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Tech Facts

LAB GUIDE
Column Separations using Resins and Adsorbents

CONTENTS:

Background

General Overview

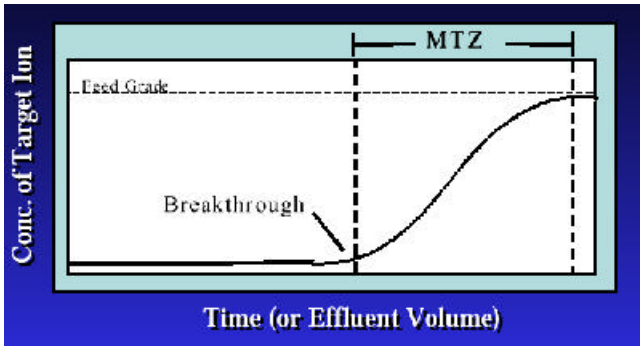
Laboratory column studies are the second step in separations process development. The first step, (Equilibrium Isotherm Testing), determines the optimal chemistry for the separation and narrows the number of candidate resins for the process. The second step, column evaluations, will elucidate the optimal engineering parameters for eventually scaling-up your process for commercial operation.

If you plan to develop a separation process in-house, or if you will be utilizing an OEM (original equipment manufacturer) or Technology House that specializes in ion exchange process development, a brief series of experiments in your own labs can save a lot of time and process development resources. Below you will find an easy to follow column-testing guide to help you quickly onto the road to a successful separation process development.

> **General Guideline 1:** Mock-up feed solutions rarely results in definitive test data. Whenever possible, use actual process feed. Actual process feeds usually contain minor constituents that can profoundly effect your separation results.

Some Theory

Column tests are performed to elucidate the shape of the breakthrough curve and provide the experimenter an avenue to evaluate the effect of changes to operating conditions during pre-scaleup optimization. For any given resin matrix, changes in the shape and duration (mass transfer zone length; MTZL) of the breakthrough curve can be manipulated by changing the average resin bead size, feed flow rate, resin bed depth, and operating temperature. The object of the column tests is to manipulate the column operating parameters in such a way as to give the "**shortest" MTZ** (on a volume basis) possible.



General Guideline 2:

- Smaller beads yield shorter MTZ.
- Higher temperature tends to shorten the MTZ.
- Slower flow velocities favor shorter MTZ.
- Increasing concentrations of competing ions, lengthen the MTZ.

The **shape** of the breakthrough curve also changes with variable parameters.

- The presence of competing ions will elongate and flatten the curve.
- Unfavorable (concave) isotherm curve flattens the breakthrough curve.
- "Higher order" molecular interactions of the target ion with the resin lengthen the curve (i.e., chelating interactions, multivalent ions, etc.).

Designing the Experiment

The equilibrium isotherm data, which you already gathered, gives you the maximum performance expectation for the feed/resin combination you are evaluating. What is missing is the shape and duration of the breakthrough curve. From the loading capacity of the target ion at equilibrium with your unique feed grade, you can easily calculate the total amount of fluid that can be treated per volume of resin.

For the sake of illustration we have chosen the following hypothetical test case:

TEST CASE --- Removal of Uranium from Mining Leach Solution

Feed Grade (ppm uranium in solution)	50
Isotherm Loading (g/l on resin)	80

It is helpful to set up your own Handy Lab Column Calculator on a computer spreadsheet. A tool such as this, makes it easy to set-up and modify your lab column operating perimeters.

Example :

Estimator for Ion Exchange Laboratory Column Evaluations

Input					Calculated fields							
Feed Grade Target Ion (ppm)	*Flow Rate* (ml/min)	*Expected Loading Capacity* (g/l)	*Resin Volume* (ml)	*Column diameter* (cm)	*Estimated Vol. To Exhaustion* (L)	*Estimated Treatment Ratio* (BV)	*Cross-sectional area* (cm2)	*Bed Depth* (cm)	*Aspect Ratio* (H:W)	*Flow Rate* (BV/hr)	*Flow Velocity* (gpm/sqft)	*Flow Velocity* (Lpm/sqmeter)
50	**2**	**80**	**10**	**1.2**	**16.0**	**1600.0**	**1.1**	**8.8**	**7.4**	**12**	**0.43**	**17.7**

In our test case, since feed grade is 50 ppm (0.05 g/L) we can calculate an approximate treatment ratio (volumes of fluid per volume of resin):

80/0.05 = 1,600 bed volumes (BVs)

General Guideline 3: While the theoretical treatment ratio can be estimated as above, The actual operational treatment ratio is usually about 65-80% of the theoretical equilibrium isotherm capacity.

In our test case the interaction of the uranyl anion with the resin is an equilibrium interaction, it is not 100% efficient with respect to time, so breakthrough of uranium into the effluent stream will occur sometime well before 1,600 BVs and complete exhaustion of the resin will occur at some point after 1,600 BVs.

Sizing the Test Column

Choosing the correct column size is essential to efficient testing.

General Guidelines 4:

- Lab column aspect ratios are best when greater than 4:1 (Height:W), however commercial column aspect ratios are best when between 2:1 (H:W) and 4:1 (H:W)
- Best flow rates to test are from 5 – 25 BV/hr. A good starting point is 8 BV/hr. Large molecules or kinetically impaired systems should be run at flow rates of 2 to 8 BV/hr.
- Best linear flow velocities to test are 5-60 m/hr (2 – 24 gpm/ft^2). A good starting point is 12m/hr (5 gpm/ft^2).
- Flow velocities slower than 1 m/hr (0.5 gpm/ft^2) may result in channeling inefficiency.
- Flow velocities faster than 50 m/hr (20 gpm/ft^2) may result in excessive pressure drop across the bed.
- Test columns with a diameter greater than 2 cm (3/4 inch) usually scale-up linearly.

Our test case has a high treatment ratio, so we don't want to make the bed too large or we will have to have a very large vessel to hold our process feed solution. A convenient column size is 1.2 cm in diameter. If we use 10 mL of resin, our bed depth will be 8.8 cm and the aspect ratio will be 7.8. We will need a little more than 16L of feed to complete a single breakthrough profile. Testing should be carried-out at 3 to 4 different flow rates and perhaps under different conditions such as varied pH or temperature. The optimized breakthrough curve can then be used as a guide to help in the scale-up of your process to practically any size required.

Commercial Scale System Configurations

Full-scale systems come in many different configurations. Guidelines for determining which configuration is appropriate for your process is outside the scope of this simple guide. Please consult with individuals or firms competent in ion exchange system design to find out which configuration is right for your technical needs and budget. Here are some General Guidelines regarding ion exchange system configuration.

General Guidelines[5]:

Single Column Systems are:

- Good for low concentration feeds.
- Useful in purification processes.
- Useful when MTZ is very short.
- Used for batch or non-continuous operations.

Multiple Column (A, B, C bed) Systems are:

- Good for medium concentration feeds.
- Useful in separation processes.
- Useful when MTZ is long.
- More efficient.
- Sized so the column length is equal to MTZ.

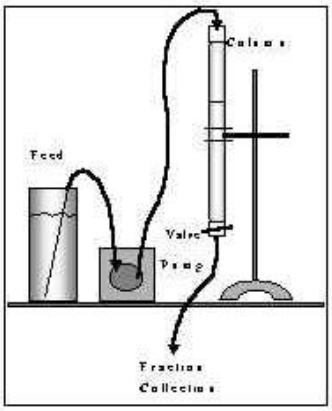
Continuous Counter Current Systems are:

- Good for medium and high concentration feeds.
- Useful in separation and chromatographic processes.
- Best when the resin-solute interaction has first-order kinetics
- Useful when MTZ is very long.
- Extremely efficient resin users.
- Use lesser amounts of chemicals for elution and rinsing.

Laboratory Guide

Lab Setup

Here are a few pointers that should help eliminate wasted lab time spent in "trial and error." Laboratory feasibility testing can usually be accomplished using a simple bench scale setup. On rare occasion, where only a few of quick screening tests are required, it may be possible to piece together a disposable column setup using a glass burette or a short piece of PVC pipe fitted with a glass wool resin support plug. However, for repeated testing and for more careful evaluations of breakthrough and elution profiles, we encourage the use of a more permanent bench testing setup.



Without a doubt, the key to getting truly usable information from the bench testing is **good analytical data**. Before investing time in column feasibility testing, make sure that you have reproducible and convenient analytical methods of analysis, appropriate for the expected composition of your column effluents.

The heart of a typical ion exchange feasibility testing setup is a variable speed pump, suitable for the flow range of the testing (we find that peristaltic pumps work well) and a glass chromatographic type column with filter disk fittings on both top and bottom. With these basic components, you can readily perform most feasibility screening tests. Consult your favorite laboratory equipment and glassware supply companies for appropriate supplies.

Additional features can be added to your test rig in order to suit the needs of the individual test. A fraction-collecting device is often invaluable for capturing a complete data set and for eliminating the need for constant operator attention. A minimum of 10 to 15 data points are needed to accurately define the shape of the mass transfer zone. For testing at temperatures other than ambient, a jacketed column and circulating constant temperature bath may be fitted.

Resin Re-hydration

It is important that the ion exchange resin is fully hydrated prior to packing into the column. If there is any doubt as to the resins state of hydration, or if you know that the resin has significantly dried in storage or on the bench-top, a re-hydration step should be performed. Generally, re-hydration can be accomplished by soaking the resin in de-ionized water for a minimum of 2 hours. Re-hydration can be greatly accelerated by placing a resin slurry in a side-arm vacuum flask and putting it under a partial vacuum for just a few minutes (resin may off-gas heavily if very dry).

Loading the Column

Always maintain the resin in a fluid slurry. Using a graduated cylinder, measure the desired amount of resin for the column test. Place about one bed volume of fluid (a volume of fluid equal to the volume of resin used) into the column, then with the outlet valve closed, pour the re-hydrated and measured resin slurry into the column.

Packing the Column

> ***CAUTION:*** *Ion exchange resins typically go through shrink/swell changes during ion exchange processing. Expanding resin can exert up to 700 bar (10,000 psi) on the vessel and internal parts, pressure far greater than most vessels can handle. Allow room for swelling and whenever possible, perform swelling steps in an up-flow mode. It is also advised to wrap glass columns with flexible tape or webbing to minimize the hazard of flying glass. Always wear appropriate protective clothing.*

For optimum flow properties, it is a good practice to backwash-stratify the resin bed prior to the introduction of feed. Backwash-stratification redistributes the resin in the column, packing the resin so that the larger beads are toward the bottom of the bed and the smaller ones are closer to the top. Backwash-stratification is accomplished by placing the column in an up-flow mode, using barren fluid (usually de-ionized water) to backwash expand the resin bed. Normally, the unused space in the top of the column (freeboard) is large enough to allow the complete expansion of the resin bed by approximately 80-100%. After allowing the bed to expand for 15 - 20 minutes, gradually reduce the flow to zero, allowing the bed to gravity settle. Do not force the bed to pack by draining the column through the outlet. This can result in extremely poor flow characteristics, possibly rendering your data useless. Also, make sure that the column is not allowed to "run dry". This will cause cracking and channeling within the resin bed. If air does happen to enter the bed, re-fluidize and re-pack the bed before continuing. Once the bed is packed it is usually a good idea to pass several bed volumes (BVs) of de-ionized water through the bed to rinse out any trace of accumulated degradation products, common in resins that are stored for long periods of time prior to use.

> ***Note:*** *Now is also a good time to convert the resin to the desired ionic form if it isn't already in the correct state. For example: if you received an anion exchange resin in the chloride form, but you need it in the hydroxide form, you can do the conversion by slowly passing several BVs of 5% NaOH solution through the resin bed, followed by several volumes of de-ionized water.*

Fill the "Freeboard"

Once the bed is packed, the freeboard space should be filled with your process feed solution in such a way that it is not diluted by residual barren packing fluid. Sometimes this is best accomplished by draining down the barren fluid level to a level just above the resin bed surface before introducing the process feed solution to the column freeboard. Care must be taken, not to disturb the resin bed while filling the freeboard with process feed (filling of the freeboard with process feed should be done with the outlet valve closed). A very small wad of glass-wool, placed just above the resin bed is often useful in minimizing the disturbance of the bed; however, the wool must be slipped completely beneath the fluid level prior to filling, or air may be trapped above the resin, causing air incursion and channeling.

Feeding and Sampling

Make sure that you have plenty of clean sampling containers ready. Sampling can be done either by collecting the entire amount of effluent, while changing the receiver at regular intervals, or by collecting small aliquots at regular intervals, and discarding the effluent in between the samplings. The data you derive from the experiment will be interpreted somewhat differently for each technique. Larger samples will require an averaging manipulation of your analytical results (A) where small samples (B) allow direct

interpretation. Regardless of the technique you choose, enough samples should be collected to completely determine the shape of the breakthrough curve (mass transfer zone).

A fraction collecting device is particularly useful since it will allow small aliquots at extremely accurate intervals and volumes to be collected.

General Guidelines 6:

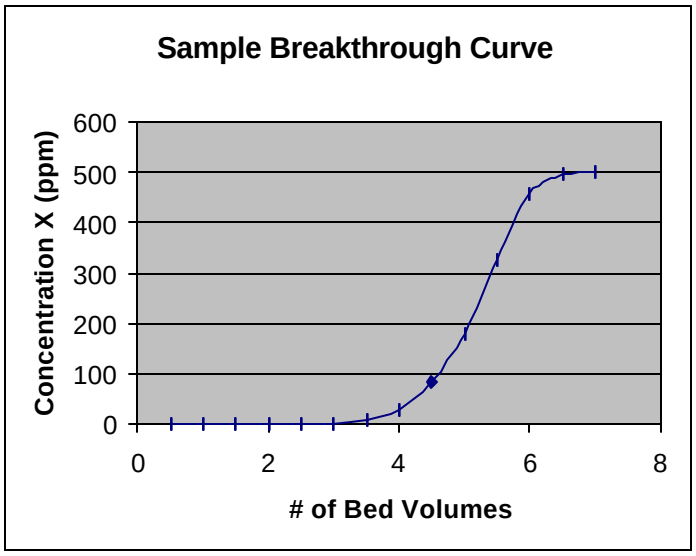
- 10 to 15 data points are needed to accurately define the shape of the mass transfer zone.
- In most cases, sampling once each BV is enough (treatment ratios between 10 and 50).
- For separations with very high treatment ratios (>1000), once every several BVs may be sufficient.
- Interpretation of data is often less ambiguous (sharper curves) if you take a larger number of small regular aliquots than if you collect the total effluent in successive containers.
- In general, the first 0.4-0.6 BVs is void volume (de-ionized water displaced by the feed).

Line-up the feed reservoir and pump without connecting to the column. Use the pump to fill the feed lines with process feed solution. Set your feed pump to the desired flow rate (e.g. stopwatch and graduated cylinder). Switch-off the pump momentarily while you connect the feed line to the column inlet. Make sure that there are no air leaks around the upper and lower column fittings. One way to do this is to open the column outlet valve (and inlet valve if there is one) and wait a few minutes checking for leaks with a tissue. When you know that there are no leaks and your first collection vessel is in place, open outlet (and inlet) valve and turn on the feed pump. Collect your samples for analysis. Monitor the test often to make sure that the flow rate remains constant and that the column never is allowed to run dry. If air does enter the column, it is best to abandon the trial and start over.

Example Spreadsheet

Feed (ppm)	500
BV (mL)	40

Sample #	volume ml	accum. vol. (mL)	BVs	Conc. (ppm)
1	20	20	0.5	0
2	20	40	1	0
3	20	60	1.5	0
4	20	80	2	0
5	20	100	2.5	0
6	20	120	3	0
7	20	140	3.5	10
8	20	160	4	27
9	20	180	4.5	83
10	20	200	5	180
11	20	220	5.5	327
12	20	240	6	458
13	20	260	6.5	495
14	20	280	7	500



Elution Profiles

Elution profiles are captured in a similar fashion, beginning with loaded resin.

General Guidelines 7:

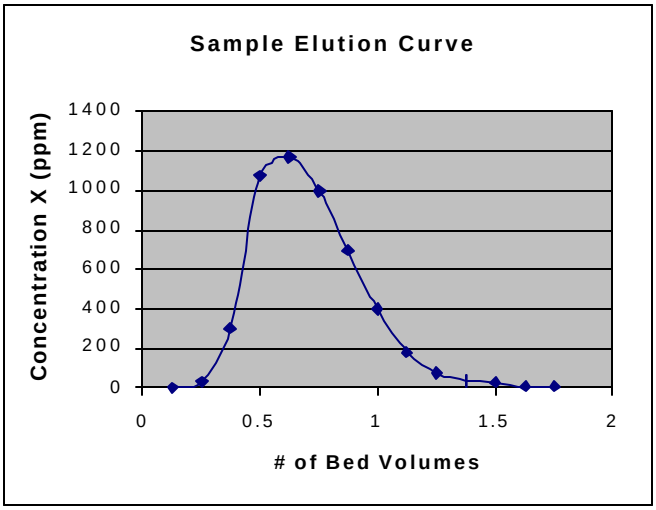
- Elution is generally done at approximately 1/4 to 1/2 the flow rate of loading.
- Faster flow rates elongate the elution profile.
- Slower flow rates sharpen the profile (higher peak elution concentrations).
- Higher temperature favor more rapid elution.
- Higher eluant chemical concentrations favor more rapid elution.

Example Spreadsheet

BV (mL) 40

Elution

Sample #	volume ml	accum. vol. (mL)	BVs	Conc. (ppm)
1	5	5	0.125	0
2	5	10	0.25	33
3	5	15	0.375	300
4	5	20	0.5	1071
5	5	25	0.625	1172
6	5	30	0.75	1000
7	5	35	0.875	692
8	5	40	1	400
9	5	45	1.125	181
10	5	50	1.25	74
11	5	55	1.375	40
12	5	60	1.5	25
13	5	65	1.625	8
14	5	70	1.75	8



Conclusions

We hope that this document will provide a good starting point for you to begin gathering meaningful ion exchange feasibility testing data. We realize that we have not given you all of the tools needed to carry-out complex (multi-component) process evaluations. Such a document would be far outside the scope of this simple guide. If you need further assistance with a tough separation, contact us.

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Warning: Oxidizing agents such as nitric acid attack organic ion exchange resins under certain conditions. This could lead to anything from slight resin degradation to a violent exothermic reaction (explosion). Before using strong oxidizing agents, consult sources knowledgeable in handling such materials.

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