Table I. Phytosterols of *Cannabis* Smoke

	%	mg of sterol/g of *Cannabis* smoked
Campesterol	16.1	0.0092
Stigmasterol	14.2	0.0081
β-Sitosterol	69.6	0.0806

marihuana was concentrated to a viscous oil weighing 6.24 g. The entire sample was taken up in 80% ethanol, stirred, and allowed to stand under refrigeration for several hours before being filtered. The precipitate was washed with 80% ethanol, and 5 ml of hot 2% digitonide in 80% ethanol added. The solution was concentrated under reduced pressure to an oil that was then allowed to cool gradually and to stand overnight. The digitonide was filtered onto a weighed sintered glass filter funnel and washed with 80% ethanol, and subsequent washing with ether gave a white solid that was satisfactory for successive treatment. The sintered funnel and sample were dried by heating at 90° for 2 hr and placed into a desiccator upon removal from the oven. After reaching ambient temperature the weights of the funnel and sample were taken and the sample weight determined: 0.1589 g of digitonide or 40.2 mg of sterols (Wall and Kelley, 1974). The sterols were isolated for gas chromatography by decomposing the digitonide with 20 ml of hot Me_2SO and extracting the cooled mixture with three 25-ml portions of hexane. The combined hexane fraction was dried ($MgSO_4$) and concentrated. The resulting solid was then made to volume in tetrahydrofuran and aliquots were subjected to gas chromatographic analysis (Grunwald, 1970; Foote and Jones, 1974). Samples were injected into a gas chromatograph (Beckman GC-45) using a flame ionization detector. The sterols were separated in a 10 ft × 4 mm glass column packed with 5% OV-101 on Gas Chrom-Q, 80–100 mesh, with a column temperature of 275° and helium carrier gas flow of 75 cm^3/min at 34 psi. Samples were injected on-column and quantitative analysis was performed by electronically integrating the peaks. The relative weight response was determined from synthetic mixtures. Only campesterol, stigmasterol, and β-sitosterol were found in the sterol fraction of the smoke from MS-13 plant material. The calculated levels of individual sterols presented in Table I are essentially of the same ratio as those in the free phytosterol fraction of the plant material (Foote and Jones, 1974) smoked in this study.

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Extraction Rate Equations for Paprika and Turmeric with Certain Organic Solvents

In order to describe concentration–time data obtained from spice extractions, it was necessary to derive extraction rate equations using a kinetic, rather than an equilibrium, approach. Three types of rate-limiting steps were tried, simple first order, diffusion controlled, and one in which the rate included a term that increased with time. The last case led to the following equation which appears to fit the data reasonably well, $c/c_0 = (1 + 2\gamma t^*) \exp[-k_1 t^*(1 + \gamma t^*)]$, where t^* is time after the start of elution from the bed, c_0 and c are initial concentration and concentration at t^*, respectively, and k_1 and γ are constants.

During a study of the rates at which various solvent systems were capable of extracting the pigment of paprika (about 46% capsanthin, 20% β-carotene, 20% zeaxanthin, 8% kryptoxanthin, and 6% capsorubin; Andre, 1973), it became apparent that it would be useful to have mathematical expressions with which to represent time–concentration data and from which "rate parameters" could be deduced. However, an examination of the literature failed to reveal expressions suitable for use for extractions of interest. From plots of the time–concentration data it appeared that for a few extractions a simple semilog representation was satisfactory, but for others a more complex representation would be required. Therefore, the objective of this work was to derive the mathematical models necessary to describe the extraction data. Since the concentration of extract eluting from the paprika bed was well below that necessary for saturation, a kinetics (rather than an equilibrium) approach was taken similar to that used for systems in which one of the reactants is a solid, e.g. polymer pyrolyses, metal oxidations, catalyst poisonings, etc. Three types of rate-determining steps were considered. (a) The first is a simple first-order process, i.e. the rate of extraction is proportional to the mass concentration of extract in the bed. (b) The second is a process controlled by diffusion of solvent into or solute out of the solid particles, which results in the rate being inversely proportional to the extent of reaction, similar to metal oxidations which form nonvolatile oxides. (c) The third is a process in which the measured concentration initially decreases less rapidly (or may possibly increase for a short time) than would be predicted from the treatment in a. Case c was necessary to treat the data from the spice ex-

tractions and may be caused by a change in the structure of the solid brought about by soaking with the solvent, thus leading to a rate term which increases with time.

NOTATION

The following symbols were used: λ, void fraction in solid bed, volume rate of solvent flow $\times$ time to pass through bed/total volume of the bed; v, linear velocity of solvent through bed, centimeters per minute; t, time, minutes; t^*, time after elution starts $(t - L/v)$; x, distance from the entrance to the bed, centimeters; L, length of solid bed, centimeters; m, mass concentration of extract in solid bed, grams per cubic centimeter; m_0, initial m, $t = 0$; c, mass concentration of extract in solvent, grams per cubic centimeter; k_i, extraction rate constants; subscripts and units depend on the rate-controlling process in each case. For the quantities m and c, cubic centimeter represents the total volume of the bed including both voids and solids. Thus, the actual concentration of extract in the solution leaving the bed equals c/λ.

DERIVATION OF THE EXTRACTION EQUATIONS

The physical conditions of the extraction experiments have certain similarities to those which pertain to the case of irreversible adsorption treated previously by Chu and Houser (1964); hence, the approach used in this study will be essentially the same. Specifically in both cases a fluid passes over a fixed, solid bed and as it moves one of the components in the fluid changes concentration by interacting with the bed. However, in the case of extraction, the mathematical treatment is significantly simplified because for a solution far from saturation, the rate at which the mass of extract in the solid changes is independent of extract concentration in the solvent. If attention is focused on a small element of volume at a given position, x, in the bed, the rate at which mass is extracted from the solid must be equal to the rate of extract concentration change in the solvent. Thus:

$$-(\partial m/\partial t) = (dc/dt) \tag{1}$$

However, concentration is differentiated totally, rather than partially, with respect to time since it is a quantity in a moving stream, and hence, has a convective part as well as the usual nonconvective part, *i.e.*:

$$(dc/dt) = (\partial c/\partial t) + v(\partial c/\partial x) \tag{2}$$

Combining eq 1 and 2 results in the differential equation to be solved for the concentration dependence on time and distance:

$$(\partial c/\partial t) + v(\partial c/\partial x) = -(\partial m/\partial t) \tag{3}$$

In this derivation it has been assumed that the temperature, linear velocity of solvent, v, and the void fraction, λ, are constant during the extraction.

The rate of extraction at any position in the bed is given by eq 4:

$$(\partial m/\partial t) = f(m,t) \tag{4}$$

The $f(m,t)$ will depend on the specific assumptions applied to the extraction process, and since the extract concentration eluting from the bed is much less than that of saturation, these functions will not depend on c.

To obtain boundary and initial conditions, it is noted that eq 3 and 4 are defined in the (x,t) plane only between the lines $x = 0$ and $x = L$, and for $x \leq vt$. Hence, the proper conditions can only be prescribed on the lines $x = 0$ and $x = vt$. It is apparent that $c = 0$ at $x = 0$ when starting with fresh solvent, and that c is proportional to x/v on the line $x = vt$ since this ratio represents the time the solvent is in contact with fresh bed. This latter

boundary condition must be consistent with the $f(m,t)$ used in eq 3.

In addition to the boundary and initial conditions, it is necessary to transform the time variable to include bed position and fluid velocity. Since the mass of extract remaining in the bed at a particular bed position depends only on the length of time the bed at that position has been exposed to the solvent, the effect of increasing x, or decreasing v, is to decrease the time of exposure for a given clock time, t. Therefore, if $m = f(t)$ at $x = 0$, then $m = f(t - x/v)$ for all x, which results in $(t - L/v) = t^*$ as the time after the start of elution from the bed.

FIRST-ORDER EQUATION

The first-order rate is the simplest to treat and eq 4 can be written

$$(\partial m/\partial t) = -k_1 m \tag{5}$$

which has the solution

$$m = m_0 \exp(-k_1 t) \tag{6}$$

for $m = m_0$ at $t = 0$. Combining eq 3, 5, and 6 and including the above variable transformation gives

$$(\partial c/\partial t) + v(\partial c/\partial x) = k_1 m_0 \exp[-k_1(t - x/v)] \tag{7}$$

the solution of which is (Hildebrand, 1965):

$$c = (k_1 m_0 x/v) \exp[-k_1(t - x/v)] \tag{8}$$

It can be seen by direct substitution that eq 8 is a solution to eq 7 and that the boundary and initial conditions are satisfied also. If the first-order assumption applies to the extraction then a plot of log c (or physical parameter proportional to c) vs. t^* will be linear with the absolute value of the slope equal to k_1.

DIFFUSION LIMITED EQUATION

If diffusion of the extract out of the solid particles (or of solvent into these particles) is rate limiting, then as the extract closer to the surface is removed, that which remains will be extracted more slowly than eq 8 would predict. Under these conditions the rate of extraction will be inversely proportional to the fraction extracted (similar to metal oxidations in which a covering layer of oxide is formed) and eq 4 will be of the form

$$(\partial m/\partial t) = -k_d m_0/(b + m_0 - m) \tag{9}$$

It is necessary to include the constant, b, so that the rate does not approach infinity at $t = 0$ when $m = m_0$. However, b is assumed small and is usually neglected in the solution of these rate equations (Laidler, 1965). Neglecting b, the solution to eq 9 is

$$m = m_0 - (2k_d m_0 t)^{1/2} \tag{10}$$

Combining eq 3, 9, and 10 and including the transformation of variable gives

$$(\partial c/\partial t) + v(\partial c/\partial x) = k_d m_0/\{b + [2k_d m_0(t - x/v)]^{1/2}\} \tag{11}$$

the solution of which is

$$c = k_d m_0 x/v\{b + [2k_d m_0(t - x/v)]^{1/2}\} \tag{12}$$

The validity of this equation can be verified as was eq 8. If diffusion is rate limiting then a plot of $1/c$ vs. $t^{*1/2}$ should be linear, the slope of which will depend on k_d and m_0.

TIME-DEPENDENT RATE EQUATION

The extractions of the red pepper were not described by either of the previous concentration–time equations. Semilog plots of these data indicated that a time-squared term

in the exponential could possibly be fruitful in describing the experimental results. Such a term can be introduced by assuming the rate is proportional to time, which may come about from a soaking effect, *i.e.* penetration of the solvent could cause the structure of the solid to expand as evidenced by the softening of the particles, thus allowing for a more rapid extraction. However, m must be included in the rate term also, since as the extract is removed from the solid the rate will decrease.

With this assumption eq 4 has the form

$$(\partial m/\partial t) = -k_1 m - 2k_s mt \qquad (13)$$

which, if $m = m_0$ at $t = 0$, has the solution

$$m = m_0 \exp[-k_1 t - k_s t^2] \qquad (14)$$

The first term in eq 13 is necessary since the rate of extraction from the surface, *i.e.* $t = x/v$, would not be zero. Combining eq 3, 13, and 14 and transforming the time variable yields

$$(\partial c/\partial t) + v(\partial c/\partial x) = [k_1 + 2k_s(t - x/v)]m_0$$
$$\exp[-k_1(t - x/v) - k_s(t - x/v)^2] \qquad (15)$$

which has the solution (verifiable as before)

$$c = [k_1 + 2k_s(t - x/v)]m_0 x/v$$
$$\exp[-k_1(t - x/v) - k_s(t - x/v)^2] \qquad (16)$$

It can be seen that it would not be possible to produce linear plots of functions of c vs. t^*. However, eq 16 can be reduced to a more usable form if $k_s = \gamma k_1$ and at $t^* = 0$, $c_0 = k_1 m_0 x/v$ which results in

$$c/c_0 = (1 + 2\gamma t^*) \exp[-k_1 t^*(1 + \gamma t^*)] \qquad (17)$$

Thus, by comparing the calculated fractional change in concentration (or in a property such as absorbance) as a function of t^* for different values of k_1 and γ to those obtained experimentally, the values of the extraction constants and functional form of the equation can be tested.

APPLICATION OF THEORY TO SPICE EXTRACTION DATA

Experimental. The spice extraction experiments were carried out at $23 \pm 1°$ using a vertical, cylindrical bed of ground raw material, the particles of which passed through a 30 mesh ASTM screen (a particle size distribution is not available); the velocity of the solvent was maintained constant by a constant fluid pressure head above the bed. The bed size was 35.0 cm $(L) \times 5.0$ cm and contained 150 g of paprika or 200 g of turmeric. The void fractions were determined (from the volume rate of flow of solvent, elution time, and bed volume) to be 0.15 for paprika and 0.32 for turmeric.

The absorbance measurements of the solutions were made using a Beckman B spectrophotometer at 460 nm for paprika and 425 nm for turmeric; therefore, the concentration ratios (absorbance/initial absorbance) reported are for the coloring agents in these materials, primarily curcumin for turmeric (Deline, 1973). During the experiments, small samples of the eluting solution were taken at the reported times, then diluted by a factor of 500 for these measurements.

Results and Discussion. The application of eq 17 to the experimental extraction results is illustrated by the summary of calculated and experimental concentration ratios listed in Table I. The equation appears to be a valid description of time–concentration data for elution times long enough to produce c/c_0 values as low as 0.05.

In general, from eq 13 and 17 it would be predicted that large values of k_1 and k_s would result in rapid extractions. Large values of k_1 will lead to a large c_0; however, this

Table I. Extraction Rate Constants

Solvent	k_1, min^{-1}	$k_s \times 10^3$, min^{-2}	t^*, min	c/c_0 (exptl.)	c/c_0 (calcd.)
Paprika					
Hexane	0.200	6.0	3.67	0.58	0.54
			7.25	0.25	0.25
			10.75	0.100	0.096
			14.34	0.031	0.031
20% EDC^a	0.075	1.12	4.55	0.79	0.79
			9.05	0.60	0.59
			13.33	0.46	0.42
			17.50	0.30	0.29
			21.75	0.19	0.19
			30.33	0.07	0.07
			47.9	0.005	0.005
Turmeric					
Methyl acetate	0.14	2.8	3.75	0.65	0.65
			7.17	0.42	0.41
			10.42	0.26	0.24
			13.50	0.14	0.14
			16.58	0.056	0.076

^{a} The solvent was a solution of hexane and 20 vol % ethylene dichloride (EDC).

would be followed by a rapid drop in concentration as t^* increases. Large values of k_s will reduce the rate at which the concentration decreases at small values of t^*. In fact, if this constant is large enough, an increase in eluting concentration may occur for a short time, followed by an even more rapid drop in concentration than that obtained with only a large k_1.

It can be concluded that eq 17 appears to fit the spice extraction data reasonably well. However, in view of the complexity of the system being examined it is possible that eq 17 may be only an empirical correlation. Additional data are required to verify the validity of the equation and its mechanistic implications.

In addition, it is believed that eq 8 and 12 may be useful in describing extraction data for other chemical systems. For example, the extraction data for iodine adsorbed on silica gel with benzene by Tovbin (1962) appear to be described by an equation similar in form to eq 8. Unfortunately, the conditions under which the experiments were conducted were not described in sufficient detail to verify this mathematical form. However, it does indicate that these equations may have wider utility.

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