Journal of Chromatography A, xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Short communication

Ion exchange column capacities. Predicting retention behavior of open tubular columns coated with the same phase

Weixiong Huang[a], Christopher A. Pohl[b], Purnendu K. Dasgupta[a,*]

[a] Department of Chemistry and Biochemistry, University of Texas at Arlington, Arlington, TX 76019-0065, United States
[b] Themo Fisher Scientific, 490 Lakeside Drive, Sunnyvale, CA, 94085, United States

ARTICLE INFO

Article history:
Received 5 February 2018
Received in revised form 26 March 2018
Accepted 27 March 2018
Available online xxx

Keywords:
Ion exchange capacity
Latex based ion exchangers
Open tubular ion chromatography

ABSTRACT

We discuss the reported capacities of available packed ion exchange columns and the different methods used for their measurement. We outline basic considerations related to both packed and open tubular columns based on ion exchange latex particles.

There is a large body of information covering the retention behavior of packed ion exchange columns based on ion exchange latex particles. We propose a parameter γ_{iex}, which is the ion exchange capacity of a column (packed or open tubular) per unit liquid volume present in the column (including accessible volume within pores) and show that the retention factor for any given ion is directly related to γ_{iex}. On this basis, if based on the same type of latex, the behavior of one type of column can be reasonably predicted from the known behavior of the other, even when the absolute capacities differ by more than 5 orders of magnitude.

1. Introduction

Perhaps the most important characteristics of an ion-exchange (IEX) material is IEX capacity. This can be as high as milliequivalents/gram (meq)/g, for a cation exchange (CEX) material, typically 1 meq/g translates to ~1 meq/mL packed bed. Some analytical CEX columns indeed have a capacity as high as 1.7 meq/mL but most have much lower capacities. The median CEX capacity of some 13 different column types offered by one manufacturer is ~0.46 meq/mL [1] while the median value of 7 CEX column types offered by another manufacturer is 0.01 meq/mL [2]. Yet a third vendor specifies *minimum* capacities (listed as "small ion capacity") directly in meq/mL, the median among 7 CEX columns offered (not based on silica) being 0.1 meq/mL [3]. See Table 1 for a detailed listing. However, the first two manufacturers measure capacity in very different manner: while the first determines capacity mostly by acid-base titration (convert all cation exchange groups to acid form, wash, determine how much standard strong base needs to be passed through the column before un-neutralized base is detected), the second manufacturer passes KCl solution through an H^+-form column and after washing to remove excess, determines the amount of potassium actually held by the column. The two determinations will produce essentially the same value for a strong acid type CEX material but a weak acid type exchanger will produce a higher value by the first measurement method. Neither one of these methods can produce a truly meaningful measure of the capacity available during actual use conditions (which depends on the actual pH and the nature of counter ions present in the eluent). However, as long as it is measured and reported in a consistent manner, at the very least, the results provide a relative measure of capacities of the columns offered by a given manufacturer.

For manufacturer 1, anion exchange (AEX) capacities of some 36 offered stationary phase types tend to be smaller than their CEX counterparts. The AEX capacities range from 6 to 460 μeq/mL (the highest one, intended for specialized carbohydrate analysis, is almost out of the distribution, the next highest one has a capacity of 180 μeq/mL) with a median value of 54 μeq/mL [1]. Capacities per column may be computed from the column volumes, e.g., 0.78 and 3.14 mL, for 250 mm long columns 2 and 4 mm in i.d., respectively. For vendor 2, the reported AEX capacities of 10 columns range from 3 to 62 μeq/mL with a median value of 30 μeq/mL. In its listing [2], this vendor also includes the capacities of two other columns offered by disparate manufacturers, measured by their method, to range from 12 to 19 μeq/mL. The offerings of the third vendor are largely geared to biomolecule separation and generally exhibits much greater capacities, ranging from 100 to 1200 μeq/mL with a median value of 200 μeq/mL [3].

* Corresponding author.
E-mail address: Dasgupta@uta.edu (P.K. Dasgupta).

https://doi.org/10.1016/j.chroma.2018.03.056
0021-9673/

Table 1
Commercial Ion Exchange columns from Major Vendors and their Capacities (Normalized to a 4 × 250 mm size).

Cation Exchange Columns		
Column type	Column Capacity	
	μeq (4 × 250 mm)	μeq/mL packed bed
Vendor 1		
CS5A	20	6.37
CS10	80	25.5
CS11	140[a]	44.6
SCS-1 Sillica	318	101
CS18	1160[a]	369
CS14	1300	414
CS17	1450	462
CS19-4 μm	2410	768
CS19	2410	768
CS15/CS16	2800	892
CS12, CS12A	2800	892
CS20	3000	955
CS16-4 μm/Fast	5370	1710
Vendor 2		
C5	19[b]	6.05
C1	20[c]	6.37
C4	25	7.96
C supp 1	30	9.55
C3	30	9.55
C6	50	15.9
Nucleosil 5 SA	190[c]	60.5
Vendor 3		
SP-STAT		23
SP-5PW		100
CM-5PW		100
Bioassist S		100
CM-STAT		100
SP-NPR		100
SCX[d]		1500

Anion Exchange Columns		
Column type	Column Capacity	
	μeq (4 × 250 mm)	μeq/mL packed bed
Vendor 1		
AS4A-SC	20	6.37
AS17C	30	9.55
CS5A	40	12.7
AS11	45	14.3
CarboPAC PA200	62[e]	19.7
AS14	65	20.7
AS12A	65[f]	20.7
Aminopac PA1	90	28.7
CarboPAC PA100	90	28.7
Fast Anion IIIA	98[e]	31.2
AS7	100	31.8
CarboPAC PA10	100	31.8
CarboPAC PA1	100	31.8
AS14A	120	38.2
CarboPAC PA20 Fast 4 μm	150[g]	47.8
AS16	170	54.1
AS16-4 μm	170	54.1
AS10	170	54.1
AS21	180[a]	57.3
AS9-HC	190	60.5
[m]AS22/AS22 Fast/–4 μm	210[h]	66.9
AS27	220	70.1
AS15	225	71.7
AS19/AS19–4 μm	240	76.4
AS26	250	79.6
AS18/AS18 Fast	285	90.8
AS11HC/AS11HC-4 μm	290	92.4
CarboPAC SA10	290	92.4
AS20	310	98.7
AS23/–4 μm	320	102
AS25	350	111
CarboPAC PA210 Fast 4 μm	350[h]	111
AS28–4 μm	383[h]	122
AS24A	560	178

Table 1 (*Continued*)

Anion Exchange Columns		
Column type	Column Capacity	
	μeq (4 × 250 mm)	μeq/mL packed bed
CaboPAC MA1	1450	462
Vendor 2		
A supp 1	9[i]	2.87
Anion Dual 3	35[g]	11.1
Anion Dual 2	43[j]	13.7
Super Sep	60[k]	19.1
A supp 15	75	23.9
A supp 5	87[h]	27.7
A supp 10	100	31.8
A supp 7	110	35.0
Anion Dual 4	185[g]	58.9
A supp 16	195	62.1
Vendor 3		
Bioassist Q		100
DEAE-5PW		100
DEAE-NPR		100
DNA-NPR		100
Super Q-5PW		130
Q-STAT		270
DNA-STAT		270
SAX[d]		1000
Sugar AXI[d]		1200
Sugar AXG[d]		1200
Misc Vendors		
PRP X100	120	38.2
Star Ion A300	38[l]	12.1

[a] based on available column 2 × 250 mm.
[b] based on available column 4.6 × 150 mm.
[c] based on available column 4 × 125 mm.
[d] poly(styrenedivinylbenzene) based, all other from this vendor are acrylate based.
[e] based on available column 3 × 250 mm.
[f] based on available column 4 × 200 mm.
[g] based on available column 4 × 100 mm.
[h] based on available column 4 × 150 mm.
[i] based on available column 4.6 × 250 mm.
[j] based on available column 4.6 × 75 mm.
[k] based on available column 4.6 × 100 mm.
[l] based on available column 10 × 100 mm.
[m] There may be multiple subtypes of a colum, e.g., Fast or 4 μm, there are no capacity differences.

A larger capacity helps the determination of a trace component with large concentrations of other ions present. There has thus been an ongoing effort to increase column capacities. The average column capacity used in suppressed IC today is an order of magnitude greater than those in the early days [4–6] and the capacities of those originally used for single column IC were even smaller.

In recent years, we have focused on open tubular (OT) ion chromatography (IC) [7–9] and suppression [10], detection [11,12] and imaging [13] systems for the same. The absolute capacities of OTIC columns are very small, of the order of nanoequivalents (neq) per column, because the active phase is typically <200 nm thick and the column inner diameter (i.d.) is <30 μm. Our interest has mostly been in anion exchange columns. We have prepared such columns in much the same manner as many commercial anion exchange columns: by electrostatically attaching positively charged AEX latex particles to a negatively charged surface. Silica itself has surface silanol groups, negatively charged at high pH; it has long been observed that AEX latex particles readily attach to silica surfaces [14–17]. Most polymer surfaces are also negatively charged: either they already have surface —COOH groups or chemical treatment is readily carried out to generate such functionality. Thus, AEX latex particles can be readily attached to polymer capillaries as well [7–9]. Although on bead surfaces positively charged latex particles are captured tenaciously whether the bead is carboxylate or sulfonate functionalized, our experience with various capillary inner

Please cite this article in press as: W. Huang, et al., Ion exchange column capacities. Predicting retention behavior of open tubular columns coated with the same phase, J. Chromatogr. A (2018), https://doi.org/10.1016/j.chroma.2018.03.056