Chromatographic Ion Exchange Resins

Ecolab chromatographic separation products for sweetener and bio-industry applications are high quality polystyrene- and acrylic-based resins with uniform spherical beads.

ECOLAB®

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This publication provides an overview of Ecolab PCR and PCA chromatographic ion exchange resins and discusses related applications.

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Product Description

Ecolab ion exchange resins for chromatography are high quality crosslinked poly(styrene)-based cation and anion exchangers and crosslinked acrylic-based anion exchangers with closely sized spherical bead form, suitable for separations which depend on relatively small differences of affinity of the materials being chromatographed. They are designed mainly for use in large industrial units or in small to medium-sized columns, and not for capillary use in e.g., HPLC equipment. The range of materials available is the result of the need to tailor the resin to the application, and represents an informed selection of the most useful ionic forms, particle sizes and distributions, and crosslinkings. General characteristics are given in the table below, followed by a more detailed individual description overpage. Note that in view of the relatively low flowrates used pressure drop is not normally a significant parameter, nor are backwash expansions relevant to closely graded chromatographic columns.

TABLE 1 Typical Chemical and Physical Characteristics

Characteristics	PCR Cation Resins	PCA Anion Resins
Polymer Matrix Structure	Styrene-DVB gel	Styrene-DVB gel and macroporous Acrylic-DVB gel
Physical Form & Appearance	Clear amber spheres	Pale yellow spheres
Whole Bead Count	>=98%	>=95%
Functional Groups	Sulphonic acid	Quaternary amine
Conversion to Ionic Form	>=98%	>=99%
Max.Operating Temp, °C	(Na^+) 140 °C [285 °F] (H^+) 120 °C [250 °F]	(Cl^-) 100 °C [210 °F] (OH^-) 60 °C [140 °F]
pH Range (Normal Operation)	2–8.5	2–8.5
Color Throw (APHA Units)	<25	<25
Fe Impurities (ppm)	<50	<50
Metals Impurities (ppm)	<40	<40

TABLE 2 Cation Separation Resins

Purolite™ Resin Product	Type	Total Volume Capacity, Na^+ Form (eq/L)	Mean Size Typical (µm)	Moisture Retention, Na^+ Form (%)	Moisture Retention, H^+ Form (%)	Remarks & Applications
PCR145	Macroporous Strong Acid Cation	1.5	260–300	55–60	60–66	Cation chromatographic separation resins can be supplied in Ca^{2+}, Na^+, K^+ or H^+ forms. Ca^{2+} form separations: Glucose-Fructose, Maltose. Na^+ form separations: Beet Molasses, Dextrose enrichment, Erythritol. K^+ form separations: Beet Molasses, Fructo-oligosaccharides, Soluble fiber. H^+ form separations: Acid-Sugar (cellulose hydrolyzate).
PCR450	Gel Strong Acid Cation	1.35	360–400	60–65	65–71	
PCR631	Gel Strong Acid Cation	1.6	210–240	52–55	55–62	
PCR632	Gel Strong Acid Cation	1.6	210–250	52–55	55–61	
PCR642	Gel Strong Acid Cation	1.6	295–335	52–56	59–62	
PCR651	Gel Strong Acid Cation	1.6	330–370	52–56	59–62	
PCR652	Gel Strong Acid Cation	1.6	320–360	52–56	59–62	
PCR732	Gel Strong Acid Cation	1.8	210–250	50–52	53–57	
PCR833	Gel Strong Acid Cation	2.0	225–275	44–48	51–55	
PCR855	Gel Strong Acid Cation	2.05	210–230	42–46	48–53	

TABLE 2 Cation Separation Resins (Cont'd)

Purolite Resin Product	Type	Mean Size Typical (µm)	Remarks & Applications
Shallow Shell SSTPCR642	Gel Strong Acid Cation	300–340	Higher purity, higher recovery and lower water.
Shallow Shell SSTPCR732	Gel Strong Acid Cation	200–240	Higher purity, higher recovery and lower water.

TABLE 3 Anion Separation Resins

Purolite Resin Product	Type	Total Volume Capacity, Cl^- Form (eq/L)	Mean Diameter (µm)	Moisture Retention, (Cl^- Form) (%)	Remarks & Applications
PCA433	Gel Strong Base Anion	1.3	150–300 (particle size range)	48–57	Anion chromatographic separation resin can be supplied in Cl-, SO_4^{2-}, OH- forms. Used for the purification process based on the acid retardation technology process.
PCA441	Gel Strong Base Anion	1.4	285–315	47–52	Xylose enrichment.
A503MBOH/4363	Macroporous Strong Base Anion	1.0	300–600 (particle size range)	61–66	Vitamin E purification.
A847DL	Gel Weak Base Anion	1.6 (FB form)	300–600 (particle size range)	56–62 (FB form)	Used for citric and lactic acid purification.
WCA100	Gel Strong Base/ Weak Acid	0.9 (Na^+ form) & 0.9 (OH- form) Amphoteric	240–280	57–62	Amphoteric resin containing balance of weakly acidic and strongly basic groups. Chromatographic applications like salt removal from caustic and sulfate removal from brine. Chlorates removal from KOH and purification of acids.

General Principles

Resins can be made with a known and well-defined crosslinking over a range of DVB contents, and with almost any required particle size from a few microns to a millimeter or more. They can show in the extreme case virtual monodispersity, though more usually a close (and specified) range of particle diameters. The resins may be based on polar or non-polar matrices, which can be either the normal gel type, or even macroporous if that is desired, with anionic or cationic groups which may be partly or, more usually, essentially fully ionized.

The main characteristics of an ion-exchange resin that determine its performance in the efficiency of a separation, once the chemistry of the separation has been determined, are its particle size and its moisture content.

The former is usually made as small as is compatible with the hydrodynamics of the system, in order that exchange rates shall be as rapid as possible, giving near-equilibrium conditions at the liquid-solid interface, and enabling the maximum number of theoretical plates to be accommodated in the column. To ensure good packing and minimise channelling, the particle size distribution should be as narrow as conveniently possible. In gel resins, it is the crosslinker content which determines the moisture content of the swollen particle, and hence the mass transfer and diffusional effects within the particle. Especially with large molecules, the higher the moisture content the greater is the intra-particle coefficient of diffusion; however, where the separation is of bulk rather than trace quantities, and the capacity of the column becomes a limiting factor, too high a moisture content becomes counterproductive as the number of exchange groups in the column are reduced. With macroporous resins the internal structural heterogeneity tends to blur the sharpness or exaggerate the diffuseness of the chromatographic front, so having an adverse effect on separation. Thus gel resins are commonly used.

Sugar Separations

The major commercial use for closely-sized resins is in the HFCS (High fructose corn syrup) production which has become the major source of sweetener for food products, such as soft drinks. The resin of choice is the Ca^{++} form of a poly(styrenesulphonate) material of moderately low DVB content, which provides sufficient crosslinking to exclude di- and poly-saccharides, and inside which ligand exchange can take place for the hydration water of the calcium counterions with the hydroxyl groups of the monosaccharide. The difference in the configuration of fructose and glucose results in preferential complexing of the fructose, and consequent retardation in the column relative to the glucose.

Organic Acid Purification

Organic acids like citric acid and lactic acid are used as food and beverage additives. They are produced via fermentation of sugars and sweeteners. The fermentation broth is filtered to remove the cultures and the organic acids are purified in one of three processes. The conventional gypsum process uses calcium hydroxide to precipitate calcium citrate or calcium lactate. The calcium precipitate is filtered to separate it from residual sugars and soluble impurities. The calcium precipitate is then treated with sulfuric acid to dissolve and acidify the citric or lactic acid, producing the less soluble gypsum, calcium sulfate, a byproduct. Residual salts are removed with demineralization resins.

The second process for organic acid purification is solvent extraction which utilizes an amine or alcohol which complexes with the organic acid. The impurities remain in the aqueous phase. The organic phase is subsequently washed with water to recover the organic acid. Residual salts are removed with demineralization resins.

The third process for organic acid purification utilizes an anion resin to separate the organic acid from residual sugars through the process of acid retardation. In the acid retardation process, the acid in solution exchanges with the anion resin functional groups and passes more slowly through the bed than the sugars. Residual salts are removed with demineralization resins.

Dietary Fiber

Dietary fiber is a prebiotic soluble dietary fiber that is incorporated into cereals, beverages, snack bars, dairy and more. One form is produced as an oligosaccharide that is resistant to digestion in the small intestine. Dietary fibers promote beneficial physiological effects.

In the production of dietary fibers, the soluble fiber solution contains an amount of smaller carbohydrates that would reduce the benefits of the fiber. Ecolab's K^+ form chromatographic separation resin removes the sugars through a molecular exclusion process where the large oligosaccharides cannot penetrate the gel structure of the resin and thus pass quickly through while the smaller saccharides diffuse in and out of the resin and pass through the bed much more slowly.

Fructooligosaccharides (FOS) are sugars naturally present in many plants and vegetables, yet their content is in low amounts. For large scale production, microbial enzymes are used to convert sucrose into FOS. However, the fermentative broth obtained is a mixture of FOS with salts and smaller saccharides. Among different purification technologies, ion exchange resins may be used in a continuous chromatographic process, such as simulated moving bed (SMB). Compared to the usual preparative processes the continuous chromatographic ones provide a better utilization of the adsorbent and less eluent consumption. In comparison with other methods, SMB process used for FOS separation has the advantage of requiring no organic eluent and achieves high production rates.

Cellulose Hydrolyzate

Cellulose is the most abundant polymer on the planet and has great potential as the basis for renewable energy, sugars and chemicals. The cellulose and hemicellulose polymers in plant structures are most commonly hydrolyzed with acid to break them down into simple carbohydrates such as glucose, xylose, arabinose and others. These sugars are then either purified, fermented or chemically altered. Prior to those steps, the residual acid from hydrolysis must be neutralized or separated from the sugars in order for the downstream processes to progress. Purolite chromatographic separation resins can be used in either an ion exclusion process or an acid retardation process to separate the acid for reuse in hydrolysis.

In an ion exclusion process, the acid is prevented from penetrating the cation resin structure in order to maintain the resin electroneutrality and pass through the bed rapidly. The sugars diffuse in and out of the resin structure and pass more slowly through the bed.

In an acid retardation process, the acid in solution exchanges with the anion resin functional groups and passes more slowly through the bed than the sugars.

Other Applications

There are many individual applications of ion exchange chromatography to be found in the literature. While most of these are of an analytical nature, commercial examples may be found in the pharmaceutical industry, or in food applications, other than sugar, where it is necessary to purify relatively small amounts of expensive and concentrated flavour essences or colourings which are, like the monosaccharides, susceptible to chromatography by ligand exchange.

Although resin requirements for any chromatographic application are generally governed by the considerations mentioned in a) above, each case is different, and optimum conditions generally have to be determined by experiment.

Laboratory Feasibility Testing of Chromatographic Separations

Pulse Testing

These systems are far removed from analytical scale, which typically use less than 15 ml of media, yet the mechanisms that allow component separation on the analytical scale also permit chromatography on the larger industrial scale.

The pulse test procedure typically uses a one-inch or two-inch diameter by six-foot tall jacketed glass column loaded with the media of interest. Several feed/rinse cycles are run to settle the media and to equilibrate it if the ionic makeup of the feed solution is different from the ionic form of the resin. This is particularly important with separations such as sucrose from beet molasses where, because of the mixed salt load, the media will equilibrate to the mixed sodium/potassium form.

The feed solution is injected at the top of the resin bed, followed by the eluent, usually water. Fractions are collected after exiting the column and are then analyzed to give the separation profile.

The degree of separation observed during these pulse tests is usually the criteria that determines whether to discontinue the work or to advance the testing to a simulated moving bed (SMB) pilot plant.

Apparatus

A. Two-inch diameter by six-foot tall glass column with water jacket

B. Pressurized and temperature-controlled deionized water supply

C. Eluent flow measurement and control capability
   1. Positive displacement pump ***or***
   2. Flow measurement and control valve with PID control ***or***
   3. Flow measurement and rate set valve with manual control

D. Fraction collection capability
   1. Automated sample collection or fraction collector *or*
   2. Calibrated sample bottles with manual collection *or*
   3. Volume totalization with auto or manual sample collection

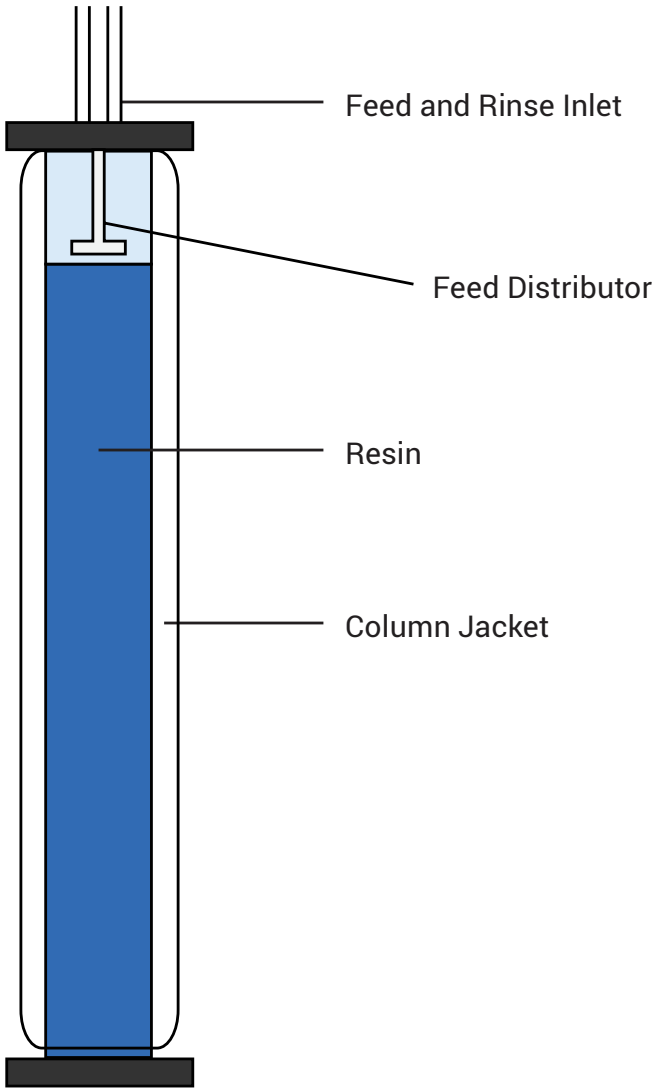
D. Controlled-temperature hot water supply for water jacket

E. Feed injection loop assembly

A schematic diagram of the column is shown in Figure 1.

FIGURE 1

Pulse Test Column



Test Conditions

Flow Rate

For SMB operations, the pulse test flow rate should be conducted at a flow similar to the average of the separation zone flows upstream and downstream of the feed introduction position (Averages of Zone 1 and Zone 2). A typical flow rate is 2 bed volumes/hour.

Temperature

Pulse testing to be conducted at temperatures similar to the anticipated actual operating temperature of the commercial scale system. The typical operating temperature is 160 °F.

Feed

Pulse test feed solution should be at a concentration and composition similar to the anticipated actual operating feed of the commercial scale system. The operating feed concentration is typically 60% DS, but internal SMB recycle flow rate dilution effectively lowers that to 40–50% DS in the separation zone so the pulse test feed solution should be run at 40–50% DS.

Rinse or Eluent Displacement

The feed pulse must be completely displaced from the test column by the eluent. Typically this will require 1.3 to 1.5 bed volumes of eluent.

Feed Pulse Volume

A feed pulse volume of 0.2 bed volumes is typically used. This normally results in incomplete resolution of feed solute components, but is representative of commercial scale equipment operations.

Critical Parameters

1. Accurate Sample Fraction Volume Measurement: Target± I% of volume: Max± 2% of volume
2. Pulse and Elution Flow: Target± 5% of flow: Max ± 10% of flow
3. Operating Temperature: Target± 2% of temperature

Test Procedure

Resin Loading and Column Packing

For reproducible test results the resins must be loaded to consistent resin bed depths. This is particularly important when a comparison of several resins is to be completed. Resin must be loaded to the proper backwashed, settled and drained (BS&D) level. NOTE: Resin levels and hydraulic packing may need to be adjusted following resin preconditioning. The total backwashed, settled and drained (BS&D) resin volume loaded in the column must be recorded.

Pulse Test Column Preconditioning

Prior to data collection five feed/rinse cycles are to be completed to equilibrate and pack the resin for reproducible test results. Additional exposure of the resin to feed material may be needed if equilibration of resin ionic form is required.

Column Free Space and Flow Distribution

It is important to avoid turbulence and backmixing of the feed pulse and the liquid in the free space above the packed resin bed. The feed pulse should be introduced very close to the top of the packed resin bed so as to avoid density inversion mixing. The flow velocity of the feed pulse should be low so as to avoid substantial turbulence and mixing.

It is preferable to introduce the feed pulse directly above the resin bed and subsequently rinse the feed pulse through the resin bed with flow from the top of the column.

Test Data Collection

A. Sample analysis of collected pulse fractions of 0.05 bed volumes each:

    1. Total Concentration
    2. % Dry Solids by Refractive Index Composition by HPLC
    3. Tracer Analysis
    4. Salts by Atomic Adsorption or Conductance

The concentration of each sample component is plotted against the displacement volume. This is a concentration vs. displacement volume plot. This plot will measure the chromatographic resolution of the various feed constituents. Peak separation, peak height and pulse width will be evaluated.

A. Resin pressure drop data

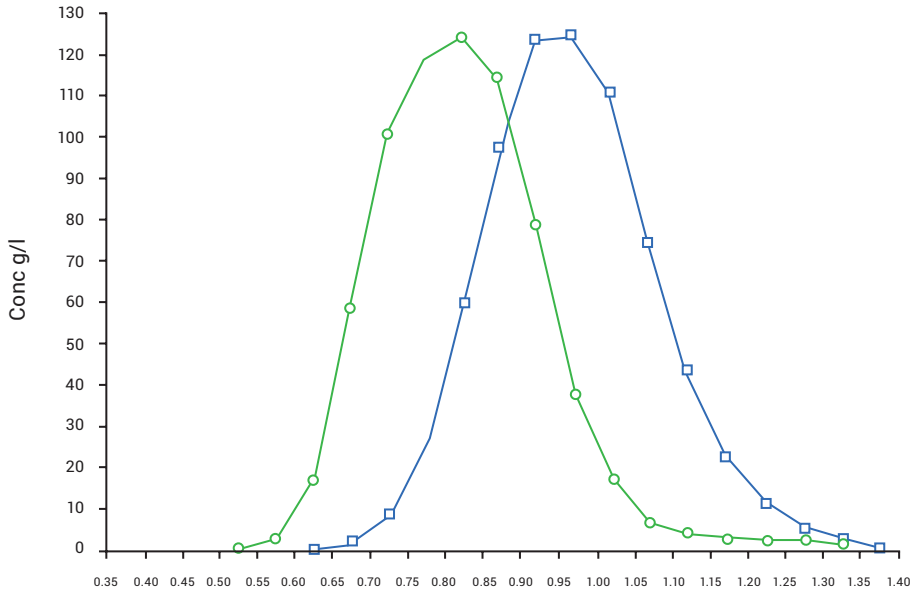
B. Resin shrink/swell

C. Bench resin analysis data
    1. Capacity
    2. Moisture
    3. Crosslinkage
    4. Ionic form
    5. Particle size distribution
    6. Mean particle size

A typical profile for a two component separation is shown in Figure 2.

FIGURE 2

Typical Pulse Test Profile



Feed Loading: 0.2 BV
Feed Concen.: 25% DS
Flowrate: 0.68 gpm/sq ft
Column Temp.: 65 °C
Resin Type: 123
Column Size: 1" x 6'

Ecolab is a global developer, manufacturer, and supplier of Purolite™ Resins including ion exchange, catalyst adsorbent and advanced polymers that make the world cleaner and healthier.

PuroliteResins.com

We're ready to solve your process challenges.

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