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SIMPLE METHOD FOR THE DETERMINATION OF LOW CATION-EXCHANGE CAPACITY AND THE TITRATION OF CATION EXCHANGERS BY CONSTANT-CURRENT COULOMETRY

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SUMMARY

The determination of the capacity of ion exchangers and their titrimetric curves by coulometry are based on the idea that the electrolyte solutions of the generating electrodes in appropriate concentrations can also serve as the solutions of the counter ions of the ion exchangers. The capacities of Dowex 50 W-X8 resin determined by both the common volumetric and the constant-current coulometric method were evaluated statistically. The difference between the mean values of the two series is not significant at the 95% confidence level. The standard deviation (S.D.), relative standard deviation (R.S.D.) and the confidence interval (C.I.) of the coulometric method are smaller (S.D. 0.131 vs. 0.211; R.S.D. 2.96% vs. 4.73%; C.I. ± 0.104 vs. ± 0.19). The rapid coulometric method was used for the determination of the low capacity (microequivalents per gram) of small amounts (milligrams) of strong cation exchangers. Coulometric titration curves are demonstrated.

INTRODUCTION

Usually the capacity of ion exchangers is determined via an ion-exchange reaction corresponding to the functional group of the resin in question¹⁻³. Approximate capacities can be determined by weighing the same amount of dried exchanger in various forms⁴. The most widely used methods for capacity determination are volumetric methods that make use of the back-titration of the excess of sodium hydroxide or hydrochloric acid in the effluent in the case of cation- and anion-exchange resins, respectively.

The volumetric methods are generally tedious, requiring multiple formation, washing, quantitative elution of the resin column and determination of the exchanged ions.

With the advent of pellicular and low-capacity resins used in ion chromatography and high-performance liquid chromatography (HPLC) systems, new levels of sensitivity and precision are required in capacity determinations. The capacity of these materials⁵ is at least an order of a magnitude less than that of conventional resins. The volumetric methods used for the capacity determinations are not suitable for these

low-capacity resins because an unrealistically large amount of the resin is necessary for the measurement. So far an indirect titration method has been used for the determination of their capacity⁶.

The above requirements prompted the present work to devise a coulometric method for capacity determination. The principle is that the electrolyte solutions of the generating electrodes also act as the counter-ion solutions of the ion exchangers. The 100% current utilization rate is ensured by the Szabellédy method⁷, developed for the determination of small amounts of acids.

EXPERIMENTAL

Materials and apparatus

Strongly acidic Dowex 50W-X8 (200–400 mesh) and phosphorylated Cellex-P cellulose ion exchangers (Bio-Rad Labs., Richmond, CA, U.S.A.) and low-capacity Bondapak-CX/Corasil (Waters Assoc., Milford, MA, U.S.A.) were tested. A Type OH-404 Universal Coulometric Analyser (Radelkis, Budapest, Hungary) was used in the amperostatic operating mode, with automatic potentiometric end-point indication. A platinum plate electrode, Type OH-935, and a silver anode, Type OH-944, were used as generating electrodes, and an OP-800-1/A combined glass electrode was used as indicator electrode (all from Radelkis). A home-made ground-glass joint glass cell with a symmetrical electrode arrangement (25 cm³) was used. Type OP-207 recording pH meter was connected to the amperostat of the coulometer to record the titration curves.

Procedure

The large K⁺ excess in the cathode area ensures that the H⁺ form of the cation exchanger introduced into the cell becomes saturated with K⁺ ions. The H⁺ ions released in this reaction are titrated by OH⁻ ions generated in the cell. From the measured charge used for the OH⁻ generation and the mass of resin introduced into the cell the capacity of the resin can be calculated.

Potassium bromide solution (0.5 M) was filled into the external cathode area and into the anode area separated by a glass frit. Nitrogen was bubbled through the solutions. The control unit and the pH meter was calibrated by Seybold pH 7.00 and NBS 0.05 M potassium hydrogen phthalate buffers.

A few milligrams of air-dried H⁺ form of the resin were carefully weighed and introduced into the cell. All titrations were carried out at a stable generating current setting of less than 10 mA. In order to avoid over-titration, end-point retardation was applied once the titration had proceeded to within 100 mV of the true end-point. This was achieved by decreasing the generating current 10-fold. The delay time of pH-sensing was 5 sec. Carbonate-free sodium hydroxide solution (0.1 M) was used for the comparative volumetric control determinations.

RESULTS AND DISCUSSION

The applicability of the method was tested with strongly and medium acidic cation exchangers.

Determination of the capacity of cation exchangers by potentiometric automatic end-point indicating coulometric titration

In order to compare the conventional and the above-described methods for capacity determination, parallel measurements were carried out on the same batch of Dowex 50W-X8 resin.

The results are shown in Tables I and II. It can be seen that the confidence

TABLE I

VOLUMETRIC DETERMINATION OF THE CAPACITY OF DOWEX 50W-X8 CATION-EXCHANGE RESIN

<i>Resin in the column (g)</i>	<i>Acid (mequiv.)</i>	<i>Capacity (mequiv./g)</i>
0.3063	1.333	4.35
0.3063	1.305	4.26
0.3063	1.319	4.31
0.2915	1.328	4.56
0.2915	1.383	4.74
0.2915	1.374	4.71
0.2971	1.337	4.50
0.2971	1.406	4.73
0.2971	1.362	4.58
0.4298	1.802	4.19
0.4298	1.818	4.23
0.4298	1,821	4.24
	Average:	4.45 ± 0.19 (<i>t</i> = 99%)
	Standard deviation:	0.211
	Relative standard deviation:	4.73%

TABLE II

DETERMINATION OF THE EXCHANGE CAPACITY OF DOWEX 50W-X8 RESIN BY AUTOMATIC END-POINT-INDICATING CONSTANT-CURRENT COULOMETRY

<i>Weight (mg)</i>	<i>Charge (mC)</i>	<i>Acid (μequiv.)</i>	<i>Capacity (mequiv./g)</i>
5.3	2197.7	22.77	4.296
5.3	2248.5	23.30	4.396
4.9	2208.1	22.88	4.669
4.8	2146.8	22.25	4.635
5.0	2137.0	22.15	4.430
4.6	1883.9	19.52	4.243
5.4	2327.1	24.12	4.467
15.5	6615.6	68.57	4.424
13.4	5944.7	61.60	4.597
15.4	6582.8	68.23	4.431
16.0	6865.5	71.16	4.448
16.5	7122.1	73.82	4.474
16.5	6741.1	69.87	4.235
15.8	6661.9	69.05	4.370
	Average:		4.437 ± 0.104 (<i>t</i> = 99%)
	Standard deviation:		0.131
	Relative standard deviation:		2.96%

TABLE III

COULOMETRIC DETERMINATION OF THE CAPACITY OF BONDAPAK-CX/CORASIL PELLICULAR CATION EXCHANGER

Weight (mg)	Charge (mC)	Capacity ($\mu\text{equiv.}/\text{g}$)
70.9	144.4	21.10
70.6	156.0	22.90
49.2	112.3	23.65
65.1	147.3	23.45
46.3	103.5	23.16
48.8	110.8	23.53
46.3	97.4	21.80
Average:		22.80 ± 1.29 ($t = 99\%$)
Standard deviation:		0.975
Relative standard deviation:		4.28%

interval, the standard deviation and the relative standard deviation of the capacity values determined by the coulometric method are smaller. The two series of data were subjected to variance analysis. It could be concluded that the difference between the two mean values is not significant.

The coulometric method is suitable for the investigation of small amounts of resin and is faster than the conventional volumetric method.

Bondapak-CX/Corasil was also examined as a representative of the low-capacity, fast kinetics resin. The results obtained are shown in Table III.

Demonstration of the coulometric titration curves

By connecting the amperostatic unit of the coulometer and the recording pH meter, the above system could be used for the continuous recording of the coulometric titration curves of the ion exchangers (Figs. 1-3).

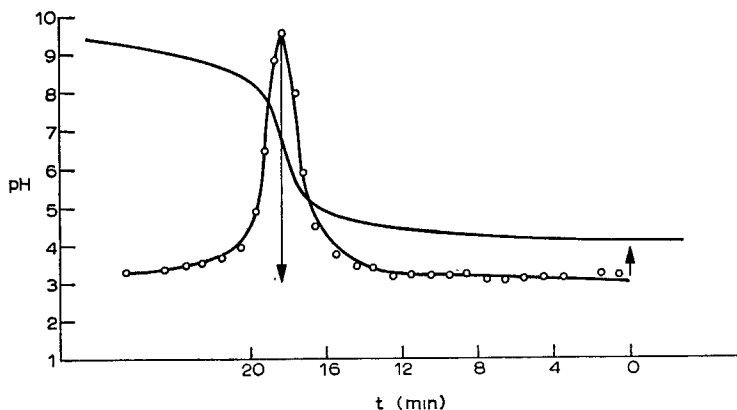


Fig. 1. Recorder trace of the coulometric titration of 20.0 mg of Dowex 50W-X8 cation exchanger. Generating current, 8 mA; —, pH vs. t ; $\circ-\circ-\circ$, $\Delta\text{pH}/\Delta t$ vs. t .

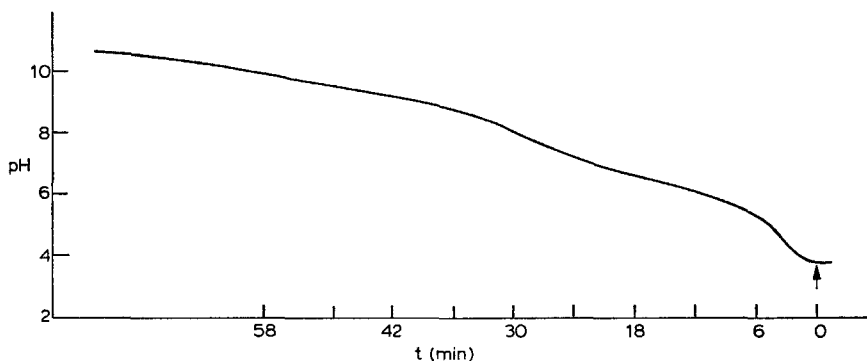


Fig. 2. Recorder trace of the coulometric titration of 120.2 mg of Cellex-P cellulose cation exchanger. Generating current, 4 mA.

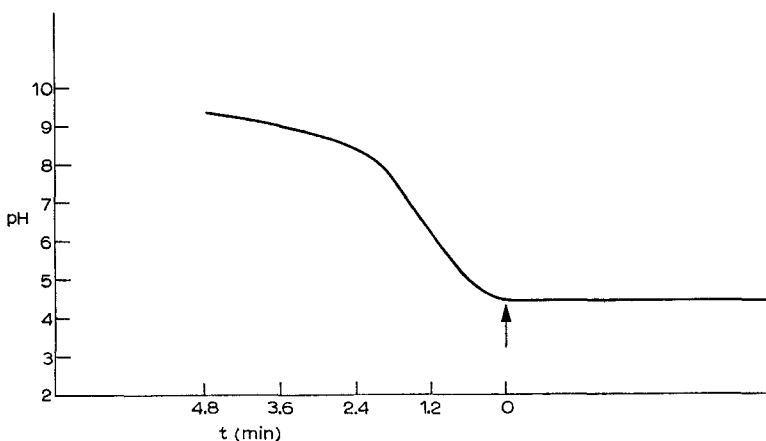


Fig. 3. Recorder trace of the coulometric titration of 202.4 mg of Bondapak-CX/Corasil pellicular cation exchanger. Generating current, 4 mA.

CONCLUSIONS

The constant-current coulometric method developed is suitable for the rapid determination of the ion-exchange capacity of both low- and high-capacity ion exchangers. Statistical evaluation proved that the precision of the method is better than that of conventional methods.

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