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Direct Tabular Method for Obtaining the Order of a Reaction of a Restricted Class

Abstract. When the rate law of a process can be written in the form $X' = dx/dt = -kX^m$, the order $m = XX''/(X')^2$ may be calculated directly, in lieu of the usual trial-and-error methods. An analytical method is used to calculate the derivatives X' and X'' from the collected data, X, and t.

Commonly, a trial-and-error procedure is employed for finding the order of a reaction (*1*). It should be possible to obtain the order directly (*2*) for reactions of that restricted class whose rate equation may be written in the form

$$x' = -kx^m \qquad (1)$$

Upon differentiating with respect to time, and rearranging, this becomes

$$m = x'' x/(x')^2 \qquad (2)$$

Data are usually collected as concentrations and so forth (that is, x), and the two differentiations can be performed by the tabular method (*3*, p. 455). Where the rates of change (that is, x') are the collected data, tabular methods of integration are available (*3*, p. 456; *4*, p. 94) for calculating x values.

In the example shown here the datum is the mass, M grams, of unreacted vitreous silica, as a function of time, in the presence of a stoichiometrically equivalent amount of hydrofluoric acid. The rate of solution in this experiment depends on the surface area, S square centimeters, of silica powder, and on the hydrofluoric acid concentration, L/V moles per kilogram of water. Thus,

$$dM/dt = -kS\ (L/V)^n \qquad (3)$$

where n is the partial order of the reaction with respect to the hydrofluoric acid concentration. From the overall reaction (*5*)

$$6\ HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O$$

and the fact that the two reactants are present initially and during the course of the reaction, in stoichiometrically equivalent amounts (at $t = 0$, $M_0 = 2.0180$ g, $L_0 = 0.2016$ mole of hydrofluoric acid, $V = 0.200$ kg of water; the solution is also 1 molal in hydrochloric acid),

$$L \text{ mole HF} = 0.09990\ M \text{ g } SiO_2 \qquad (4)$$

The assumption is made that the surface S varies as the ⅔ power of the mass of remaining silica (*6*),

$$S = S_0\ (M/M_0)^{\frac{2}{3}} \qquad (5)$$

where $S_0 = 680$ cm²/g.

By substitution of Eqs. 4 and 5 into Eq. 3, this last becomes

$$dM/dt = -k\ (S_0/M_0^{\frac{2}{3}})\ (0.4995)^n\ M^{n+\frac{2}{3}} \qquad (6)$$

which is in the same form as Eq. 1.

The equations for differentiation (*2*) are

$$(dM/dt)_i = \frac{1}{h}\left[\Delta M_i - \frac{1}{2}\Delta^2 M_i + \frac{1}{3}\Delta^3 M_i - \ldots\right] \qquad (7a)$$

$$(d^2M/dt^2)_i = \frac{1}{h^2}\left[\Delta^2 M_i - \Delta^3 M_i + \ldots\right] \qquad (7b)$$

where h is the common interval of the time variable (in this case, 1800 sec). Table 1 lists the calculations needed for obtaining the order and the rate constant. Since second and third order differences are used, precise data which are either accurate or amenable to smoothing techniques (*4*, p. 6) are required. Column 3 in the table is the data after one smoothing process. Not all smoothing processes lead to the same results. Two other attempts gave, for the partial order, $n = 0.93$, and $n = 1.11$, and, for the rate constant, $k = 7.12 \times 10^{-8}$ and 7.16×10^{-8} g of SiO_2 per square centimeter, per second, per HF molality. The latter were calculated from Eq. 6, where $n = 1$. These results agree with those obtained by other methods (*6*).

From Eq. 1 or Eq. 6 it is apparent that plotting log $(-M')$ versus log M should give a straight line whose slope

Table 1. Table for obtaining the order of a reaction of a restricted class (T = 32.1 °C).

t (sec)	M_{exp}(g)	$M_{smoothed}$	ΔM	$\Delta^2 M$	$\Delta^3 M$	M'	M''	$n + \frac{2}{3}$	$k\left(\frac{\text{g } SiO_2}{\text{sec cm}^2 \text{ HF molality}}\right)$
0	2.0180	1.9916							
1800	1.9124	1.9129	−0.0787						
3600	1.8265	1.8393	−0.0736	+0.0051					
5400	1.7742	1.7704	−0.0689	0.0047	−0.0004	-3.94×10^{-5}	1.57×10^{-9}	1.79	7.14×10^{-8}
7200	1.6931	1.7056	−0.0648	0.0041	−0.0006	-3.72×10^{-5}	1.45×10^{-9}	1.79	7.18×10^{-8}
9000	1.6378	1.6447	−0.0609	0.0039	−0.0002	-3.50×10^{-5}	1.26×10^{-9}	1.69	7.18×10^{-8}
10800	1.5904	1.5874	−0.0573	0.0036	−0.0003	-3.29×10^{-5}	1.20×10^{-9}	1.76	7.17×10^{-8}
12600	1.5467	1.5332	−0.0542	0.0031	−0.0005	-3.11×10^{-5}	1.11×10^{-9}	1.76	7.18×10^{-8}
14400	1.4911	1.4821	−0.0511	0.0031	.0000	-2.93×10^{-5}	0.96×10^{-9}	1.66	7.15×10^{-8}
16200	1.4462	1.4338	−0.0483	0.0028	−0.0003	-2.76×10^{-5}	0.96×10^{-9}	1.81	7.13×10^{-8}
18000	1.3699	1.3881	−0.0457	0.0026	−0.0002	-2.62×10^{-5}	0.86×10^{-9}	1.74	7.13×10^{-8}
								1.75 ± .04	$7.16 \pm .02 \times 10^{-8}$
								$n = 1.08 \pm .04$	

is m, and whose intercept is log k. This graphical method gives results identical with those presented in Table 1. However, once the M' values have been calculated, it is a simple matter to get the M'' values, then m and k.

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Intestinal Transport of Selenium-75 Selenomethionine

Abstract. When measured simultaneously, selenium-75 selenomethionine accumulated identically with sulfur-35 methionine across everted hamster intestinal sacs in the presence of carrier methionine. The apparent K_m for L-methionine transport was 0.8×10^{-3} M, as calculated from the beta emissions of S^{35}-methionine or the gamma emissions of Se^{75}-selenomethionine. Absorption of Se^{75}-selenomethionine from the gastrointestinal tract of man also occurred, with peak blood levels being reached in about 3 hours. Because of the 122-day half-life of selenium-75 and its multiple gamma emissions, Se^{75}-selenomethionine may serve as a tool in evaluating amino-acid absorption.

Availability of an amino acid labeled with a gamma-emitting radioisotope would be an aid to studies of intestinal absorption, since the emission could be detected without extensive preparation and fragmentation of the sample. Although I^{131}-tyrosine (*1*) and its derivatives have been employed during in vitro studies of absorption, the short half-life of iodine-131 (and consequently its short shelf-life) and the cleavage of iodine from the molecule in biologic systems have limited its applicability for in vivo studies. The report of biosynthesis of Se^{75}-selenomethionine (CH_3-Se^{75}-CH_2•CH_2•$CHNH_2$•$COOH$) with the description of some of its biological properties has provided another amino acid labeled with a gamma-emitting isotope (*2*).

In the experiment reported here, in vitro transport of Se^{75}-selenomethionine against a concentration gradient was compared with that of S^{35}-methionine; everted hamster intestinal sacs, as described by Wilson and Wiseman (*3*), were utilized. Hamsters were sacrificed, and the small gut of each was made into three everted sacs containing 1 ml inside (serosal fluid) and 5 ml outside (mucosal fluid). Initially, serosal and mucosal fluids contained solutions of identical composition. A stock solution contained L-methionine ($8 \times 10^{-3}M$), S^{35}-methionine (0.05 μc/ml), and Se^{75}-selenomethionine (0.02 μc/ml) in Krebs-bicarbonate buffer at *p*H 7.4 (without calcium, magnesium, or glucose). From the stock solution successive dilutions were made with Krebs-bicarbonate buffer to provide L-methionine concentrations of 4, 2, and $1 \times 10^{-3}M$. Two animals (six intestinal sacs) were studied at each concentration. An incubation period of 1 hour in an oscillating water bath at 37°C was employed after preliminary gassing with 95 percent oxygen and 5 percent carbon dioxide.

Sacs were removed from the bathing fluid, drained, and weighed. Mucosal and serosal solutions were centrifuged to remove sloughed tissue and were then assayed. Mucosal and serosal solutions (0.5 ml each) were counted in a Tracerlab gamma ray spectrometer and corrected for background. The S^{35} beta emissions did not interfere with assaying the Se^{75} gamma emissions. However, some of the weaker gamma rays of Se^{75} were recorded by a Packard Tri-Carb scintillation counter as though they were beta emissions [0.05 ml of solution to be analyzed, 10 ml of toluene containing 0.5 mg of 1,4-bis-2-(5-phenyloxazolyl)-benzene, 40 mg of 2,5-diphenyloxazole, and 3 ml absolute ethanol]. Accordingly, the S^{35}-methionine beta counts were in each case corrected for the Se^{75}-selenomethionine present on the basis of the counts recorded from a known amount of Se^{75}-selenomethionine and the gamma counts of each sample. The correction was small (about 3 percent) but was made in each case.

Shown in Table 1 are the ratios of serosal concentration to mucosal concentration calculated in each case by the beta counts of S^{35}-methionine and the gamma counts of Se^{75}-selenomethionine. The values are practically identical, indicating that S^{35}-methionine and Se^{75}-selenomethionine are handled identically by the everted hamster intestinal sac under these conditions. Initial chromatographic studies of the mucosal and serosal solutions have revealed but one gamma-emitting peak, suggesting that Se^{75}-selenomethionine is not appreciably degraded during its transmural transport. A Lineweaver-Burk type plot of the transport data is shown in Fig. 1.

Table 1. In vitro intestinal concentration of L-methionine measured by S^{35}-methionine and Se^{75}-selenomethionine. Each value for the ratio of serosal concentration to mucosal concentration is the mean of six determinations. The standard deviations were about 0.5. The original concentrations of L-methionine are given in italic type.

Serosal concn./mucosal concn. (at 1 hour)		Concn. ratio by β / Concn. ratio by γ
By β activity	By γ activity	
8×10^{-3}M L-methionine		
2.11	2.20	0.96
4×10^{-3}M L-methionine		
3.86	3.70	1.04
2×10^{-3}M L-methionine		
4.51	4.33	1.04
1×10^{-3}M L-methionine		
7.60	8.20	0.93
	Mean	0.99

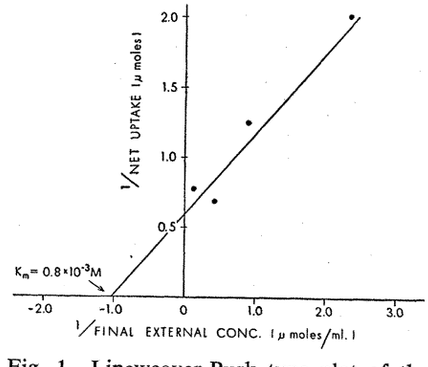

Fig. 1. Lineweaver-Burk type plot of the net serosal uptake of L-methionine as a function of the final mucosal concentration.

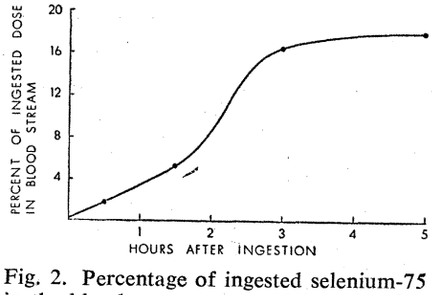

Fig. 2. Percentage of ingested selenium-75 in the blood stream of an adult male after ingestion of 15 μc of Se^{75}-selenomethionine in 0.53 g of L-methionine (0.1 g of L-methionine per 15 kg body weight).