Biotechnology and Bioprocess Engineering **2004**, 9: 362-368

Comparing the Performance of One-column Process and Four-zone Simulated Moving Bed by Computer Simulation

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Abstract A new one-column chromatography process, analogous to a four-zone simulated moving bed (SMB), was presented. The basic principle of the process was identical to that of a four-zone SMB. The process consisted of one chromatographic column and four tanks, instead of the four columns in the four-zone SMB (1-1-1-1), and has been used for the separation of two amino acids, phenylalanine and tryptophan, using an ion exchange resin. The operating parameters for the one-column process and four-zone SMB were obtained from equilibrium theory. Computer simulations were used to compare the performances of the new one column process to that of the general four-zone SMB, using Aspen Chromatography™ v 11.1. The differences between the one-column and SMB processes in terms of the purities and yields of phenylalanine and tryptophan were less than 4 and about 6%, respectively. The lower purities of the one-column process were due to the loss of the developed concentration profiles in the column when the liquid was stored in tanks. The one-column process gave great flexibility, and would be useful for reconstructing an existing conventional chromatography process to one of a SMB.

Keywords: simulated moving bed, one-column process, computer simulation, amino acid

INTRODUCTION

Simulated moving bed (SMB) technology has been used for decades in the petrochemical and sugar industries [1,2]. SMB has recently become of increasing interest for application to new areas, and has been adopted for separation of bio-products and fine chemicals, such as proteins [3], amino acids [4,5], organic acid and enantiomers [6,7]. The SMB process is an especially powerful tool for the fractionation of enantiomers, due to their inherent attributes (binary mixture), and for the development in chiral stationary phases.

SMB system simulates continuous countercurrent chromatography between the mobile and the stationary phases. The concept of SMB is best understood in terms of a true moving bed (TMB) system. A four-zone TMB system is presented in Fig. 1. The feed is continuously supplied to the center of the column, with the mobile phase flowing upward, and the solid phase flowing downward. The lower affinity solute (B) moves in the direction of the mobile phase, while the higher affinity solute (A) moves in the counter direction; A is withdrawn at the extract port and B at the raffinate port, as illustrated in Fig. 2. A continuous counter-current flow, with a series of packed columns, is simulated by periodically advancing the inlet and outlet ports along the solvent flow direction [8].

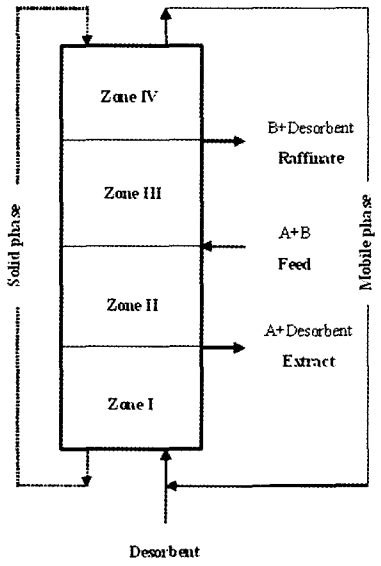

Fig. 1. Four-zone true moving bed (TMB) system.

The main advantage of SMB chromatography, over that of batch chromatography, is that a continuous mode operating [9] chromatographic separation can achieve a high yield and purity, with low desorbent and adsorbent

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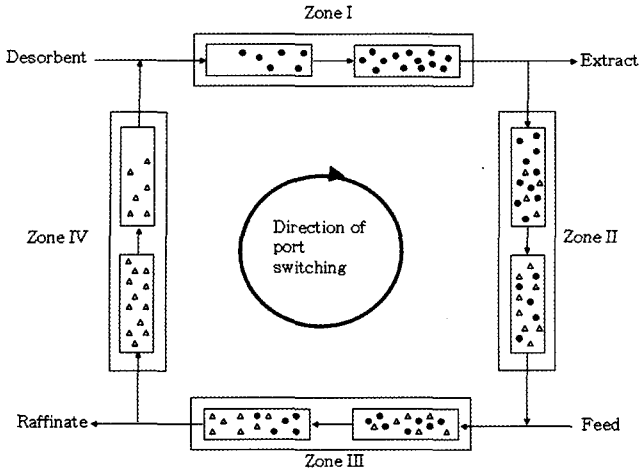

Fig. 2. Schematic diagram of a four-zone Simulated Moving Bed.

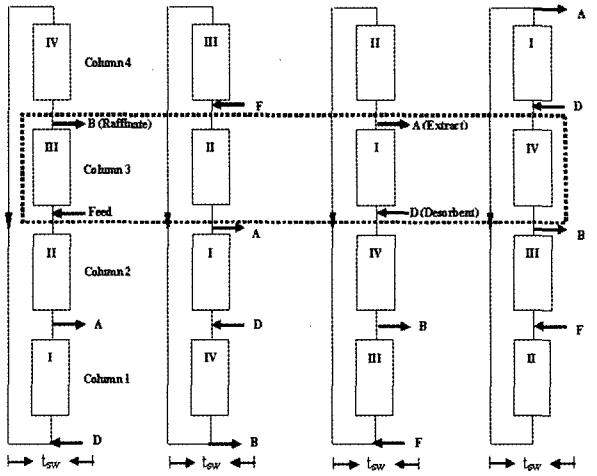

Fig. 3. Schematic diagram of a four-zone SMB, with one column per zone, during one cycle.

consumption. The main drawback is the expensive fixed costs and complex process operation. These disadvantages are overcome by studying different classical four-zone SMB schemes, applying modified operation and optimization strategies for the SMB process, and developing computer simulations. Many different classical four-zone SMB schemes and modified operation strategies have been studied. Ching *et al.* [10] compared a classical four-zone SMB with a three-zone SMB system, and with the five-zone SMB of Navarro *et al.* [11], the nine-zone SMB of Ma and Wang [12], for separating ternary mixtures, with the nonsynchronous switching of the inlet and outlet ports, otherwise known as the Varicol process of Ludemann-Homburger *et al.* [13], the temperature gradient operation of Morbidelli *et al.* [14] and the partial feed of Zang and Wankat [15].

In this study, a novel process, able to simulate a conventional four-zone SMB (1-1-1-1) system, using a single column and four tanks, has been proposed. This "one-column process" would be more economic and easier to apply to industrial applications due to the simplicity of the process equipment. An additional advantage over the SMB process is the homogenous column conditions. All of the columns in a SMB process should be identically packed, otherwise this can cause errors. The operating conditions were obtained using equilibrium theory, assuming a negligible mass transfer resistance. The flow rate ratio selection was achieved using the "triangle theory" developed by Morbidelli *et al.* [16,17]. The performance of the one-column process was compared, by simulation, with a four column four-zone SMB.

THEORY

One-column Process

The one-column process was developed on the basis of a conventional SMB process, divided into four zones, with one column per zone. A cycle of the conventional SMB process consists of four switching periods, as shown in Fig. 2. Every column plays a different role in each switching period. For example, column 3 plays the role of zone III during the first switching period, zone II during the second switching period, zone I during the third switching period and zone IV during the fourth switching period. A column can perform the role of four zones during one cycle, *i.e.* four switching period. This is the key concept of the one-column process. To keep the effluent from the column during a cycle, four tanks are proposed, so a single column can perform as a SMB. A simplified schematic diagram of the one-column process is given in Fig. 3, with the arrangement for the one-column process simulation shown in Fig. 4. The system consists of two solenoid valves and two time controllers for flow path control, and four tanks for effluent storage. In the process, a complete cycle consists of four switching periods. In the first switching period of a cycle, the feed and solution from T_2 simultaneously enter the column. The effluent from the column is collected to the raffinate and T_1. In the second switching period, the solution in T_3 enters the column, and effluent from the column is stored in T_2. In the third switching period, desorbent and the solution in T_4 enter the column, and the effluent from the column is collected at the extract and to T_3. In the last switching period, the solution in T_1 enters the column, and the effluent from the column is stored in T_4. The feed and desorbent were periodically pumped into the column. Samples were also periodically collected during the first and third periods of each cycle. As T_1 receives solution from T_2 for the first period, all the tanks, except T_1, were initially filled with DI. The solution in a tank was introduced into a column, and had a uniform concentration as each tank was thoroughly mixed.

Models

An equivalent countercurrent model was used, which

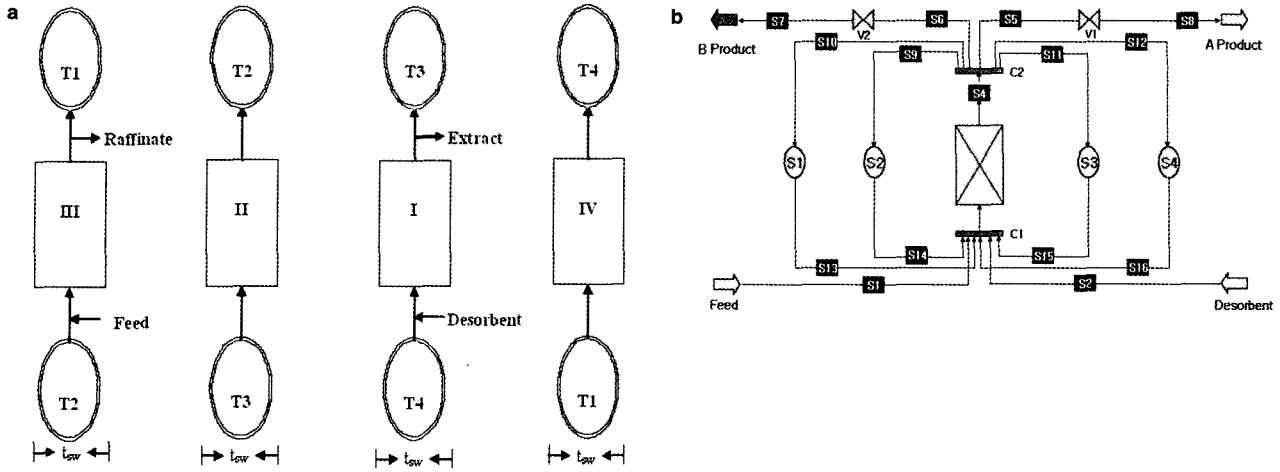

Fig. 4. (a) A simplified diagram of the one-column process, using a single column and four tanks. (b) Physical arrangement of the one-column process.

assumed solid particles flow counter-currently to the direction of the fluid flow along the column [18]. The material balance equations are as follows:

$$\varepsilon^* \frac{\partial C_i}{\partial t} + (1-\varepsilon^*)\frac{\partial q_i}{\partial t} + v_l \frac{\partial C_i}{\partial Z} = \varepsilon^* E_z \frac{\partial^2 C_i}{\partial Z^2}$$

$$\frac{\partial q_i}{\partial t} = K_f (q_i^* - q_i)$$

$$q_i^* = f_{eq}(C_i)$$

where C_i and q_i are solute concentrations of the mobile and solid phases, respectively, v_l the superficial velocity of the fluid, ε^* the total column porosity, E_z the axial dispersion coefficient, K_f the lumped mass transfer coefficient and q^* represents the adsorbed phase concentration at equilibrium with the mobile phase. The lumped mass transfer parameter, assuming a linear driving force, was used as the mass transfer between mobile and solid phases.

Design of Operating Conditions

The operating parameters were chosen to achieve successful operation in terms of maximum productivity and minimum desorbent consumption. The triangle theory, developed by Morbidelli's group [16], was used, which suggests operating conditions that lead to a complete separation of the products, based on the relative flow rates of the fluid and solid phases. The designs of the operating conditions of the SMB units have been developed under ideal conditions, where the mass transfer resistance and axial dispersion are neglected. The optimum operating conditions for the SMB and one-column processes in this study were obtained using the triangle theory. The separation performance was controlled by the flow rate ratios between each zone of the SMB unit.

$$m_j = \frac{Q_j t^* - V\varepsilon^*}{V(1-\varepsilon^*)}$$

where m_j is the flow rate in the four zones of the SMB, Q_j the volumetric flow rate in zone j, V the volume of the column and t^* the switching time. The complete separation region is defined by m_2 and m_3, which are independent of m_1 and m_4. The detailed condition of constraints has previously been presented in the literature [17]. The triangle theory is acknowledged as one of the most effective tools for SMB design. Although the theory neglects the mass transfer resistance and axial dispersion, it provides a useful starting point for SMB experiments. The purity and yield are obtained by the following equations:

$$P_{Phe} = \frac{C^R_{Phe}}{C^R_{Phe} + C^R_{Trp}} \qquad P_{Phe} = \frac{C^R_{Phe}}{C^R_{Phe} + C^R_{Trp}}$$

$$Y^R_{Phe} = \frac{R \times C^R_{Phe}}{R \times C^R_{Phe} + E \times C^E_{Phe}} \qquad Y^E_{Trp} = \frac{E \times C^E_{Trp}}{E \times C^E_{Trp} + R \times C^R_{Trp}}$$

where E and R are abbreviations for the extract and raffinate flow rates, respectively.

RESULTS AND DISCUSSION

The separation of two amino acids [4,5], phenylalanine and tryptophan, was used in a simulation to compare the one-column and conventional SMB processes. The mass transfer coefficients were obtained from Wilson-Geankoplis correlation, and the adsorption isotherms of the two amino acids from previous work [4].

$$q_{Phe} = \frac{1.61 C_{Phe}}{1 + 0.01534 C_{Phe} + 0.16103 C_{Trp}}$$

$$q_{Trp} = \frac{10.73 Grp}{1 + 0.01534 C_{Phe} + 0.016103 C_{Trp}}$$

As the basic principle of the one-column process is identical to that of the four-zone SMB, the operating parameters for the simulation of both processes were iden-

Table 1. System parameter for the four column, four-zone SMB and the one-column SMB processes

System parameter	
Column length (cm)	21.6
Column internal diameter (cm)	2.5
Liquid viscosity (cP)	0.89
Mass density of eluent (kg/m^3)	1000
Interparticle porosity (ε_i)	0.35
Intraparticle porosity (ε_p)	0.55
Adsorbent particle radius (μm)	211
Bed density (kg/m^3)	530
Feed concentration (mg/mL)	
Phenylalanine	2.0
Tryptophan	1.0
Mass transfer coefficients (min^{-1})	
phenylalanine	1.83
tryptophan	1.83

tical, and are listed in Table 1. The operating conditions, such as the flow rates of each zone and the switching times, for the one-column and SMB processes were obtained using the triangle theory, which neglects the mass transfer resistance and axial dispersion. The computer simulator used in this work was that of Aspen Chromatography™, which considers the mass transfer resistance and axial dispersion. The triangle theory is a design method for separation under ideal conditions in a SMB process. Hence, the complete separation region in a simulation should be smaller than that under the ideal conditions obtained by the triangle theory. In order to obtain high purity and yield in a simulation, eight points inside the triangle were chosen (A~H), with the SMB and one-column processes simulated by Aspen Chromatography™. The feed flow rate was fixed at 5 mL/min. The flow rate of each zone and the switching time (A~H) are

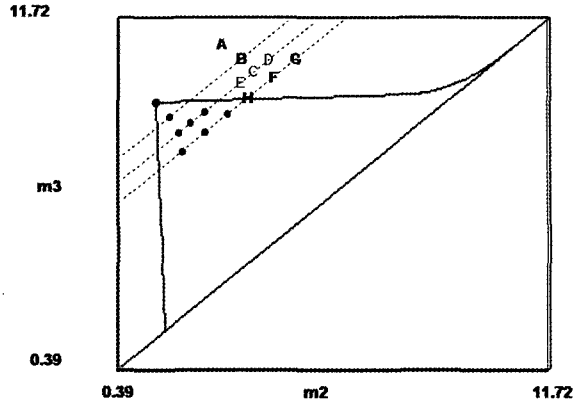

Fig. 5. Complete separation region in the (m_2, m_3) plan for amino acids.

presented in Table 2. The triangle region, based on the system parameters [19] and isotherms of the two amino acids, is presented in Fig. 5. The values of m_2 and m_3, shown in Fig. 5, were A (1.393, 9.004), B (1.799, 8.650), C (2.248, 8.338), D (2.611, 8.700), E (1.886, 7.976), F (2.611, 7.9382), G (3.184, 8.514) and H (2.034, 7.362). The simulation results of the SMB and one-column processes are summarized in Table 3. The differences in the purities and yields between the one-column and SMB processes for the phenylalanine and tryptophan were less than 4 and about 6%, respectively, based on the points A~H. Further, point F was selected to compare the concentration profiles of the extract and raffinate and the effluent histories of both processes. According to Figs. 6(a) and (b), the one-column process almost reached a cyclic steady state after the seventh cycle, while this was attained after the second cycle of the SMB process. This is the reason the one-column process has a discontinuous average concentration built into the tank losing separation, instead of maintaining a concentration profile, as in the column of the SMB process. Fig. 6 shows similar results for the two processes, which are the SMB histories of the raffinate (a) and the extract (b) profiles at point F.

Table 2. Summary of operation parameters for four column four-zone SMB and one-column process at point A~H

	Q_I	Q_{II}	Q_{III}	Q_{IV}	t_{sw} (min)
A	8.63	2.50	7.50	2.61	47.21
B	9.60	3.08	8.08	2.91	42.49
C	10.79	3.83	8.83	3.27	37.77
D	10.80	4.13	9.13	3.27	37.77
E	10.79	3.53	8.53	3.27	37.77
F	12.34	4.72	9.72	3.74	33.05
G	12.34	5.26	10.26	3.75	33.05
H	12.34	4.18	9.18	3.74	33.05

Table 3. Summary of simulation results for SMB and one-column SMB at point A~H

	P_{Phe} (%)		P_{Trp} (%)		Y_{Phe} (%)		Y_{Trp} (%)	
	SMB	One-Column	SMB	One-Column	SMB	One-Column	SMB	One-Column
A	93.1	90.7	86.7	80.8	93.4	90.3	86. 2	81.6
B	93.8	91.3	89.3	83.0	94.7	91.6	87.5	82.5
C	94.3	91.7	90.9	85.1	95.6	92.7	88.5	83.2
D	93.4	90.6	92.1	87.0	96.3	94.0	86.5	80.5
E	95.0	92.6	89.0	82.6	94.4	91.0	90.1	85.6
F	94.8	92.3	91.4	86.0	95.8	93.1	89.5	84.4
G	93.5	90.5	92.6	88.1	96.5	94.1	86.6	80.1
H	95.7	93.6	88.9	82.3	94.3	90.6	91.6	87.7

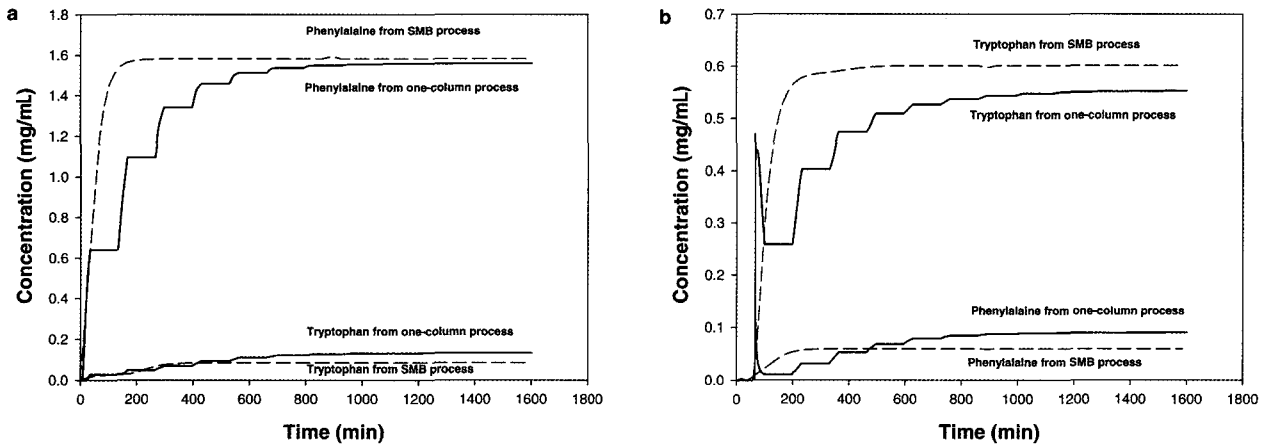

Fig. 6. Comparison of the effluent histories in the one-column and SMB processes at the raffinate port (a) and extract port (b). The solid and dashed lines are for the one-column and SMB processes, respectively.

Before the process reached a cyclic steady state, the concentration steadily increased. In the one-column process, the average concentration of the effluent collected by the tanks showed a stepwise increase. Also, the one-column process led to a loss in the recovery yield and an increase in contamination in the extract and raffinate. At the raffinate port, the concentration of the phenylalanine in the one-column process was 0.04 g/L lower than that of the SMB process, but that of the tryptophan was 0.04 g/L higher. This means that in the one-column process the contamination of the tryptophan at the raffinate was higher than that in the SMB process. At the extract port, the concentration of the phenylalanine in the one-column process was 0.03 g/L higher than that of the SMB process, but that the tryptophan was 0.04 g/L lower. The effluent histories of the one-column and SMB processes are shown in Fig. 7. In the one-column process, the column effluent histories are the same as the concentration profiles entering the tanks. Therefore, the average concentrations of the profiles during each period corre-

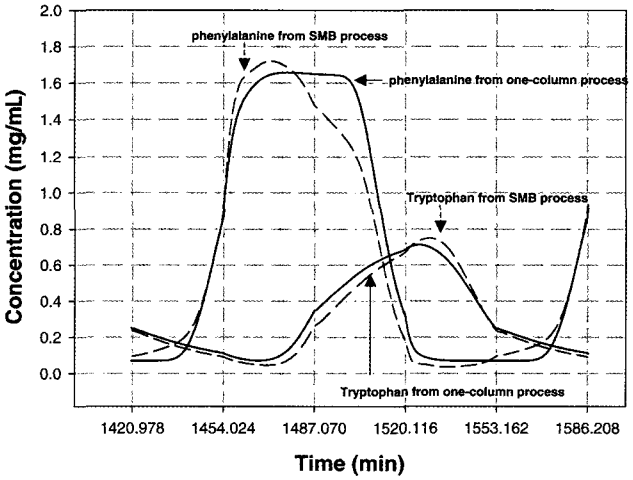

Fig. 7. Comparison of the effluent concentration profiles in the one-column and SMB processes. The solid and dashed lines are for the one-column and SMB processes, respectively.

sponded to the concentrations of each tank.

CONCLUSION

A one-column process was developed to simulate a four-zone SMB, using just one column and four storage tanks. A systematic design for the one-column process was carried out for the separation of two amino acids, phenylalanine and tryptophan. The process was compared with a four-zone SMB by a computer simulation using Aspen Chromatography™. The differences in the purities and yields for phenylalanine and tryptophan between the one-column and SMB processes were less than 4 and about 6%, respectively. In general, the purity of the one-column process was lower than that of a conventional SMB, due to the concentration profiles developed in the column being lost when the solution was stored in tanks. The separation would be improved by using additional tanks to reduce the mixing in each tank. The SMB process clearly has advantages if very high purities are required, but the one-column process has several advantages compared to conventional SMB process. The one-column process has powerful flexibility, in that various configurations of the SMB can be applied by the one-column process. For example, an 8 column four-zone SMB (2-2-2-2) can be applied using a single column and eight tanks. In addition, the one-column process has a simple design and is inexpensive. The one-column process can be applied for the reconstruct of an existing conventional chromatography to a SMB process.

Acknowledgement This study was supported by the ERC for the Advanced Bioseparation Technology, KOSEF.

NOMENCLATURE

C = Solute concentration of mobile phase (g/L)
D = Desorbent flow rate (mL/min)
D_p = Effective intraparticle diffusivity (cm^2/min)
D^∞ = Brownian diffusivity (cm^2/min)
E = Extract flow rate (mL/min)
E_p = Effective pore diffusivity (cm^2/min)
E_z = Axial dispersion coefficient (cm^2/min)
F = Feed flow rate (mL/min)
K_f = Film mass transfer coefficient (min^{-1})
m_j = Ratio of mobile phase flow rate over stationary phase flow rate in zone j
Q_j = Volumetric flow rate in zone j (mL/min)
q = Solute concentration adsorbed (mg/mL solid volume)
q^* = Adsorbed phase concentration at equilibrium with the mobile phase (g/L)
R = Raffinate flow rate (mL/min)
Re = Reynolds number
t^* = Switching time (min)
V = Total column volume (mL)
$V_{F,i+1}$ = Retention volume of the inflection point of $(i+1)$ front (mL)
V_0 = Column void volume (mL)
V_D = The system dead volume (mL)
V_a = The volume of adsorbent in the column (mL)
v_l = Superficial velocity of the fluid (cm/min)
ε_i = Interparticle porosity
ε_p = Intraparticle porosity

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[Received May 3, 2004; accepted September 2, 2004]