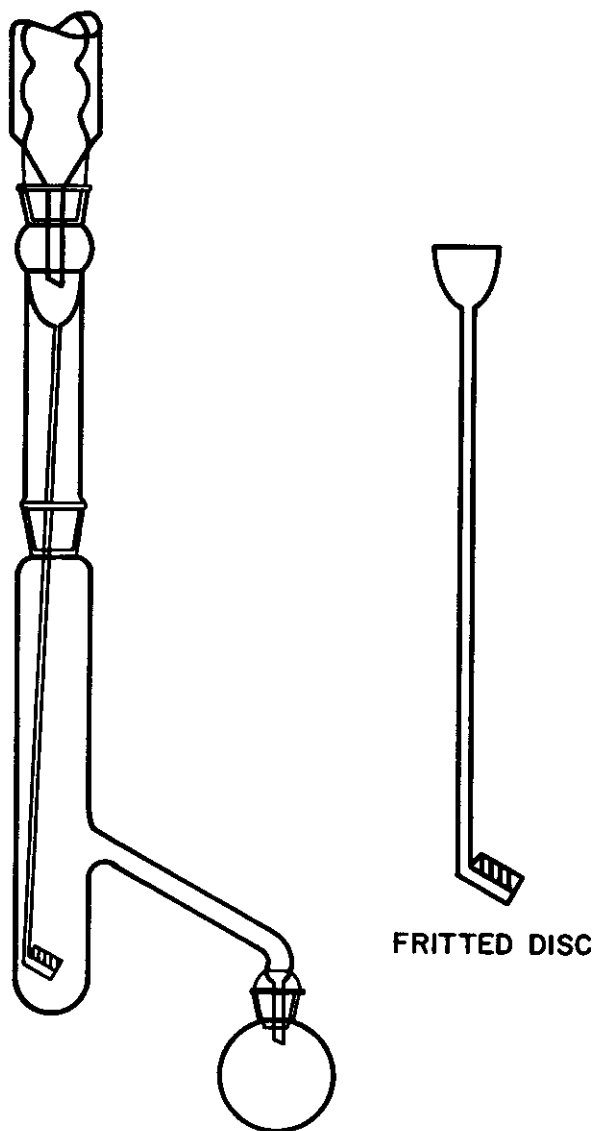
Morrison GH, Freiser H: Solvent Extraction in Analytic Chemistry. New York, John Wiley & Sons, 1957, p. 23.

Figure 18-1. Continuous Extractor for Use with a Solvent Lighter Than Water.

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**Figure 18-2. Continuous Extractor for Use with a Solvent Heavier Than Water**

The fraction $T_{n,r}$ of the solute present in the $r$th stage for $n$ transfers can be calculated from

$$T = \frac{n!}{r! \, (n\text{-}r)!} \frac{(DR_v)^r}{(1+DR_v)^n} \qquad (5)$$

A modification of CCD useful for laboratory purposes involves the use of a small number of separatory funnels (e.g., three) together with a larger number of transfers of upper phase portions (e.g., eight) and collecting the first upper phase portions as the product fraction. This means it would be possible to separate quantitatively a substance with a D of 10 from one whose D is 0.1.

**Experimental Techniques:**

(1) Introduction

Selection of a particular extraction method from the large number of methods available involves consideration of the behavior of interferences that might be present as well as that of the substance of interest. Another factor of importance is the means to be employed in the analytical determination of the species in question.

Some of the chelate systems, e.g., dithizone, are colored sufficiently to provide the basis of a spectrophotometric determination. If the extract is to be aspirated into the flame of an atomic absorption apparatus, however, a dithizone solution would not be as desirable as a non-benzenoid reagent because of its behavior in the flame.

The problem is simplified greatly by the existence of abundant literature which permits the selection of a method on the basis of s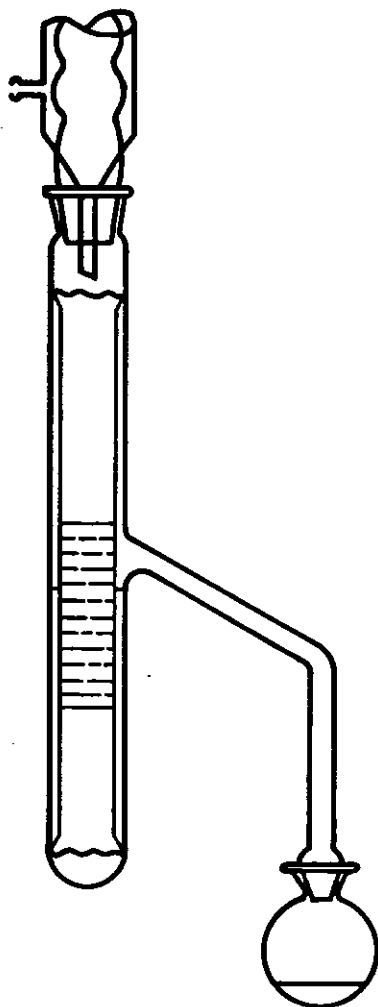imilarity or even matching of separation problems. Although even those experienced in extraction methods generally proceed in a new problem by following published precedents, a better understanding of the design of an extraction procedure can benefit from the careful study upon which previous work is based.

(2) Choice of Solvent

Solvents differ in polarity, density and ability to participate in complex formation. Generally it is more convenient to use a solvent denser than water when the element of interest is being extracted and a less dense solvent when interferences are extracted away from the element of interest.

Ion association complexes in which one of the ions is strongly solvated, such as the hydrated hydronium ion, $O(H_3O)_3^+$, as in the extraction of chloride complexes from HCl solutions (e.g., $H^+$, $FeCl_4^-$), can be extracted most effectively with oxygen-containing solvents such as alcohols, esters, ketones and ethers. Similarly, with coordinatively unsaturated chelates; i.e., in which the coordination number of the metal ion is greater than twice its oxidation state, such as $ZnOx_2$ (where Ox refers to the 8-hydroxyquinolinate anion), use of an oxygen-containing solvent will increase extractability significantly over that obtainable with hydrocarbon and chlorinated hydrocarbons.

On the other hand, ion association complexes involving quaternary ammonium, phosphonium or arsonium ions, and chelates that are saturated coordinatively may be readily extracted in hydrocarbons as well as in oxygenated solvents. In such cases, the principle of "like dissolves like," as expressed by the Hildebrand "solubility parameter," $\delta$, (defined as the heat of vaporization of one cc of a liquid) offers a guide to extractability. Simply expressed, in the absence of specific chemical interactions, a substance will be more extractable in a solvent whose $\delta$ value most closely matches its own. Thus, 8-hydroxyquinoline ($\delta = 10$) is more extractable into benzene ($\delta = 9.2$) than $CCl_4$ ($\delta = 8.6$) than heptane ($\delta = 7.4$). The absence of $\delta$ values for many extractable species hampers the full applicability of this principle.

It must not be assumed that the best solvent to use is always that which gives the highest extractability because a poorer solvent is often more selective.

(3) Stripping and Backwashing

Occasionally it is of advantage to remove the extracted solute from the organic phase as part of the analytical procedure. This process, called stripping, may be accomplished by shaking the organic phase with a fresh portion of aqueous

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solution containing acids or other reagents which will decompose the extractable complex.

Backwashing is the technique of contacting the organic extract with a fresh aqueous phase. The combined organic phase, containing almost all the desired element and some of the impurities (extracted to a smaller extent), is shaken with small portions of a fresh aqueous phase containing the same reagent concentrations in'tially present. Under these conditions, most of the desired element remains in the organic phase whereas the bulk of the impurities are back-extracted (backwashed) into the aqueous phase because of their lower distribution ratios.

### (4) Treatment of Emulsions

Rapid reappearance of a sharp phase boundary after shaking two immiscible liquids depends on the avoidance of emulsion formation. Tendency to form emulsions decreases with increasing interfacial tension. With liquids of relatively high mutual solubility or in the presence of surfactants, the interfacial tension is low and the tendency to form emulsions correspondingly high. Also of importance in avoiding emulsions is the use of solvents of low viscosity and whose densities are significantly different from water. With systems that tend to form emulsions, repeated inversion of the phases rather than vigorous shaking is helpful. In an extreme case, use of a continuous extractor rather than a separatory funnel is often successful. Tendency to emulsion formation can be reduced by addition of neutral salts or an anti-emulsion agent.

### Important Experimental Variables

#### (1) Chelate Experimental Variables

As seen from Table 18-1, many chelating extractants are weak acids and can be represented as HR. For a chelate extraction process

$$M^{n+} + nHR \text{ (org)} \overset{K_{ex}}{\rightleftharpoons} MR_n \text{ (org)} + nH^+$$
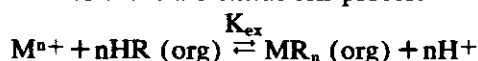
the extent of extraction is described by the expression

$$D_M = \frac{C_{M(o)}}{C_M} = \frac{K_f K_{DC} K_a^n}{K_{DR}^n} \frac{[HR]_o^n}{[H^+]^n} \alpha_M = K_{ex} \frac{[HR]_o^n}{[H^+]^n} \alpha_M \tag{6}$$

where $K_f$ is the formation constant of the metal chelate $MR_n$, $K_a$ the acid dissociation constant of the chelating agent HR, $K_{DR}$ and $K_{DC}$ the distribution constants of reagent and chelate, respectively. The combination of constants in equation (6) is called the overall extraction constant, $K_{ex}$. Representative values of $K_{ex}$ are listed in Table 18-2.

Equation (6) shows that the value of D increases with the concentration of the reagent in the organic phase and decreases with the hydrogen ion concentration in the aqueous phase. From this we see the importance of pH control in chelate extractions. Inasmuch as the extractions of different metal ions with a given reagent are characterized by different extraction constants, the extraction curves (%E vs pH) will be similar but displaced in pH. Figure 18-3 shows a typical set of extraction curves for various metal dithizonates. It will be noted that, while the curves of all of the

divalent metal ions are parallel, those for Ag(I) and Tl(I) are less steep, as a result of $n$ in equation (6) being 1. From the curve we can conclude that at pH 2, Hg (II) is 100% extracted; Ag, Cu, Bi are fractionally extracted, and the other ions listed not extracted at all. It would be simple to separate Hg(II) from Sn(II), Pb, Zn, Tl(I) and Cd in a mixture by extracting with dithizone at pH 2 but difficult to separate it from Ag, Cu and Bi. Since Bi is only 10% extracted at this pH, backwashing several times with fresh aqueous (pH 2) portions would quantitatively remove Bi (90% of remaining amount each time) from the extract without appreciably affecting the extracted Hg.

Table 18-2   Extraction Constants, $K_{ex}$, and $pH_{1/2}$ Values of Selected Metal Chelate Systems

| | Extractant | | | |
|---|---|---|---|---|
| | 8-Quinolinol 0.10M CHCl₃ | | Dithizone $10^{-4}M$ CCl₄ | |
| Metal Ion | log $K_{ex}$ | $pH_{1/2}$ | log $K_{ex}$ | $pH_{1/2}$ |
| Ag⁺ | — | 6.5 | 7.18 | −3.2 |
| Al³⁺ | −5.22 | 2.87 | Not extracted | |
| Ca²⁺ | −17.9 | 10.4 | Not extracted | |
| Cd²⁺ | — | 4.65 | 2.14 | 2.9 |
| Cu²⁺ | 1.77 | 1.51 | 10.53 | −1.3 |
| Fe³⁺ | 4.11 | 1.00 | Not extracted | |
| Pb²⁺ | −8.04 | 5.04 | 0.44 | 3.8 |
| Zn²⁺ | — | 3.30 | 2.3 | 2.8 |

One useful way to condense extraction information from curves such as in Figure 18-3 or from expressions such as equation (6) is to specify the $pH_{1/2}$ (called "pH one half") value for the metal ion obtained with a particular concentration of the reagent. The $pH_{1/2}$ is the value of the pH at which half the metal is extracted. Thus from Figure 18-3, the $pH_{1/2}$ values for the dithizonates are 0.3 for Hg, 1.0 for Ag, 1.9 for Cu, 2.5 for Bi, 4.7 for Sn, 7.4 for Pb, 8.5 for Zn, 9.7 for Tl and 11.6 for Cd. For a single batch extraction, a minimum of three units difference in $pH_{1/2}$ is required to permit the quantitative separation of two metal ions, although as mentioned above the technique of backwashing can reduce this requirement.

The factor $\alpha_M$ in equation (6) which represents the fraction of the total metal concentration in the aqueous phase that is in the form of the simple hydrated metal ion, points to the importance of masking agents in improving selectivity of extraction. Masking agents are auxiliary complexing agents which form charged water-soluble complexes whose effectiveness in inhibiting other reactions (e.g., extraction) of metal ions increase with the formation constants of the masking complex, the concentration of the masking agent, and, for the many masking agents which are bases, with the pH. A number of representative values are listed in Table 18-3.

As an illustration of masking let us consider a mixture of Ag⁺ and Cu²⁺ from which we wish to extract Ag⁺ selectively. As can be seen from Figure 18-3, Ag⁺ can be extracted quantitatively
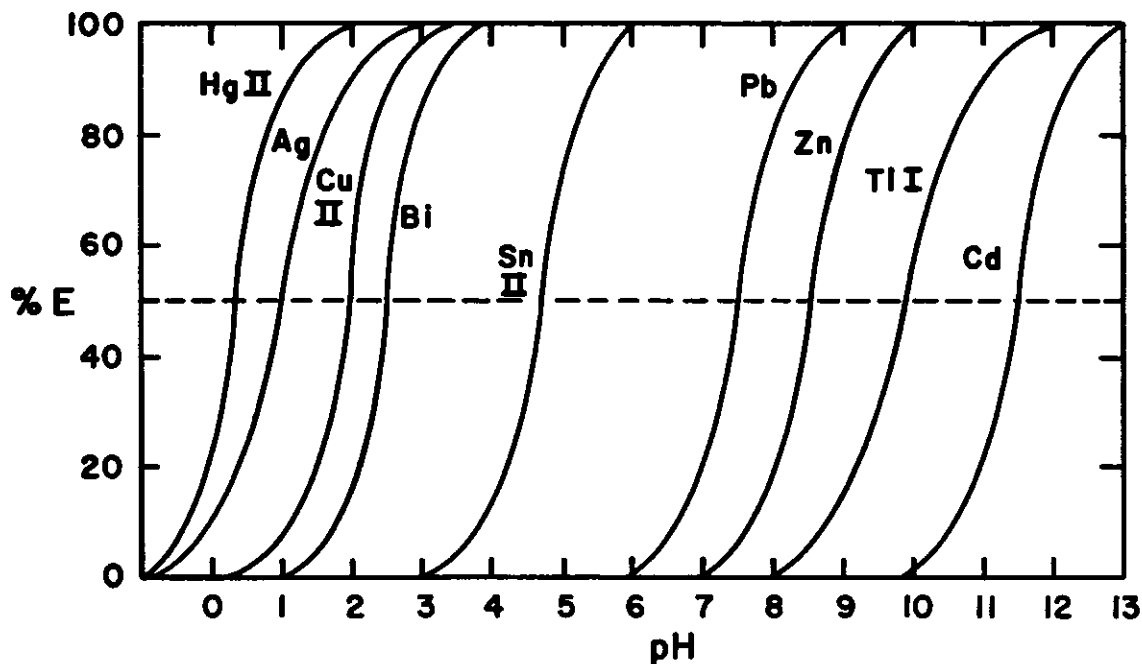
**Figure 18-3.   Qualitative Extration Curves for Metal Dithizonates**

at pH 3 but without any masking agent present, $Cu^{2+}$ is also appreciably extracted. In the presence of 0.1M EDTA, the value of log $\alpha_{cu}$ = $-6.6$ (estimated from Table 18-3) which would displace the extraction curve of copper dithizonate to the right increasing $pH_{1/2}$ by 3.3 units [according to equation 6)]. Since the value of log $\alpha_{Ag}$ under these conditions is about $-0.2$, EDTA has little effect on the extraction curve of Ag dithizonate. Hence, in the presence of 0.1M EDTA at pH 3, $Ag^+$ will be selectively extracted from $Cu^{2+}$. Similarly the use of cyanide as masking agent will permit the selective extraction of $Al^{3+}$, which does not form a $CN^-$ complex, by 8-hydroxyquinoline in the presence of such transition metal ions as Cu, Fe, as well as Ag which form strong cyanide complexes. Other examples of successful masking can be predicted with the help of Table 18-3. We will return to the use of masking in the discussion of ion exchange separations.

Kinetic factors may be important in all types of extraction, but since they are observed most frequently with chelate extraction systems, they will be discussed here. Generally, extraction equilibrium can be achieved in one or two minutes of normal shaking because mass transfer rates are reasonably rapid. Occasionally it is observed, particularly with some chelates, that the formation of an extractable complex or the dissociation of a masking complex is slow enough to affect the course of the extraction. For example, most substitution reactions of $Cr^{3+}$ are very slow, so that although $Cr^{3+}$ forms stable chelates it is rarely extracted in the usual chelate extraction proce-

dure. Less dramatic but of analytical utility is the significant difference in the speed of formation of other metal dithizonates which makes it possible to separate $Hg^{2+}$ from $Cu^{2+}$ and $Zn^{2+}$ from $Ni^{2+}$ by limiting the shaking periods to one minute.

(2)  Ion Association Extraction Systems

As with chelate systems, ion association extraction equilibria involve a number of contributing reactions. For example, for the extraction of $Fe^{3+}$ out of HCl solutions into ether:

$$Fe^{3+} + 4\ Cl^- \rightleftharpoons FeCl_4^-$$

$$H(H_2O)_4^+ + FeCl_4^- \rightleftharpoons H_9O_4^+,\ FeCl_4^-$$

$$H_9O_4^+,\ FeCl_4^- \rightleftharpoons H_9O_4^+,\ FeCl_4^-\ (ether)$$
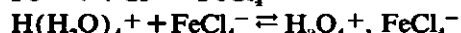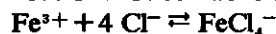
From these equations, the importance of chloride and acid can be seen. About $6M$ HCl is required for optimum iron extraction. Ether, as an oxygen containing solvent, is needed to stabilize the $H_9O_4^+$ ion. If $(C_4H_9)_4N^+$ is used, then the iron can be extracted out of a much less acidic solution (provided that the chloride concentration was about $6M$) and, more significantly it would be possible to use benzene, $CCl_4$ or $CHCl_3$ as well as oxygen-containing solvents for the extraction.

In many ion association extraction systems, high electrolyte concentrations are found effective in increasing the extent of extraction. The addition of such salts, referred to as salting-out agents, serves two purposes. The first, and more obvious, is to aid in the direct formation of the complex by the mass action effect. That is, the formation of a chloro or nitrato complex, for instance, is promoted by increasing the concentration of $Cl^-$

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Table 18-3  Values of Masking Factor
[-log $\alpha_M$ from Equation (6)]
For Representative Metal Ions and 0.1M
Masking Agents at Various pH Values

| | pH= | 2 | 5 | 8 | 10 |
|---|---|---|---|---|---|
| Ag | EDTA | 0 | 0.5 | 3.7 | 5.5 |
| | NH₃ | 0 | 0.1 | 4.6 | 7.2 |
| | CN | 4.7 | 10.7 | 16.7 | 19.0 |
| Al (no masking NH₃ or CN⁻) | | | | | |
| | EDTA | 1.8 | 8.2 | 14.5 | 18.3 |
| | OH⁻ | 0 | 0.4 | 9.3 | 17.3 |
| | F⁻ | 10.0 | 14.5 | 14.5 | 17.3 |
| Ca (no masking NH₃ or CN⁻) | | | | | |
| | EDTA | 0 | 3.2 | 7.1 | 8.9 |
| | Citrate | 0 | 1.8 | 2.5 | 2.5 |
| Cd | EDTA | 1.8 | 7.9 | 12.2 | 14.0 |
| | NH₃ | 0 | 0 | 2.3 | 6.7 |
| | CN | 0 | 0.7 | 10.1 | 14.5 |
| Cu (II) | | | | | |
| | EDTA | 4.6 | 10.7 | 15.0 | 16.8 |
| | NH₃ | 0 | 0 | 3.6 | 8.2 |
| Fe (III) | | | | | |
| | EDTA | 10.3 | 17.2 | 22.0 | 26.4 |
| | OH⁻ | 0 | 3.7 | 9.7 | 13.7 |
| | F⁻ | 5.7 | 8.9 | 9.8 | 13.7 |
| Pb (no masking NH₃ or CN⁻) | | | | | |
| | EDTA | 4.2 | 10.2 | 14.4 | 16.2 |
| | OH⁻ | 0 | 0 | 0.5 | 2.7 |
| | Citrate | 1.0 | 4.2 | 4.2 | 5.3 |
| Zn | EDTA | 2.8 | 8.8 | 12.9 | 14.7 |
| | NH₃ | 0 | 0 | 0.4 | 0.7 |
| | CN⁻ | 0 | 0 | 7.5 | 12.3 |

or $NO_3^-$. Second, as the salt concentration increases, the concentration of "free", i.e., uncomplexed, water decreases because the ions require a certain amount of water for hydration. Because $Li^+$ is more strongly hydrated than $K^+$, $LiNO_3$ is a much better salting-out agent than $KNO_3$ for nitrate extraction systems even though equimolar solutions supply the same nitrate concentration.

**Metal Extraction Systems**

In this section the application of a few representative extractants are described in periodic array. Elements extractable as diethyldithiocarbamates are shown in Figure 18-4. The number under each element represents the lowest pH at which it will be extracted. Because the reagent is non-aromatic, solutions of its chelates can burn with a smokeless flame so this reagent is widely used as a separation or preconcentration step preparatory to atomic absorption spectrometry.

The application of dithizone is shown in Figure 18-5. Because of the highly conjugated reagent, the chelates are all highly colored in the visible range, which provides the basis of sensitive spectrophotometric determinations.

Extractions with 8-quinolinol (8-hydroxyquinoline, oxine) are described in Figure 18-6. These chelates also are used in spectrophotometric and fluorimetric determinations.

The extraction of metal ions from hydrochloric acid into ethyl ether is shown in Figure 18-7.

**Outline of Illustrative Extraction Procedures**

In this section several extraction procedures will be outlined as a means of illustrating the application of principles discussed above. Naturally for a working method, more detailed procedures in the references should be consulted. Precautions

Sodium Diethyldithiocarbanate



$(C_2H_5)_2N-C\overset{\displaystyle S}{\underset{\displaystyle S^-}{\diagup}}$ , Na⁺

| H | | | | | | | | | | | | | | | | | He |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | A |
| K | Ca | Sc | Ti | V 3 | Cr 0 | Mn 6.5 | Fe 0 | Co 6 | Ni 6 | Cu 1 | Zn 3 | Ga 3 | Ge | As | Se 3 | Br | Kr |
| Rb | Sr | Y | Zr | Nb ~5 | Mo 3 | Tc | Ru | Rh | Pd | Ag 3 | Cd 3 | In 3 | Sn 5 | Sb | Te -0.7 | I | Xe |
| Cs | Ba | La | Hf | Ta | W 1 | Re -1 | Os | Ir | Pt | Au | Hg 3 | Tl 3 | Pb -0.2 | Bi 1 | Po | At | Rn |
| Fa | Ra | Ac | | | | | | | | | | | | | | | |

| | | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Th | Pa | U 6.5 | Np | Pu 3 | Am | Cm | Bk | Cf | E | Fm | Mv | 102 | 103 |

Morrison GH, Freiser H: Solvent extractions in radiochemical separations. Ann. Rev. of Nuclear Sci., vol. 9, 1959.

**Figure 18-4. Elements Extractable with Sodium Diethyithiocarbamate. The number under an element symbol indicates the pH value at which the element can be completely extracted.**

## Dithizone

H and structure (dithizone):

$$\text{N(H)}-N,\ C-SH,\ N=N$$

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|----|----|----|----|----|----|----|----|----|
| H | | | | | | | | | | | | | | | | | He |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | A |
| K | Ca | Sc | Ti | V | Cr | Mn ~11 | Fe 6 | Co 7 | Ni 8 | Cu 1 | Zn 8 | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd <0 | Ag <0 | Cd 13 | In 8 | Sn 6 | Sb | Te | I | Xe |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | P 2 | Au <0 | Hg <0 | Tl 3 | Pb 8.5 | Bi >2 | Po <0 | At | Rn |
| Fa | Ra | Ac | | | | | | | | | | | | | | | |

| Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | E | Fm | Mv | 102 | 103 |

Morrison GH, Freiser H: Solvent extractions in radiochemical separations. Ann. Rev. of Nuclear Sci., vol. 9, 1959.

**Figure 18-5. Elements Extractable by Dithizone. See Figure 18-4 for explanation of numbers.**

peculiar to trace element determinations must be observed carefully.

**(1) Extraction of Cd with Dithizone**

It is possible to separate Cd from Pb or Zn by using a highly alkaline solution during extraction and from Ag, Hg, Ni, Co and Cu by stripping the Cd at a pH of 2 where these other dithizonates are stable.

A solution containing up to 50 $\mu$g Cd is treated with tartrate (to avoid hydroxide precipitation) and made basic with an excess of 25% KOH. This is now shaken with successive 5 ml portions of

## 8-Quinolinol

Structure: quinoline ring with OH

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|----|----|----|----|----|----|----|----|----|
| H | | | | | | | | | | | | | | | | | He |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg 10 | | | | | | | | | | | Al 5 | Si | P | S | Cl | A |
| K | Ca 13 | Sc 6.5 | Ti 4 | V 3 | Cr | Mn 7 | Fe 2 | Co 7 | Ni 4.5 | Cu 3 | Zn 4 | Ga 3 | Ge | As | Se | Br | Kr |
| Rb | Sr 11 | Y | Zr 5 | Nb 6 | Mo 1.5 | Tc | Ru 9 | Rh | Pd 1 | Ag | Cd 5 | In 3 | Sn 2.5 | Sb | Te | I | Xe |
| Cs | Ba | La | Hf 5 | Ta | W 2.5 | Re | Os | Ir | Pt | Au | Hg | Tl | Pb 85 | Bi 4 | Po | At | Rn |
| Fa | Ra | Ac | | | | | | | | | | | | | | | |

| Ce 10 | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
|-------|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Th 5 | Pa 10 | U 5 | Np | Pu 4 | Am | Cm | Bk | Cf | E | Fm | Mv | 102 | 103 |

Morrison GH, Freiser H: Solvent extractions in radiochemical separations. Ann. Rev. of Nuclear Sci., vol. 9, 1959.

**Figure 18-6. Elements Extractable by 8-quinolinol**

H                                                                                                    He

| Li | Be |    |    |    |    |    |    |    |    |    |    | B  | C  | N  | O  | F  | Ne |
| Na | Mg |    |    |    |    |    |    |    |    |    |    | Al | Si | P  | S  | Cl | A  |
| K  | Ca | Sc | Ti | V  | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | Y  | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I  | Xe |
| Cs | Ba | La | Hf | Ta | W  | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| Fa | Ra | Ac |

| Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu  |
| Th | Pa | U  | Np | Pu | Am | Cm | Bk | Cf | E  | Fm | Mv | 102 | 103 |

Morrison GH, Freiser H: Solvent extractions in radiochemical separations. Ann. Rev. of Nuclear Sci., vol. 9, 1959.

**Figure 18-7. Elements Extracted in Chloride System: Solid Blocks—Appreciably Extracted, Broken Blocks—Partially Extracted**

dithizone in $CHCl_3$ until the aqueous layer remains yellowish brown (to indicate excess dithizone). The combined extracts are shaken for two minutes with an aqueous solution buffered at pH 2 which will strip the Cd quantitatively. To remove small amounts of Cu and Hg that may accompany the Cd, reextract with a fresh portion of dithizone at pH 2. The Cd will remain in the aqueous phase.

(2) Extraction of Pb with Dithizone

A slightly acid solution containing up to 100 µg Pb is treated with aqueous $NH_3$ and KCN prior to extraction with dithizone in $CHCl_3$. Under these conditions no metal other than Bi, Tl or $Sn^{+2}$ will interfere.

(3) Cu with Sodium Diethyldithiocarbamate

Adjust the pH of a solution containing up to 50 µg Cu to 4.5 — 5.0 with acetate buffer, add sodium EDTA, followed by Na diethyldithiocarbamate and shake mixture for one minute. Add butyl acetate and shake again for one minute. Backwash the extract with dilute $H_2SO_4$. There is essentially no interference.

(4) Fe with 4,7-Diphenylphenanthroline (Bathophenanthroline)

Add $NH_2OH \cdot HCl$ to a solution containing up to 10 µg Fe to produce Fe(11), adjust the pH to 4 with sodium acetate, add bathophenanthroline dissolved in ethanol. Add n-hexanol and shake to extract. The iron complex absorbs strongly at 533 nm.

(5) Germanium with Hydrochloric Acid

To the sample, which may be dissolved in $H_3PO_4$ and $HNO_3$, add concentrated HCl. The $GeCl_4$ that forms may then be extracted with portions of $CCl_4$. To return Ge to an aqueous phase prior to determination, a solution of ammonium oxalate-oxalic acid may be used for stripping.

**Suggestions for Further Reading**

In addition to reference (1) which is a general text covering the principles of solvent extraction and its applications to separation and analysis, the Biennial Reviews (2) published in even-numbered years from 1958 to the present include comprehensive surveys of newly published extraction reviews; the references listed in (2) are very helpful.

(1) G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry." John Wiley & Sons, New York (1957).

(2) See Anal. Chem. *30*, 632 (1958); ibid *32*, 37 (1960); ibid *34*, 64R (1962); ibid *36*, 93R (1964); ibid *38*, 131R (1966); ibid *40*, 522R (1968).

## ION EXCHANGE

### General Principles and Terminology

Ion exchange is a process in which ions of the same sign are exchanged between a (usually aqueous) solution and an immobilized phase, not necessarily a crystalline solid, which consists of macromolecular species having many ionizable functional groups, called exchange sites. The earliest ion exchange materials used, clays and zeolites, are indeed solid, but currently most widely used ion exchangers are synthetic resins that are high molecular weight polymers having a high concentration of ionizable functional groups, (3-6 meq/g dry resin). Both cationic and anionic exchange resins are available in granular bead form in a variety of mesh sizes.

A cation exchange resin contains either strong (sulfonic) or weak (carboxylic) acid groups as the fundamental exchange site, with the former being more commonly used. The cation exchange reaction can be written

$$H^+, R^- + 1/nM^{n+} \rightleftharpoons 1/nM^{n+}, R^- + H^+$$

where $H^+$, $R^-$ signifies the resin in the acid or H form and $M^{n+}$, $nR^-$ the resin in the $M^{n+}$ form. The equilibrium constant of the exchange reaction, $K_{IX}$, called the exchange constant, is

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$$K_{IX} = K_H^{M^{1/n}} \frac{[M^{n+}]_R^{1/n}[H^+]}{[M^{n+}]^{1/n}[H^+]_R} \quad (7)$$

where brackets signify concentrations in the aqueous and resin (subscript R) phases. It is convenient to use milliequivalents per gram of resin to describe resin concentrations and milliequivalents per milliliter (Normality) for solution concentrations. It should be noted that $K_{IX}$ is expressed in terms of concentrations rather than the more rigorously correct activities. This is not only more practical but, because the resin phase is equivalent to an extremely concentrated electrolyte solution (e.g., about 5-6 molar in NaCl) activity, coefficients are difficult to evaluate accurately. Representative values of $K_{IX}$ for cation exchange are listed in Table 18-4.

Similarly, the equilibrium of an anion exchange process

$$R^+, Cl^- + \frac{1}{n}X^{-n} \rightleftharpoons R^+, \frac{1}{n}X^{-n} + Cl^-$$
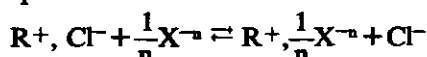
can be expressed by

$$K_{IX} = K_{Cl}^{X^{1/n}} = \frac{[X^{-n}]_R^{1/n}[Cl^-]}{[X^{-n}]^{1/n}[Cl^-]_R} \quad (8)$$

The extent of cation exchange may be expressed by a distribution ratio, $D_M$, which like equation (2) for extraction, is the ratio of total metal concentration in the resin phase, $C_{M(R)}$, (meq/g), to the total metal concentration in the aqueous phase, $C_M$ (normality)

$$D_M = \frac{C_{M(R)}}{C_M} \quad (9)$$

Usually the metal ion in the resin phase is uncomplexed and can be represented as $[M^{n+}]_R$ but in the aqueous phase the frequent use of complexing agents suggests the use of the same masking factor that is incorporated in equation (6). Hence, equation (8) becomes

$$D_M = \frac{[M^{n+}]_R}{[M^{n+}]}\alpha_M \quad (10)$$

A major difference between masking in ion exchange and solvent extraction is the requirement that the masking complex for the metal cation be anionic, because cationic metal complexes (e.g., $M(NH_3)_6^{2+}$ or $M(phenanthroline)_3^{2+}$) are also strongly absorbed on the resin.

If the resin is initially in the $H^+$ form the distribution ratio may be related to the exchange constant by the following equation [note analogy to (6)]

$$D_M = \frac{[M^+]_R}{[M^{n+}]} \cdot \alpha_M = \left[K_H^{M^{1/n}}\frac{[H^+]_R}{[H^+]}\right]^n \cdot \alpha_M \quad (11)$$

When the exchanged ion is present in small quantities, the resin loading, i.e. the $[H^+]_R$, remains substantially constant so that $D^M$ is inversely proportional to $[H^+]^n$ which signifies the importance of dilution on the extent of exchange, particularly as the charge (n) of the metal ion increases.

Another important means of describing the extent of exchange is F, *the fraction exchanged*, which is given by (note resemblance to equation (3))

$$F = \frac{C_{M(R)} \cdot W}{C_{M(R)} \cdot W + C_M \cdot V} = \frac{D_M(W/V)}{D_M(W/V) + 1} \quad (12)$$

where W is the weight of the resin in grams and V, the volume of the aqueous phase in milliliters. The fraction of metal remaining in solution is 1-F or $[D_M(W/V) + 1]^{-1}$.

## Properties of Ion Exchange Materials

Typical commercial cation exchange resins of the strong acid type are Dowex 50 and Amberlite IR-120, while Amberlite IRC 50 is weakly acidic. The strong acid types can function throughout the pH range but Amberlite IRC 50 must be used at a pH of 7 or higher.

Commercial anion exchange resins of the strong base type include Dowex 1, Dowex 2, Amberlite IRA-400 which can be used throughout the pH range but the weakly basic resins such as Dowex 3 or Amberlite IR-4B must be used at pH 7 or below.

The exchange capacities for the strong acid and base resins is of the order of 3-5 meq/g dry resin whereas that of the weak acid and base resins is about 10 meq/g.

These ion exchange resins are available with different degrees of crosslinking which affects both the hardness of the resin beads and their selectivity. Typically the resin is about 8% crosslinked with divinylbenzene (denoted in the listing of the resin as Dowex 50-X8), but at higher crosslinking a significant drop of exchange of larger ions imparts a greater ion size selectivity to the resin. This can be seen from Table 18-4 by the insensi-

Table 18-4  Concentration Exchange Constants, $K_H^{M^{1/n}}$, For Some Metal Ions on Dowex 50 Resins of Different Extents of Crosslinking (Measured in Terms of Percent Divinylbenzene (DVB)).

|         | 4% DVB | 8% DVB | 16% DVB |
|---------|--------|--------|---------|
| $Li^+$   | 0.76   | 0.79   | 0.68    |
| $Na^+$   | 1.20   | 1.56   | 1.61    |
| $NH_4^+$ | 1.44   | 2.01   | 2.27    |
| $K^+$    | 1.72   | 2.28   | 3.06    |
| $Ag^+$   | 3.58   | 6.70   | 15.6    |
| $Mg^{2+}$ | 0.99   | 1.15   | 1.10    |
| $Zn^{2+}$ | 1.05   | 1.21   | 1.18    |
| $Co^{2+}$ | 1.08   | 1.31   | 1.19    |
| $Cu^{2+}$ | 1.10   | 1.35   | 1.40    |
| $Cd^{2+}$ | 1.13   | 1.36   | 1.55    |
| $Pb^{2+}$ | 2.20   | 3.46   | 5.65    |
| $Ni^{2+}$ | 1.16   | 1.37   | 1.27    |
| $Ca^{2+}$ | 1.39   | 1.80   | 2.28    |
| $Sr^{2+}$ | 1.57   | 2.27   | 3.16    |
| $Ba^{2+}$ | 2.50   | 4.02   | 6.52    |
| $Cr^{3+}$ | 1.6    | 2.0    | 2.5     |
| $Ce^{3+}$ | 1.9    | 2.8    | 4.1     |
| $La^{3+}$ | 1.9    | 2.8    | 4.1     |

From O.D. Bonner et al., J. Phys. Chem., 61, 326 (1957) and 62, 250 (1968).

**Table 18-5**  Concentration Exchange Constants, $K_{Cl}^{X^{1/n}}$ For Some Anions on Dowex 1 and Dowex 2.

| Ion | Dowex 1 | Dowex 2 |
|-----|---------|---------|
| $OH^-$ | 0.09 | 0.65 |
| $F^-$ | 0.09 | 0.13 |
| $Br^-$ | 2.8 | 2.3 |
| $I^-$ | 8.7 | 7.3 |
| $CN^-$ | 1.6 | 1.3 |
| $NO_3^-$ | 3.8 | 3.3 |
| $CNS^-$ | — | 18.5 |
| $ClO_4^-$ | — | 32 |
| $H_2PO_4^-$ | 0.25 | 0.34 |
| $HCO_3^-$ | 0.32 | 0.53 |
| $HSO_3^-$ | 1.3 | 1.3 |
| $HSO_4^-$ | 4.1 | 6.1 |
| $SO_4^-$ | 2.55 | 0.55 |
| $HCOO^-$ | 0.22 | 0.22 |
| $CH_3COO^-$ | 0.17 | 0.18 |

From O.D. Bonner et al., J. Phys. Chem., 61, 326 (1957) and 62, 250 (1968).

tivity of a small ion such as $Li^+$ to degree of crosslinking, whereas for a large ion such as $K^+$ or $Ag^+$, the $K_{H^+}^M$ changes significantly. The effect is not as dramatic with the more highly charged ions but may still be observed with $Ba^{2+}$ and $Pb^{2+}$.

### General Experimental Techniques

Two means of employing ion exchange resins are the batch technique, in which a portion of the resin is added to the solution to selectively remove an ion of interest, and column techniques which may involve either "column filtration" or chromatography. Both column techniques can serve to separate ions too similar to permit use of the batch technique; chromatography is both more powerful and more inconvenient than column filtration. The following typical values of the extent of removal by a batch ion exchange using a Dowex 50 x 8 resin are illustrative. (These values could be derived from equations (11) and (12)).

(1) For 1 g of resin in the H form equilibrated with 100 ml 0.1 $M$ HCl which is 0.02$M$ in Ca, Sr, or Ba to be 97%, 98%, and 99.3% removal, respectively. If only trace levels of the metal ions were present, the percent removal would be 98.8%, 99.3%, 99.8% of these metal ions. Hence, when resin loading is kept low the exchange is more efficient.

(2) The effect of ionic charge may be seen from the value of $NH_4$ remaining in solution = 4% when a gram of resin is equilibrated with 40 ml of 0.01$M$ $NH_4Cl$. The corresponding Mg is 0.01% if 40 ml of 0.005$M$ Mg $Cl_2$ is used.

(3) The effect of the concentration of the counter ion may be seen from a comparison of the 0.01% Mg remaining in solution mentioned in (b) where the aqueous phase would then be 0.01$M$ in HCl and the value of 4% Mg remaining if the aqueous phase were 0.1$M$ in HCl at equilibrium.

With the help of values in Tables 18-4 and 18-5 and equations (11) and (12), one can calculate the feasibility of separating various pairs of ions. For example, from equation (12) for removal of 99% of a metal ion $M_1$, (assuming a V/W value of 25:1) a value of $D_{M_1}$, of at least 2500 is needed. Under similar experimental conditions a $D_{M_2}$ of 0.25 or less for a second metal ion, of which 99% or more will remain in the aqueous solution.

For metal ions of the same charge, it is evident from the similarity of values of $K_{1x}$ as well as the form of equation (11) that, unless great variation in $\alpha_M$ for the pair of ions can be achieved, quantitative separation of the ions using a simple batch process is hopeless. A number of interesting and useful batch separations can be carried out, however, by adjusting conditions to obtain sufficiently different values of the masking factor, $\alpha_M$, of the pair of metal ions.

For example, a mixture of $Ca^{2+}$ and $Cu^{2+}$ at concentrations of $10^{-3}M$ or lower can be separated using Dowex 50-X8 in the Na- form by adding 0.1$M$ EDTA and adjusting the pH suitably. In the absence of EDTA the distribution values are $D^{Ca} = 40,000$ and $D^{Cu} = 25,000$, so that both metal ions would be quantitatively removed from solution. From Table 18-3 we can estimate that at pH 3, $\alpha_{ca}$ is between 1 and 0.1 but $\alpha_{cu}$ is $10^{-6.6}$. Hence under these conditions $Ca^{2+}$ ($D_{Ca} > 4000$) will be quantitatively taken up by the resin while $Cu^{2+}$ ($D_{Cu} \sim 0.008$) will remain entirely in solution (as Cu-EDTA complex).

When differences in $D_M$ values for a pair of ions cannot be made large enough to permit use of a batch technique, an ion exchange column must be used. Although column chromatographic methods represent the ultimate separation efficiency these are rather complicated, requiring either close attention or automatic fraction collectors. The technique of column filtration, however, offers both speed and simplicity while providing significantly greater separating efficiency than the batch process.

In preparation of an ion exchange column for analytical use several precautions should be observed. The resin, usually about 8% crosslinked and about 50-100 mesh, is slurried in water in a beaker. After allowing the mixture to stand for a few minutes to settle the large particles, the turbid supernatant liquid is poured off. This process is repeated a few times in order to remove the fine particles which would otherwise clog the column. The resin is slurried again with water and poured into a tube which is provided with a plug of glass wool or sintered glass disk (coarse porosity) on which the ion exchange bed will rest. Because air bubbles in the column interfere with the flow of liquids through the tube and can lower column efficiency drastically, the miniscus of the liquid must never be allowed to fall below the top of the column. This, as well as the desired flowrate, is controlled by a stopcock or pinchclamp at the bottom of the tube.

All columns should be conditioned prior to general use to remove impurities. For both strong cation and anion exchange resins, conditioning is

carried out by passing through the column, in succession, about 3-4 bed volumes each of $1M$ NaOH, $1M$ HCl, water, 95% ethanol and water for two to three cycles. The conditioning ends with either NaOH or HCl depending whether the cation exchange resin is to be used in either the Na- or H-form (for the anion exchange resin this is either the -OH or Cl-form), and then rinsed with water until a qualitative test (with a suitable indicator) verifies completeness of rinsing.

Regeneration of the column after some use is necessary in order to avoid leakage of exchanged ions into the effluent. This can be carried out by passing either HCl (from 1-3$M$) for cation exchange resins or NaOH (1-3$M$) until tests of the effluent reveals the completeness of ion removal. If a particularly strongly held metal ion is on the cation exchange column, a complexing agent like ammonium citrate or EDTA can be used effectively in the regenerative solution.

It is useful to keep in mind that the theory of ion exchange column chromatography behavior is almost identical with that of other chromatographic systems. The concentration profile of a particular ion moving down the column under the influence of a solvent (eluent) resembles a Gaussian (bell shaped) curve. When enough eluent has been added, the ionic component will emerge. The elution volume corresponding to the peak (maximum concentration) of the curve is described by the relation

$$V_{max} = D_M \cdot W \quad (13)$$

where $D_M$ is the distribution ratio of the ion under the conditions of the elution and W is the weight of the resin in the column. The peak concentration, $C_{max}$, is given by the equation

$$C_{max} = \frac{(meq) \times}{V_{max}} \left( \frac{N}{2\pi} \right)^{1/2} \quad (14)$$

where (meq) is the number of meq of the ion on the column and N is the number of theoretical plates. Since $V_{max}$ and N are both linearly related to W and hence to column length at constant column width, the value of $C_{max}$ is inversely proportional to the square root of column length. The width in milliliters of an elution band (i.e., the concentration-volume profile of an eluted ion) is proportional to the square root of the column length. Hence, the relative width of a particular elution band decreases with the square root of column length.

Column filtration is a process involving separation of two ions on an ion exchange column by passing a given (reasonable) volume of an eluent through the column to quantitatively remove one of the ions but essentially none of the other.

Two ions can be successfully separated by column filtration provided that the D value for the ion retained on the column is at least 100 (compared to at least 2500 for batch) while the D for the ion washing through the column may be three or smaller (0.25 for batch). Even such large differences in D are unusual for metal ions of the same charge unless $\alpha_M$ values can be modified by suitable masking agents. If the ratio of $D_{M_1}/D_{M_2}$ is below 30, column filtration may not

be used and a full-fledged chromatographic procedure must be used.

## Outline of Illustrative Ion Exchange Procedures

As in the corresponding section on extraction, several ion exchange procedures will be outlined to illustrate the principles and indicate the range of applications.

(a) Non-Chromatographic Applications

The determination of phosphate is simplified and improved by the removal of cations. Passing an acidified solution of the sample through a cation exchanger (H- form) removes all interfering cations. Analogously, phosphate interferes with the determination of a number of cations. For example, the atomic absorption determination of $Ca^{2+}$ is preferably carried out after removing phosphate by passing the sample through an anion exchanger (Cl- form).

Fluoride can be separated from all interfering cations prior to determination with the $F^-$ selective electrode.

Sodium or potassium can be determined in the presence of transition metal ions such as $Ni^{2-}$, $Cu^{2+}$, $Co^{2+}$, $Fe^{3+}$, $V^{4+}$ by passing the mixture through a column of Dowex 2 in the citrate form which will remove interfering metals as anionic citrate complexes. Utilization of column filtration with an anion exchanger in the CyDTA form, permits the separation of Ca and Mg from $Al^{3+}$, $Cu^{2+}$, $Fe^{3+}$, $Mn^{2+}$, and $Zn^{2+}$.

A series of several concentrations of HCl can be used to wash the metal ions of the NH$y$OH group successively through an anion exchange column in the chloride form. With 9M HCl, $Ni^{2+}$ will come through, with 4M HCl, $Co^{2+}$; with $1M$ HCl, $Fe^{3+}$, and finally using water, $Zn^{2+}$ will wash through. This order is a consequence of the increasing stability (Ni→Zn) of the chloroanionic complexes of these ions.

(b) Chromatographic Applications

As differences in D value decrease, separations naturally become more difficult. This implies longer columns, slower flowrates, more carefully controlled conditions and almost continuous monitoring of the column effluent or automated fraction collectors. One of the most promising new developments in liquid chromatography of all types (adsorption, partition, etc., as well as ion exchange) is that involving exceptionally long and narrow columns through which the eluent is forced under very high pressure. This renders practical the use of columns of very great separating efficiency (large number of theoretical plates) in procedures which give sharply defined bands without excessively long run times. High pressure liquid chromatography should make it possible to extend the present scope of application of ion exchange (as well as other types) chromatography to almost any organic or inorganic electrolyte mixture.

## Suggestions for Further Reading

Samuelson (1) is the classic text on ion exchange and its application to analytical chemistry. Ringbom (3) is responsible for the excellent treatment of the role of complexation in improving ion exchange separations.

A wealth of references to current develop-

ments is to be found in the biennial ion exchange review in Analytical Chemistry (4).

(1) O. Samuelson, "Ion Exchange Separations in Analytical Chemistry," Second Ed., John Wiley & Sons, New York (1963).

(2) W. Rieman and H. Walton, "Ion Exchange in Analytical Chemistry," Pergamon Press, Oxford (1970).

(3) A. Ringbom, "Complexation in Analytical Chemistry," John Wiley & Sons, New York (1963).

(4) H. Walton, Analytical Chemistry, *42*, 86R (1970).

## Other Separation Processes

Although it is impossible in this brief chapter to do more than simply mention other methods of separation, it might be of some value to point these out as having useful application and high potential in problems of environmental analysis.

*Liquid-liquid partition chromatography* which is based on the selective distribution of solutes between two liquids: an immobilized liquid spread thin on a largely inert solid support in contact with a mobile eluent liquid with which the immobilized liquid may or may not be miscible. This process which can be carried out on either a column or paper and can best be understood as a modified multistage countercurrent solvent extraction process. Many of the recently published methods for separating inorganic ions, particularly those of so-called *reverse phase partition* (the immobilized phase is organic — the eluent is aqueous) are direct adaptations of extraction systems.

*Thin layer chromatography* analogous to paper but makes use of noncellulosic materials, e.g., silica, alumina, which are capable of being heated (for activation of substrate or development reactions) to much higher temperatures. TLC is more often the two dimensional analog of columnar adsorption chromatography (but not exclusively so) in which the immobilized phase is a solid of high surface area.

*Exclusion chromatography* is a separation process based on the relative size of adsorbate molecules and adsorbent pores or channels. Molecular sieve materials such as the inorganic zeolites and the organic gels are used successfully as column packing materials for chromatographic fractionation of both relatively small and large molecular weight mixtures. Zeolites are open silicate networks with highly uniform pore sizes that can be available in diameters from 4.2Å to about 9.0Å. For example, molecular sieve 4Å will adsorb molecules whose diameter is under 4Å ($H_2O$, $CO_2$, $H_2S$, $SO_2$, and hydrocarbons containing one or two carbon atoms) but will exclude all others. Type 5A sieve will adsorb straight chain hydrocarbons and derivatives up to about fourteen carbon atoms but will exclude all branched chain and cyclic compounds. Because of their silicate character, zeolite sieves will exhibit a strong preference for polar over non-polar molecules of equal size. Zeolite sieves are frequently used in gas-solid chromatography.

*Gel permeation chromatography* which may utilize either hydrophilic gels like Bio-Gel (a polyacrylamide) or Sephadex (a cross-linked dextron) or hydrophobic gels such as Styragel (a sponge-like cross-linked polystyrene), are generally used as a column packing in liquid chromatography. This technique is particularly useful for size separation of high molecular weight mixtures such as protein and polymeric fractions, although a mixture of mono-, di- and tri-saccharide can be easily separated (Sephadex).

A number of separation processes are based on the differential migration of charged species in solution when subjected to an electric field gradient. Of particular interest is electrophoresis carried out on a supporting medium of filter paper, cellulose acetate, or gel layer which is soaked in a buffered electrolyte and subjected to a d.c. voltage with electrodes placed at each end of the paper (or gel). A sample of the material to be separated breaks up into zones because of the differential migration rate influenced by the charge, size and shape of the species. Greater variation in behavior of inorganic ions and, hence, improvement in separation can be brought about by variation of pH, oxidation state, and the ability to form complexes.

Interposing a thin perm-selective membrane between two solutions forms the basis of *dialysis* and, with the addition of an electric field gradient, *electrodialysis* which have been used for separations used more for recovery and purification than analysis per se. Nevertheless, as a means of removing interferences, such methods can be of value.

Fractional distillation is a separation process for liquid mixtures based on differences in volatility. By the addition of a non-volatile component that can interact with the volatile components in a differential manner, (called extractive distillation) such volatility differences can be increased.

*Zone refining* involves countercurrent fractional recrystallization by moving a narrow band heater slowly along a column of the solid material. The small melted zone contains most of the impurities so that the cooled recrystallized material becomes significantly purer, while the impurities concentrate at one end of the column. The process can be repeated several times. This technique could be useful in concentrating trace level impurities.

*Thermal diffusion,* which does not involve phase separation, can be used to separate gas or liquid mixtures by virtue of the concentration gradient produced in a homogenous fluid mixture to which a temperature gradient is applied. Thermal diffusion is a sufficiently powerful technique to permit separation of the gaseous isotopes of helium, of chlorine, and of $C^{13}H_4$ from $C^{12}H_4$ as well as the components of liquid hydrocarbon mixtures.

## Preferred Reading

1. CASSIDY, H. G., Fundamentals of Chromatography, Vol. 10 of *Techniques of Organic Chemistry*, A. Weissberger, edit.

2. BLACK, R. J., E. L. DURRUM and G. ZWEIG, *Manual of Paper Chromatography and Paper Electrophoresis*, Academic Press, New York (1958).

3. KIRCHNER, J. G., *Thin Layer Chromatography*, Interscience Publ., New York (1967).

4. T. L. THOMAS and R. L. MAYS, Separations with Molecular Sieves, in Vol. IV, *Physical Methods in Chemical Analysis*, W. Berl, edit., Academic Press, New York (1961).

5. DETERMANN, H., *Gel Chromatography*, Springer Verlag, New York (1968).

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7. MICHL, H., Techniques of Electrophoresis in *Chromatography*, E. Heftmann, edit., Reinhold, New York (1967).

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9. PFANN, W. G., *Zone Refining*, John Wiley & Sons, New York (1958).

10. DICKEL, G., Separation of Gases and Liquids by Thermal Diffusion in Vol. IV *Physical Methods in Chemical Analysis*, G. Berl, edit., Academic Press, New York (1961).