Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article King, C. Judson(1974) 'Selection and Sequencing of Separations', Separation Science and Technology, 9: 6, 493 — 503
To link to this Article: DOI: 10.1080/00372367408055595
URL: http://dx.doi.org/10.1080/00372367408055595

SEPARATION SCIENCE, 9(6), pp. 493–503, 1974

Selection and Sequencing of Separations

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Abstract

Selection criteria are reviewed for choosing the most promising methods of separation for accomplishing a given separation of chemical components. The degree of separation attainable is governed by the separation factor, which in turn is related to molecular or ionic properties. Various separation processes are contrasted with regard to general desirablilty of using them, both on an industrial scale and on a laboratory scale. Heuristic rules for synthesizing sequences of separations to create multiple products are also considered. Criteria which have proven useful for generating separation sequences on an industrial processing scale are contrasted with those which may be useful for choosing sequences of separation steps in the laboratory.

INTRODUCTION

The problems of selecting a method of separation to accomplish a given goal and of selecting the optimal ordering of separations are both common to industrial chemical processing and to laboratory chemical analyses. The purpose of this short review is to consider methods which are useful for picking separation methods and sequences, and to contrast criteria suitable for industrial processing with those applying to the laboratory scale.

Common Features of Separation Processes

Common features of separation processes have been discussed by the author (*1*) as well as by others. Any separation must be based upon a *separation factor*, akin to the relative volatility for a distillation, which denotes the extent to which the products from the separation differ in composition. The separation factor α_{ij} is defined by

$$\alpha_{ij} = \frac{x_{i1}x_{j2}}{x_{i2}x_{j1}} \tag{1}$$

where subscripts i and j refer to the components being separated and subscripts 1 and 2 refer to two different products. x is mole fraction or any other suitable composition parameter.

The separation is generally effected by means of a *separating agent*, which is a stream of matter or energy fed to the process to cause the separation to occur. Since separation is the opposite of mixing and since mixing is an irreversible process, purposeful design and a certain minimum energy consumption are required for a separation process. This energy is usually provided by means of the separating agent.

Categorizations of Separation Processes (*1*)

Some separations simply segregate two phases already present in a mixture on the microscale into two collected products, one of each phase. These are known as *mechanical* separation processes. We shall be concerned here with separations of homogeneous mixtures, which may include a mechanical separation of phases as a final step.

Separation processes may be categorized as being either *equilibration* processes or *rate-governed.* An equilibration process is based upon the approach of two immiscible phases toward equilibrium compositions which differ from one another. Rate-governed processes are based upon different rates of transport of different species through some medium, often a barrier between feed and product.

Separation processes can also be categorized according to the type of separating agent, with *mass separating agent* processes (such as absorption and extraction), which utilize solvents or other streams of matter, being distinguished from *energy separating agent* processes (such as distillation and crystallization), which supply the separating agent as heat, cooling, or compression work.

Differences between Industrial Processes and Laboratory Analyses

The choice and design of industrial separation processes are dominated by economics, whereas the choice and design of separations used for analytical purposes in the laboratory are more influenced by convenience (short time, little effort), flexibility, and attainable completeness of separation. Industrial processing separations tend to be continuous flow processes, while those in the analytical laboratory are for the most part batch processes. Industrial separations most often involve large quantities of material, whereas analytical separations involve small quantities. In fact, the ability to handle extremely small quantities is often a prime virtue in analytical methods.

For purposes of chemical analysis it is not necessary that the various species analyzed be separated from one another into products of different composition. Techniques such as spectrometry and NMR allow quantitative identification of relative amounts of different species without formal separation. Such approaches depend upon the degree of resolution between components rather than the degree of separation. Methods of chemical analysis can often be destructive, in that the chemical nature of the species being separated or identified can be changed or lost, as in pyrolysis. On the other hand, the usual purpose of industrial separations is to isolate individual components as salable products, as reactor feeds, or as recycle streams. In all these situations the chemical nature of the different components should not be changed.

SELECTION OF SEPARATION PROCESSES

Separation Factor

The separation factor results from differences in appropriate physical properties, such as vapor pressure and solubility. These differences result in turn from differences in molecular properties, a list of which is given in Table 1. In order for separation to be possible the separation factor must be different from unity, the more removed the better.

Different separation processes involve separation factors which are dependent to different extents upon the different molecular properties listed in Table 1 (*1*, Table 14–1). For example, separation by distillation depends upon differences in volatility, which in turn come from differences in molecular weight and in intermolecular forces, reflected by dipole moment and polarizability. Crystallization, on the other hand, involves the ability of molecules to fit into an ordered solid-phase structure and thereby relies more upon differences in molecular volume and molecular shape for determining separation factors. Electrophoresis requires differences in molecular charge, ultracentrifugation requires differences in

TABLE 1

Molecular Properties upon Which Separations May Be Based

Molecular weight
Molecular volume
Molecular shape
Dipole moment
Polarizability
Electrical charge
Chemical reactivity

molecular weight, and ion exchange requires differences in chemical reactivity with the exchange resin. Solvent extraction provides separation factors through differences in activity coefficients of the components within the solvent and feed phases; these differences in turn usually result from differences in dipole moment and polarizability. Foam or bubble fractionation requires differences in surface activity which in turn result from differences in intermolecular forces.

Since separation factors for different processes depend to different extents upon differences in different molecular properties, one can judge a priori which separation processes are likely to give the most favorable separation factors by evaluating the molecular properties in which the species to be separated differ to the greatest extent.

Nature of the Process

There are certain inherent features of different separation processes which favor or disfavor use of the process for industrial-scale processes and for laboratory analytical separations. In fact, it is striking to observe that only rarely is the same separation method for a given component mixture used in a chemical process and for laboratory analyses.

Certain processes are inherently better suited to large-scale or to small-scale operation. For example, gas–liquid chromatography sees widespread use for analyses because of its flexibility and ability to handle multicomponent systems in a single operation, but it has for the most part resisted efforts to achieve economical operation upon scale-up. Similarly, electromagnetic separation with the mass spectrometer is one of the most successful separation methods for analysis, but is generally not suitable for separations on an industrial scale. An exception is the use of the Calutron for production-scale separation of radioisotopes; however, that usage is a result of a unique historical situation (*2*).

Some separations are better adapted to batch operation than to fully continuous operation. A good example again is chromatography of any sort, and this is another reason why chromatography sees much more use in the laboratory than on a production scale.

Distillation, on the other hand, is a process which sees more use for industrial separations than for chemical analyses. Distillation is well-suited to large-scale, continuous operation and is usually a relatively inexpensive separation with considerable economies of scale. Batch distillation is used for analyses in some cases, especially for complex petroleum mixtures, but suffers from relatively incomplete separations resulting from the lack of a stripping section.

For industrial separations, energy-separating-agent processes tend to be relatively favored over mass-separating-agent processes because of the extra quantities of material to be handled in the case of mass separating agents and because of the expense associated with subsequent separation and regeneration of the mass separating agent from one of the products. These considerations are much less important for laboratory analyses; in fact, it is usually not necessary to regenerate a mass separating agent when one is used. For this reason, precipitation sees much more widespread use as a separation process for laboratory analyses than for industrial separations. Precipitation is the basis of the classical qualitative analysis schemes and of all gravimetric analysis. When used on a large scale, however, precipitation suffers from the facts that the material being separated is chemically converted and that there is a net consumption of a precipitant which will often be a major process expense. Furthermore, there must usually be an excess of precipitant added, and this will appear in a product, often contributing further separation problems.

Another characteristic of gas–liquid chromatography is the considerable dilution of the species being separated with the carrier gas, which is a mass separating agent. This is of little concern for analyses but represents a large economic burden if the process is to be used where recovery of the components in pure form is needed.

Requirement of extreme processing conditions can be a deterrent on both the laboratory and industrial scales. Thus one does not ordinarily contemplate separating a mixture of salts by distillation in either case. Extreme conditions of temperature or pressure lead to expense and can lead to product damage; both these aspects tend to discourage the use of extreme conditions on an industrial scale even more than for laboratory analyses.

Use of large-scale separations involving a solid phase poses problems.

Usually truly continuous-flow operation for both phases is not possible in an economic way, and the approach instead is to use a fixed-bed process, involving intermittent operation and regeneration of solid material in the fixed bed. Handling and transport of solids and slurries also poses problems. These difficulties are of much less concern for laboratory analyses, and therefore separations with solid phases (e.g., adsorption chromatography and precipitation) are much more common.

Some separation methods lend themselves much more readily to multiple staging than do others Rate-governed separation processes, such as reverse osmosis, are difficult to stage because of the need for using a separate device for each stage and supplying separating agent in the form of energy to each stage. Thus rate-governed processes are relatively more preferred when only one or a few stages are necessary. Since separations for chemical analysis often require very high degrees of resolution of components and hence many stages, rate-governed processes see less utilization for analyses.

Two other pertinent selection criteria apply both to industrial-scale separations and to laboratory analyses. One of these is a desire to choose separations which are capable of providing the desired grouping of components into products. As an example, we may want to separate a mixture of aromatic and paraffinic hydrocarbons of approximately the same molecular weight range. Boiling points of the aromatics and paraffins will overlap, so that it will not be possible to achieve the desired component grouping into the products of a single distillation. On the other hand, solvent extraction with a relatively polar solvent will often be able to remove all the aromatics preferentially to the paraffins in a single step. No matter what the scale of operation, additional separation steps beyond the minimum necessary will incur a penalty in expense and/or effort.

Another criterion involves experience. For good reason the industrial designer and the laboratory analyst stick with tried and true processes, since development of a new separation method for each design or each analysis is inefficient.

An Example—Separation of Xylene Isomers (*1*)

Different xylene isomers are used for different purposes in the chemical industry. *p*-Xylene is a raw material for the manufacture of terephthalic acid, an intermediate for polyesters. *o*-Xylene sees use for the production of phthalic anhydride and thereby plasticizer compounds and other derivatives. *m*-Xylene is largely recycled and isomerized into the para and ortho compounds, although there are some developmental uses of the meta isomer. Thus separations of the isomers are important to the petrochemical industry, as well as being important for analyses.

Referring to Table 1, the xylene isomers do not differ in molecular weight, molecular volume, polarizability, or electrical charge. They differ slightly in dipole moment, since the ortho isomer and to a lesser extent the meta isomer do possess nonzero moments. They differ significantly in molecular shape and consequently differ in chemical reactivity with some reactants where steric effects are important. Molecular shape has the greatest influence upon separations involving a solid phase, such as crystallization and adsorption. Correspondingly, one finds that the most established process for industrial separation of *p*-xylene from *m*-xylene is crystallization, which is based upon a substantial difference in freezing points—+56 and −55°F for *p*-xylene and *m*-xylene, respectively. Another successful new process is based upon adsorption.

The slight dipole moment (0.62×10^{-18} esu) of *o*-xylene gives a boiling point (291.2°F) which is significantly greater than those of *m*-xylene (282.7°F) and *p*-xylene (281.3°F). Even though the resultant relative volatility of the other isomers to the ortho isomer is only 1.16, distillation is commonly used for the recovery of *o*-xylene industrially. A reflux ratio of 15:1 and 100 or more plates are required. This is an example of the very great attractiveness of distillation compared to other separation processes industrially, since much better separation factors are available with several other processes. The very small relative volatility (1.02) between *m*-xylene and *p*-xylene renders distillation uneconomical for their separation industrially. Again, because of the small difference in dipole moments, the addition of polar solvents for azeotropic distillation of the meta and para isomers has not been successful, with the best solvent among 40 tested merely improving the relative volatility to 1.03.

It is interesting to observe that none of these approaches are used for laboratory analyses of xylene isomers. Instead, one frequently takes advantage of the fact that the original chemical nature of the isomers need not be preserved. Thus the isomer mixture is often converted by $KMnO_4$ oxidation to the dicarboxylic acids, which have quite different melting points from one another. The same is true of the nitro derivatives. The other common laboratory procedure, of course, is gas-liquid chromatography, which takes advantage of the incentives which have already been noted for chromatography. Even though quite low relative volatilities between the isomers are achieved with most solvents and column substrates used, the ability of GLC to provide the effects of very large numbers of stages in improving the separation allows a quantitative resolution of the isomers to be made with sufficiently good chromatographic systems.

SEQUENCING OF SEPARATIONS

When several products containing specified groupings of components are to be obtained from a mixture, the number of possible sequences of separators becomes quite large. Table 2 illustrates the number of possible sequences (S_R) for separating a mixture of R components into single-component products. It is assumed in Table 2 that a single method of separation is available, in which case the series

$$S_R = \sum_{j=1}^{R-1} S_{R-1} S_j \qquad (2)$$

is obeyed. When several different kinds of separators may be considered for use, the numbers become even larger. For example, if N different separators may be considered at each constituent step in the sequences, and if the ordering of separation factors is the same for all separation methods, then the number of different sequences grows by a factor of N^{R-1}, since each of the $R - 1$ separators in each scheme could be replaced by any of the other separation methods.

The situation becomes more complex in the case where the different products should contain specified mixtures of components and/or the separation factors for different methods of separation have different orderings. Because of the orderings of separation factors, only certain combinations of separators will have the capability of producing the desired components groupings in products without splitting sets of components that may remain together. If a sequence is used which separates

TABLE 2

Number of Separator Sequences

No. of components, R	No. of separators, $R - 1$	No. of sequences, S_R
2	1	1
3	2	2
4	3	5
5	4	14
6	5	42
8	7	429
10	9	4862

components unnecessarily, then more than the minimum number of separators will be employed. In general, using extra separations will lead to greater expense on the industrial scale, and almost certainly will lead to greater effort on the laboratory analytical scale. Thompson and King (*3*) describe a systematic procedure which may be implemented by computer if desired, and which has the capabiity of identifying those sequences which can make the desired separations into products with the minimum number of separators. Two matrices, a pair compatibility matrix and a product separability matrix, are employed. If no sequence can lead to the desired component groupings in products without splitting a product, then the procedure identifies those sequences which involve the least number of product splits.

The separator selection problem has a tree structure in that there are subproblems corresponding to the separation of lesser numbers of components into products. After the initial separation steps in a sequence have been fixed, certain of these subproblems remain. The same subproblems can show up following various different initial steps. If a single cost can be attached to the use of a particular separator for separating a particular mixture into a particular set of products, no matter what separations come before or after, then dynamic programming may be used as a very efficient procedure for determining the optimal separation sequence (*4*). The assumptions necessary for this approach can be significantly limiting for industrial separation problems, but are probably better fulfilled for separation sequences used for laboratory analyses, such as classical qualitative and quantitative analysis schemes.

For separation problems where a large number of alternative sequences are possible, it is usually true that the difference in cost or amount of laboratory effort does not differ much from the true optimal sequence for the next several sequences closest in attractiveness to the optimal sequence. In such cases the incentive for finding the single optimal sequence diminishes, and it is probably satisfactory just to find a sequence which is close to optimal, or to find a number of near-optimal sequences and make the final judgment among them on the basis of other qualitative factors. In these instances heuristic rules are useful for synthesizing separation sequences.

A listing of heuristic rules which have been found useful for the selection of distillation sequences on an industrial scale is given in Table 3 (*1*). The desirability of using the minimum number of separators follows from the discussion above. Performing difficult separations, in terms of either separation factor or product purities, last is desirable from the standpoint of

TABLE 3

Heuristic Rules for Sequencing Distillation Columns

Minimum number of separators (or products)
Perform tight (low separation factor) separations last, as binaries
Make high purity products last
Take one component at a time overhead
Use descending pressure level of columns
Favor approximately equal product flows

minimizing the amount of additional components present, since difficult separations require many stages and/or much separating agent. Taking one component at a time overhead in distillation sequences leads to the minimum vapor generation rate, if the relative volatilities for all separations are about the same, and also leads to the least number of high-pressure columns if pressures above atmospheric are required. On the other hand, taking approximately equal amounts of both products is desirable from the standpoint of properly utilizing the balance between the reflux rate in the rectifying section and the vapor boil-up rate in the stripping section of a distillation column. These last two heuristics often conflict. The use of heuristic rules for the assembly of separation sequences has been explored by Thompson and King (*3*). One finding is that an effective heuristic is to use next the cheapest separator from among that group of potential next-separators which have the capability of leading to the minimum number of products. This heuristic combines several of those from Table 3.

The synthesis of industrial separation schemes has been reviewed recently by Hendry, Rudd, and Seader (*5*).

The heuristics to use for laboratory analytical separation sequences would be largely different. The incentive for utilizing the minimum total number of separations should remain valid. For any analysis one would seek separations which can give a high resolution between components, and which can create the desired split between components without great effort or extreme conditions. For qualitative analysis it should be desirable to seek sequences which have the potential of confirming the absence of large groups of components and of dividing the possible components into groups each containing a substantial number of components. One can see this factor at play in the design of the standard qualitative analysis schemes. For example, if a precipitate is not obtained for any major group, then all those components are known to be absent. In the case of quantitative analyses of components that are already known to be present, there is a greater incentive for separating one component at a time and doing it in such a way (e.g., precipitation) so as to allow for the quantitative determination of that component as it is separated. Finally, perhaps the most important point to be made regarding separations for analyses is that a single-operation multicomponent separation—such as chromatography—has by far the greatest efficiency and is satisfactory for the purpose desired.

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Received by editor April 25, 1974