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Author
Cantelow, H.P.

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Ernest O. Lawrence Radiation Laboratory

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ABSTRACT

Performance characteristics of two activated charcoal columns at room temperature in separating fission-product xenon from an air stream were investigated by installing each column in the exhaust from an enclosure in which irradiated slugs were dissolved. Breakthrough curves are presented and the variation in xenon concentration within the columns is examined. Theoretical treatments of adsorption columns in the literature are found to agree well with the experimental data. Performance of the columns is evaluated in terms of "concentration factor" and number of effective theoretical plates.

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INTRODUCTION

As the atomic energy industry expands, more and more attention is focused on the problem of radioactive waste disposal. Often overlooked in considering this problem is the disposal of radioactive noble gases, probably because these gases are less toxic than many radioisotopes encountered in particulate or liquid form and because noble gases are easily dispersed into the atmosphere without fear of fallout, although tall stacks are usually required.

Two noble gases are among the fission products of heavy elements: krypton and xenon. From the half life and cumulative fission yield, the production rate in a nuclear reactor and the total amount present at equilibrium can be calculated for the several isotopes of these noble gases. The radioisotopes of these elements whose half lives are greater than one day are:[1]

Isotope	Half life	U-235 fission yield (%)	Per megawatt of reactor power: Production (curies/day)	Per megawatt of reactor power: Equilibrium amount (curies)
Kr^{85}	10.3 yrs	0.3	0.47	2,500
Xe^{131m}	12 days	0.03	15	250
Xe^{133m}	2.3 days	0.16	410	1,300
Xe^{133}	5.3 days	6.5	7200	54,000

If reactor fuel elements are allowed a sufficiently long cooling period before reprocessing, the shorter-half-life xenon isotopes will decay and offer no disposal problem. Krypton-85 with its 10.3-year half life cannot be treated this way, and if this gas is released into the atmosphere, eventually 2500 curies will be found in the atmosphere for every megawatt of reactor power. If fuel elements (or irradiated transuranic slugs) cannot be allowed an adequate cooling time before processing, xenon also becomes a major problem, particularly xenon-133.

The forecast expansion in atomic energy and radioisotope production strongly suggests that pollution of the atmosphere with these radioactive gases could very well some day become intolerable. It seems worthwhile, then, to look into possible methods of control so that the necessary information and experience will be at hand when required.

Truly controlled disposal of radioisotopes, including gases, requires concentration, not dispersion. One of the promising ways of concentrating noble gases is by adsorption on activated carbon.[2, 3] To obtain an idea of how activated carbon might perform in extracting fission-product xenon from a hot-cell exhaust air stream, a charcoal column was included as part of the ventilation equipment set up for processing irradiated slugs at Lawrence Radiation Laboratory.

The first obvious result obtained was the realization that the use of radioactive gases greatly facilitates the study of the behavior of an adsorption column. The only instrumentation required consisted of simple ionization chambers in the inlet and outlet of the column. Actually, it was found that significant data concerning adsorption in the column could easily be obtained with nothing more than a portable survey meter.

The data obtained are set forth in this report and compared with theoretical treatments found in the literature to show the excellent agreement possible. This was particularly gratifying in view of the simple instrumentation used and the complex nature of an adsorption column.

The invaluable encouragement and assistance of Messrs. Nelson B. Garden, Myron D. Thaxter, John E. Bowen, and other members of the Health Chemistry Group at Berkeley are gratefully acknowledged.

EXPERIMENTAL DATA

A 5-inch-diameter column of activated charcoal 25 in. long was installed in the ventilation train handling the exhaust from a shielded enclosure in which a number of MTR-bombarded transuranic slugs were dissolved and processed. The slugs were dissolved in two batches (a few days apart) so that it was possible to get data on two different activated charcoals.

The enclosure was designed to be as tight as practical, with a rate of air leak into the enclosure less than 1 liter per minute at the operating pressure of -0.5 in. w. g., in order to permit high-efficiency filtration of the exhaust air stream. Exhaust air was passed at very low velocity through two high-efficiency filters in series and then through a millipore filter with a 0.7-micron pore size. No detectable particulate activity was present in the exhaust after the filters.

Ionization chambers were installed in the inlet and outlet of the column as shown in the flow sheet, Fig. 1. The gas flow rate was calculated as 630 cm^3/min from the known volume of the system and the measurements of pressure as a function of time when the system was momentarily isolated from the suction source.

The two different activated charcoals studied were "Cliffchar" 4-10 mesh and "BC Adsorbite" 6-14 mesh. Bulk densities measured were

Cliffchar, 0.23 g/cm^3,

BC Adsorbite, 0.54 g/cm^3.

Dissolution of the slugs released the fission-product gases into the enclosure atmosphere.* In each case roughly 1 curie of xenon-133 was released, producing a concentration of about 1 $\mu C/cm^3$ in the box exhaust gas. No other active gas was present in any appreciable quantity, as indicated by calculations from bombardment time, flux, and cooling time and confirmed by half-life and γ pulse-height analyses of gas samples.

Figure 2 shows the ionization chamber data obtained from the first run, using the Cliffchar column. Ionization chamber data from the BC Adsorbite column are shown as Fig. 3. Because of limited available time and the press of other considerations, the complete breakthrough curve was not obtained for this second column. It was possible to supplement these data, however, with a series of readings with a Juno survey meter at different locations along the outside of the column (as will be shown in Fig. 5.)

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*In equipment currently employed at Berkeley, gaseous products are directly withdrawn into a small evacuated vessel containing charcoal, thus preventing dilution by the enclosure atmosphere. See M. D. Thaxter, H. P. Cantelow, and C. Burk, Off-Gas Treatment in Berkeley Enclosures, UCRL-3635, Jan. 1957, pp. 5-7.

INTERPRETATION OF DATA

At least two different equations are found in the literature which express the concentration of a solute in the effluent from an adsorption column as a function of feed concentration, time or throughput volume, and column parameters.

Glueckauf[4] starts by considering the adsorption column divided into "effective theoretical plate units," that is, units of length within which the concentration of solute in both solution and sorbent phases is treated as uniform, the two being in equilibrium. This discontinuous picture of the column is then reduced to differential form so that in essence the column is treated as though it were continuous.

The expression he derives for the elution curve is

$$\frac{C}{C^o} = 1/2 - \bar{\Phi}_e\left\{\sqrt{N}\,\frac{\bar{V}-V}{\sqrt{\bar{V}\,V}}\right. \quad \text{(for } N > 3\text{)}, \qquad (1)$$

in which C = effluent concentration,

C^o = feed concentration,

N = number of effective theoretical plates,

V = volume of solution put through column,

$\bar{V}$ = volume of solution at the center of the S-shaped breakthrough curve, where $\frac{C}{C^o} = 1/2$,

$\bar{\Phi}_e(\theta)$ = the error function,

$$= \frac{1}{\sqrt{2\pi}} \int_0^{\theta} \exp\left(-\frac{\theta^2}{2}\right) d\theta .$$

Jury[5] has given another equation for the breakthrough curve which may be written as

$$\frac{C}{C^o} = 1/2 - \overline{\Phi}_e \left\{ a\sqrt{h} - b\sqrt{t} \right\},$$

where h = column length,

t = time,

a and b are constants.

Since $\overline{V} = kAh$ and $V = Lt$,

$$\text{where} \qquad k = \frac{f_v(C)}{C},$$

$f_v(C)$ = total amount of solute per unit column volume at equilibrium,

A = cross-sectional area of column,

L = gas flow rate,

$$\frac{C}{C^o} = 1/2 - \overline{\Phi}_e \left\{ \frac{a}{\sqrt{ka}} \sqrt{\overline{V}} - \frac{b}{\sqrt{L}} \sqrt{V} \right\}.$$

By definition, $\frac{C}{C^o} = 1/2$ when $V = \overline{V}$, therefore

$$\frac{a}{\sqrt{kA}} = \frac{b}{\sqrt{L}} = a', \text{ and Jury's equation may be written}$$

$$\frac{C}{C^o} = 1/2 - \overline{\Phi}_e \left\{ a' \left(\sqrt{\overline{V}} - \sqrt{V} \right) \right\} \qquad (2)$$

In fitting these two equations to the experimental data it is convenient to use the measured value of $\overline{V}$ and the slope of the elution curve,

$\frac{d\frac{C}{C^o}}{dV}$, at $V = \bar{V}$. Differentiating Eq. (1) and (2) gives equations for the slope as follows:

For Eq. (1),

$$\left(\frac{d\frac{C}{C^o}}{dV}\right)_{\bar{V}} = \frac{\sqrt{N}}{\bar{V}\sqrt{2\pi}} ;$$

For Eq. (2),

$$\left(\frac{d\frac{C}{C^o}}{dV}\right)_{\bar{V}} = \frac{a'}{2\sqrt{\bar{V}}\sqrt{2\pi}} ;$$

and therefore $a' = 2\sqrt{\frac{N}{\bar{V}}}$.

The observed elution curve from the Cliffchar column is plotted in terms of $\frac{C}{C^o}$ and V in Fig. 4. From the value of $\bar{V}$ (128 liters) and the value of the slope at this point (0.0156 liter^{-1}), the two equations can be determined and are also plotted in Fig. 4. These equations are

$$\text{Glueckauf, } \frac{C}{C^o} = 1/2 - \Phi_e\left\{\sqrt{25}\,\frac{(128-V)}{\sqrt{128\,V}}\right\}, \qquad (1)$$

$$\text{Jury, } \frac{C}{C^o} = 1/2 - \Phi_e\left\{0.884\,(\sqrt{128} - \sqrt{V})\right\}, \qquad (2)$$

where V is in liters.

It is seen that both curves fit the data quite well, although the Glueckauf Eq. (1) gives the better fit.

The data obtained by survey meter on the BC Adsorbite column can be used to calculate the elution curve for this column. (Only Glueckauf's

equation will be used, since the two equations are so similar.) By assuming that the length of column for one theoretical plate unit is the same throughout the column and that the rate of movement of a point of constant concentration along the column is constant,[6] one can calculate N and $\overline{V}$.

Figure 5 shows survey meter readings plotted against time for several different distances, χ, from the inlet end of the column. The center of the curve for χ = 16 in. occurs at t = 365 minutes, where the survey meter reading is one-half the maximum. The measured slope of the curve at this point is 0.012 $\frac{r/hr}{min}$. The survey meter indicates the total xenon activity per unit column volume, which is proportional to the xenon concentration in the gas phase. From this,

$$\frac{d\frac{C}{C^o}}{dt} = 0.005 \text{ min}^{-1},$$

leading to

$$\frac{d\frac{C}{C^o}}{dV} = 0.00794 \text{ liter}^{-1}$$

By extrapolating to the end of the column, where $\chi = h = 25$ in., $\overline{V}$ and N can be determined:

$$\overline{V} = 0.630 \left(365 + \frac{25 - 16}{0.0454}\right) = 355 \text{ liters},$$

$$\left(\frac{d\frac{C}{C^o}}{dV}\right)_{\overline{V}} = 0.00794 \sqrt{\frac{25}{16}} \times \frac{365 \times 0.630}{355} = 0.00644;$$

since $\left(\frac{d\frac{C}{C^o}}{dV}\right)_{\overline{V}} = \frac{1}{\sqrt{2\pi}} \frac{\sqrt{N}}{\overline{V}}$, $N = 2\pi (0.00644 \times 355)^2 = 33$.

Substituting these values for $\overline{V}$ and N in Eq. (1) results in the curve drawn in Fig. 6. The data obtained from ionisation chambers at the beginning of the breakthrough curve are also plotted, and again, the agreement with the calculated curve is quite satisfactory.

Since the equations for the breakthrough or elution curve are error functions, it is convenient to plot these data on probability paper. Such a plot is shown as Fig. 7 for both adsorption columns.

DISCUSSION

In order to characterize the operation of an adsorption column, it is necessary to specify only N and $\overline{V}$. For a given column, $\overline{V}$ is a function of only the adsorption isotherm. From the values of $\overline{V}$ determined in these two experimental runs, values of k can be computed from $\overline{V} = k\bar{A}h$. In summary:

	$\frac{k}{16}$	$\frac{N}{25}$
Cliffchar,		
BC Adsorbite,	44	33

From the literature, the value of the constant k_w in the adsorption isotherm $f_w(C) = k_w C$ is 76 $\frac{cm^3}{g}$ at 20°C, where $f_w(C)$ is the amount of solute adsorbed per gram of charcoal at gas concentration C:[7]

$$k = k_w \rho_B + a ,$$

where ρ_B is bulk density and a is fraction of voids.

From the literature one would calculate the following values for k:

Cliffchar, $k = 76 \times 0.23 + 0.89 = 18.3$,

BC Adsorbite, $k = 76 \times 0.54 + 0.74 = 42$,

showing reasonably good agreement with the observed values of k tabulated above.

The constant k might be termed the "concentration factor," since it represents the ratio of the amount of xenon contained in a charcoal column (at equilibrium) to the amount contained in the same volume without charcoal. In other words, a certain volume of charcoal will hold as much solute as an empty container whose volume is k times as large.

The sharpness of the breakthrough curve depends on N, as well as $\bar{V}$, the midpoint slope being proportional to $\sqrt{N/\bar{V}}$. From Jury's treatment, one would expect N to vary directly as the volume of charcoal in the column and inversely as the flow rate, for a given system of charcoal and adsorbed gas.

As more data of this nature are obtained and evaluated, leading to more complete understanding of the effect of various parameters on k and N, it should be possible to reliably predict the performance of any charcoal column in retaining any of the noble gases. This report is presented with the hope that it will stimulate further investigation in this field. The use of radioactive gases makes data collection quite easy and the results are satisfying in that they seem to conform to theory.

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6. Don DeVault, Theory of Chromatography of a Single Solute, JACS 65, 532 (1943).
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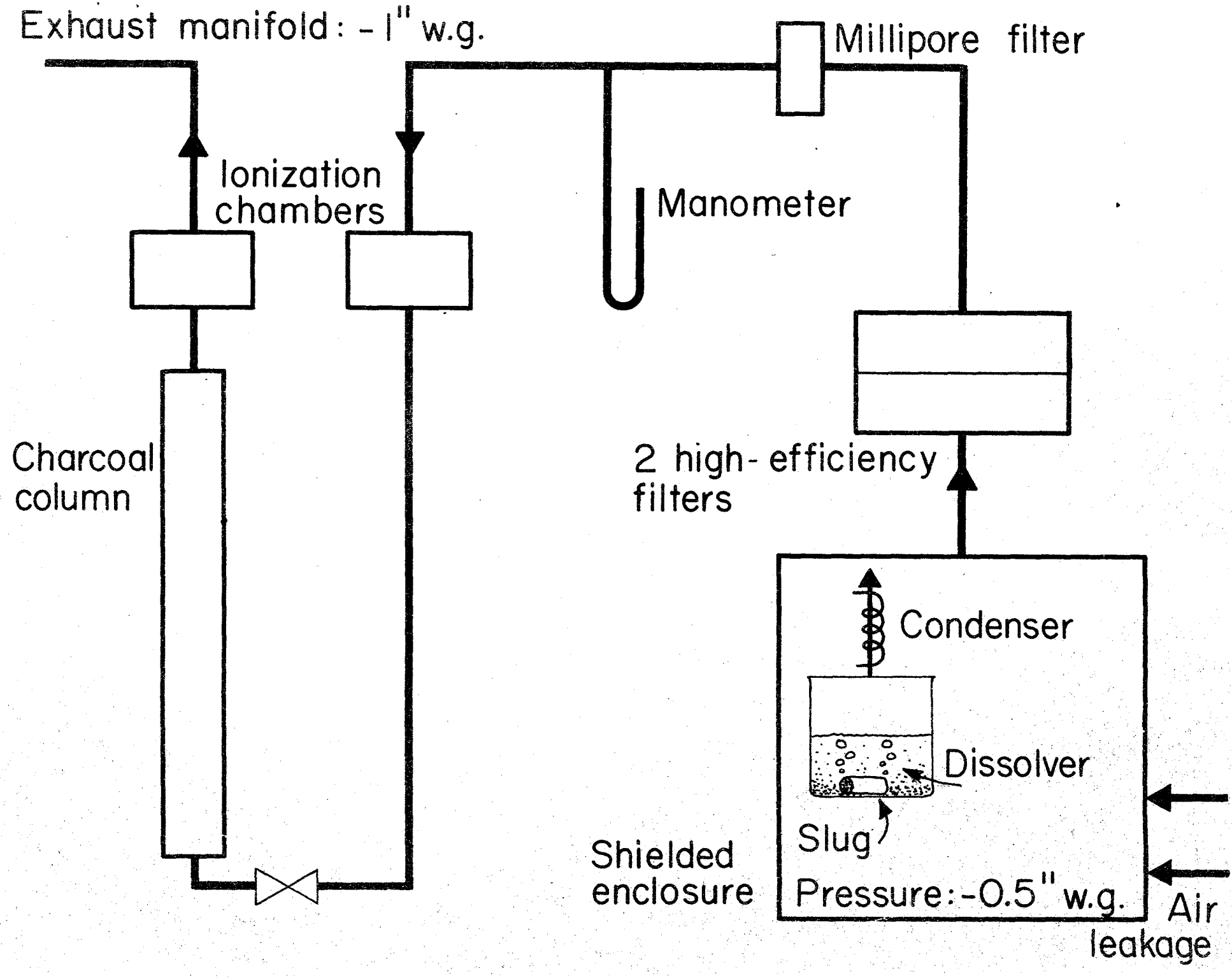
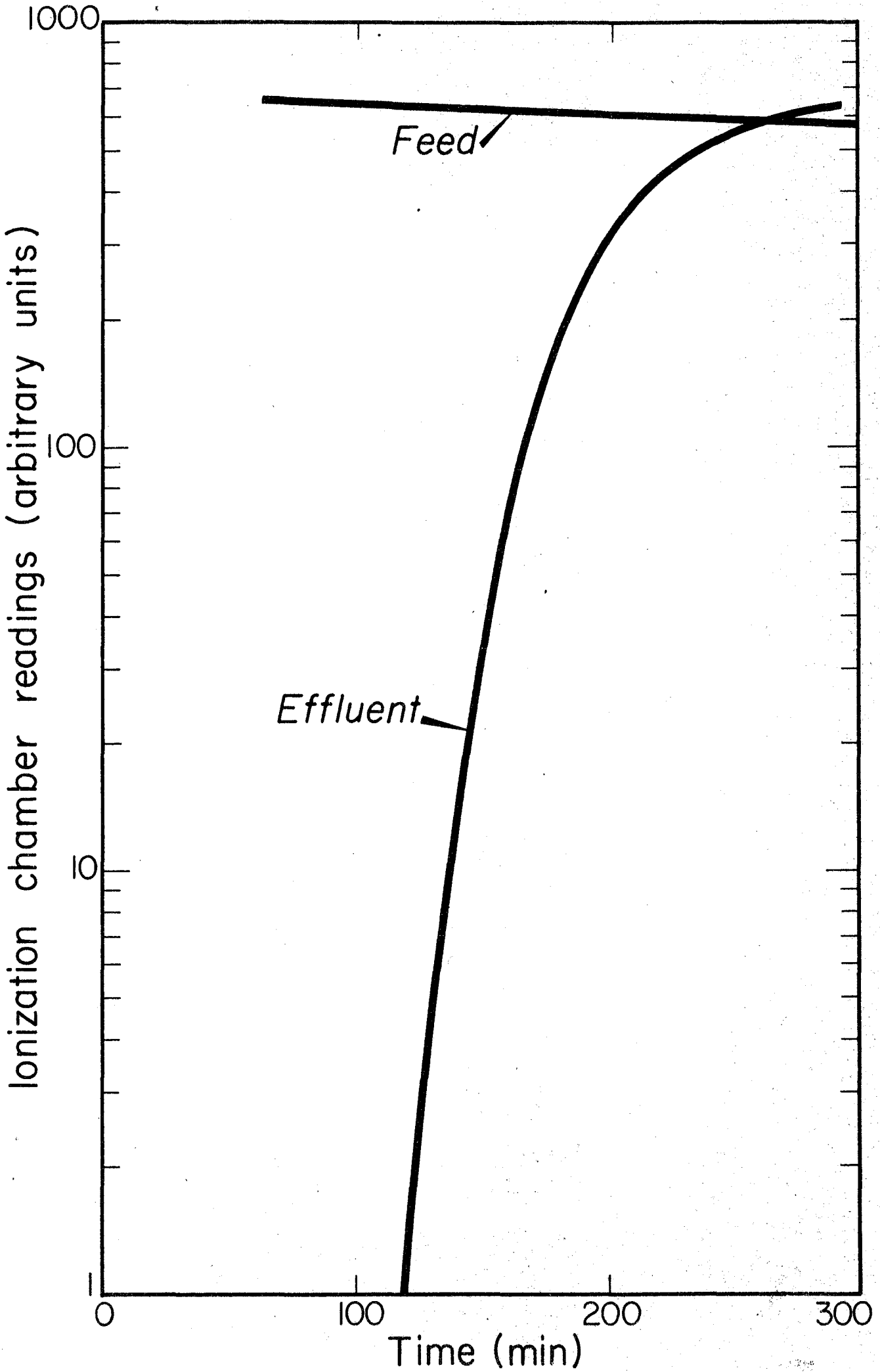
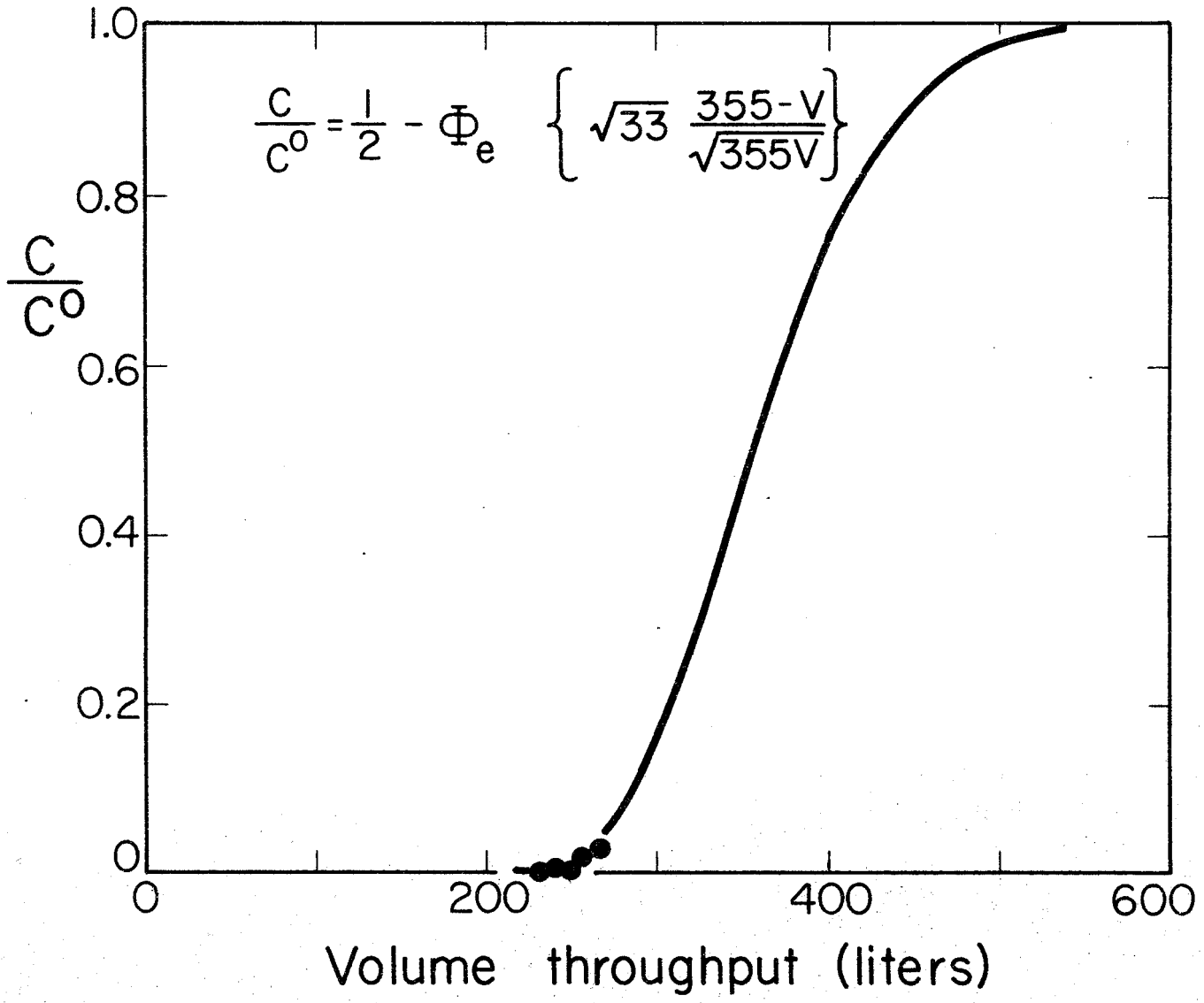
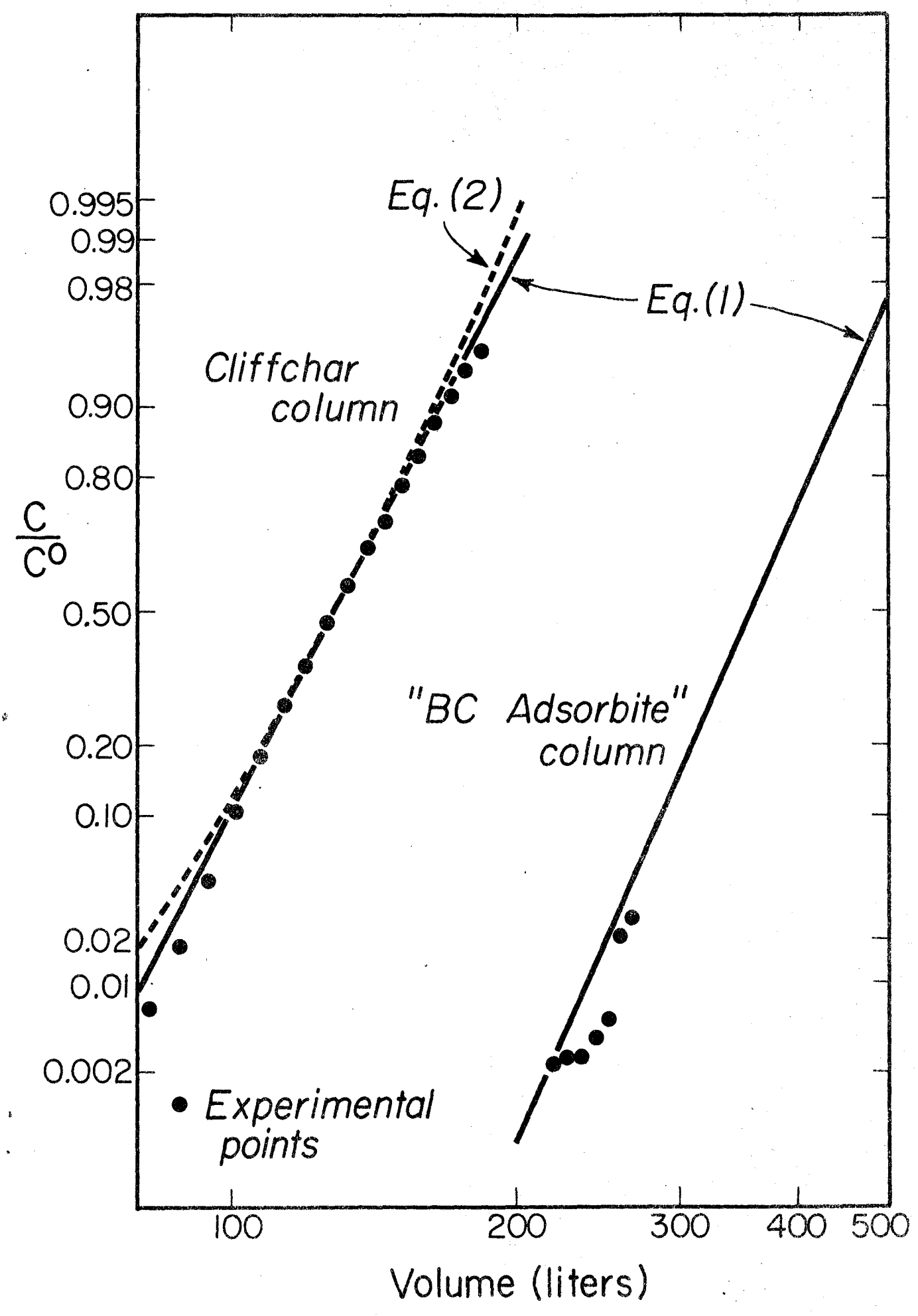
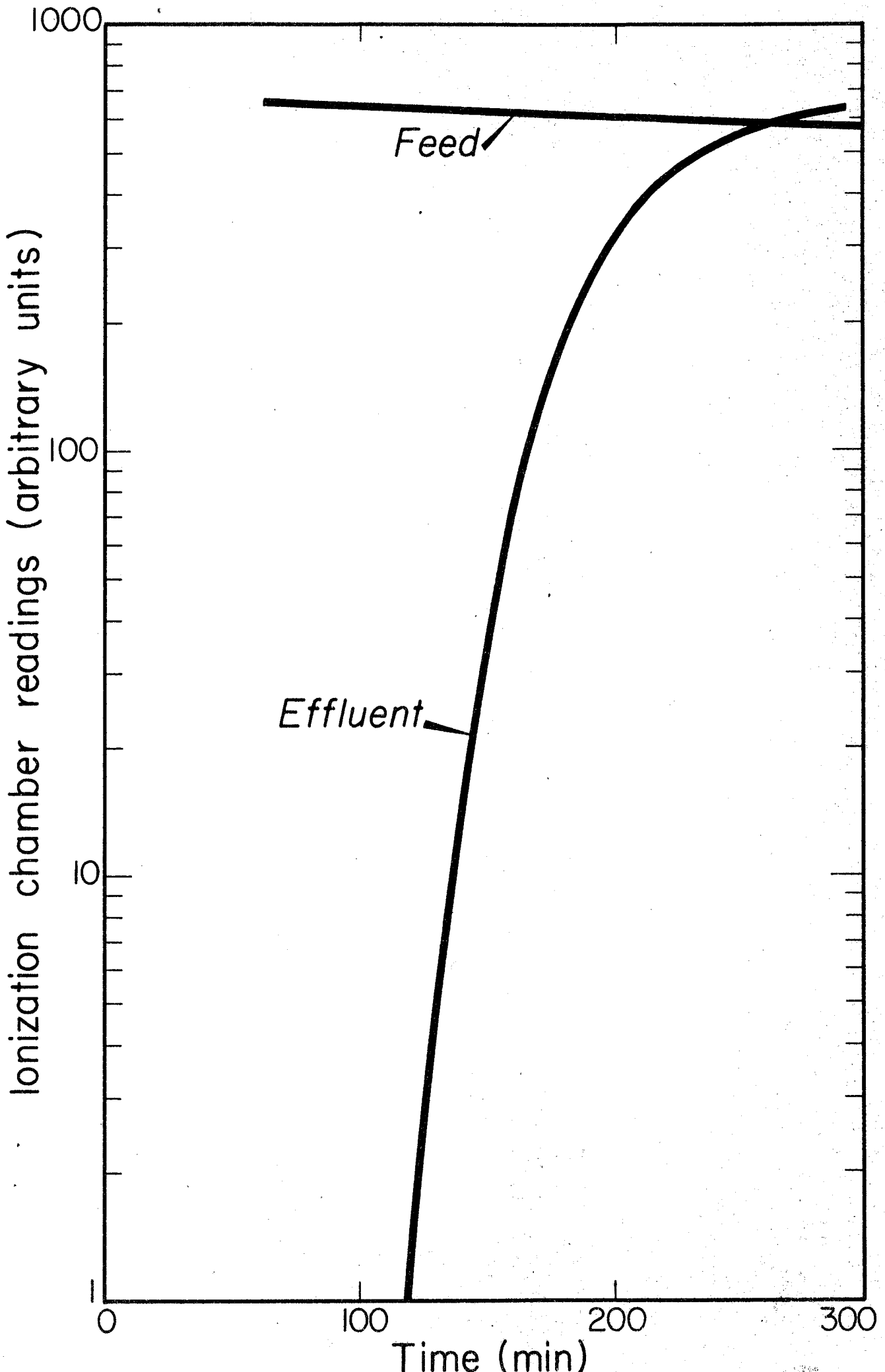

Exhaust manifold: - 1" w.g.
Millipore filter
Ionization chambers
Manometer
Charcoal column
2 high-efficiency filters
Condenser
Dissolver
Slug
Shielded enclosure
Pressure: -0.5" w.g.
Air leakage

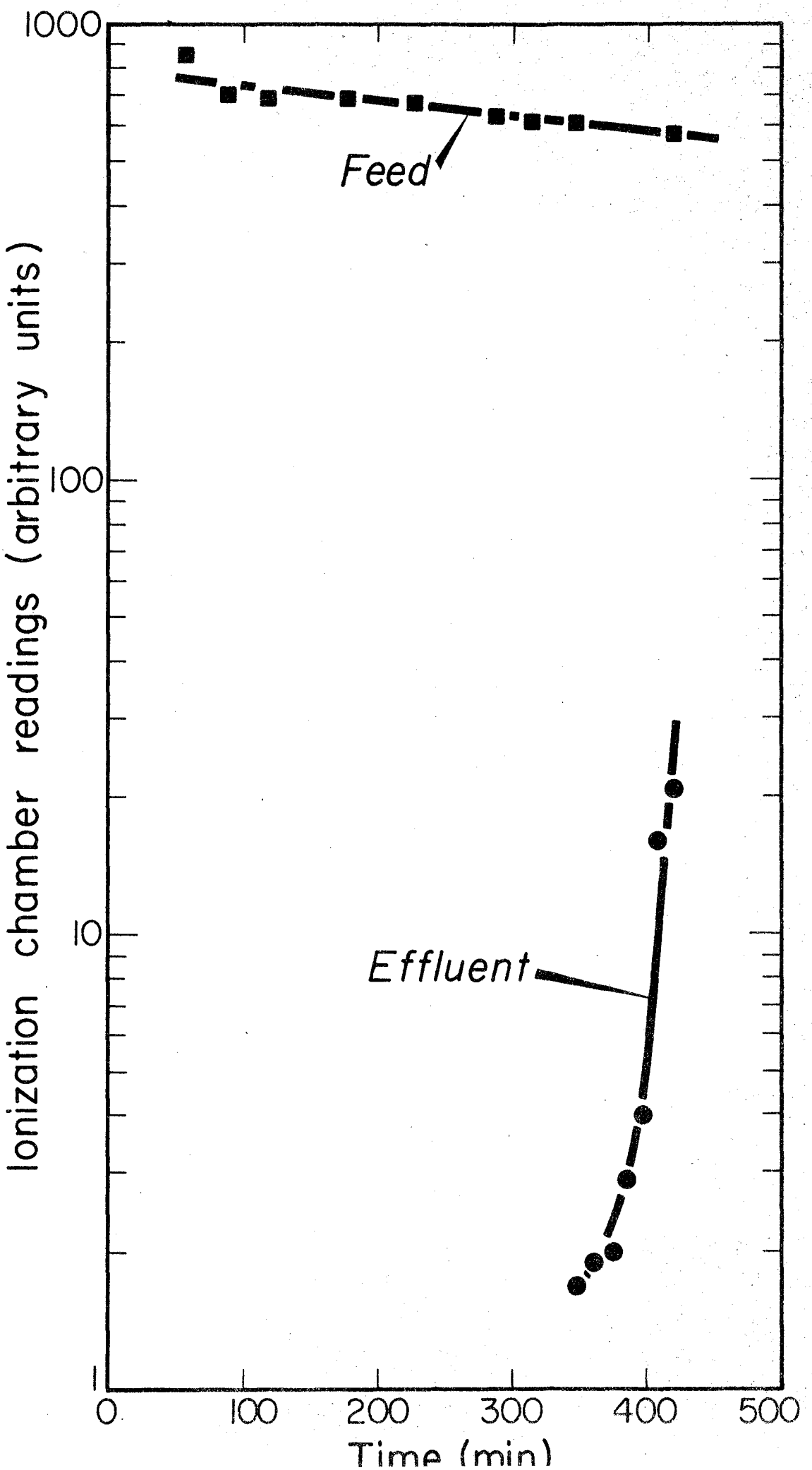

1000
100
10
1
Ionization chamber readings (arbitrary units)
Feed
Effluent
0
100
200
300
Time (min)

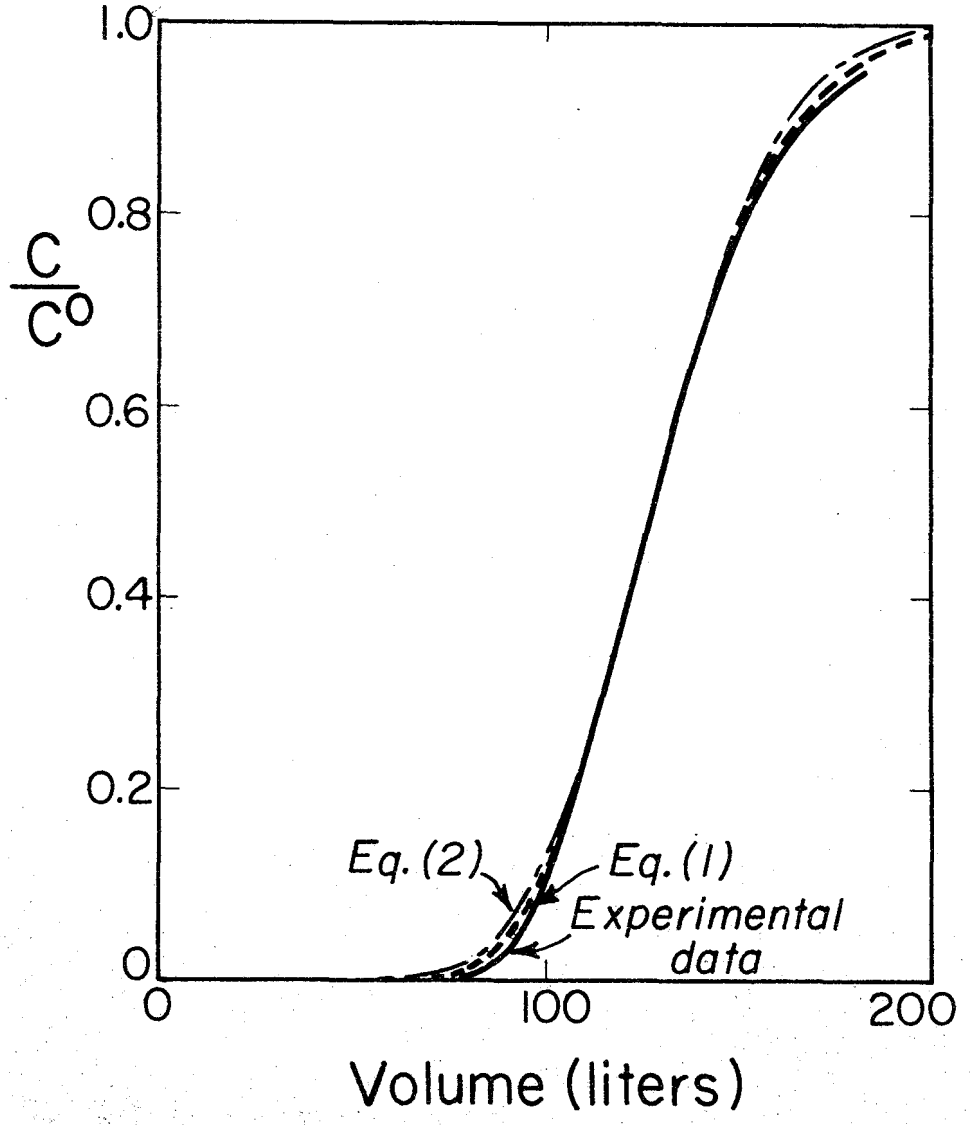

$\frac{C}{C^o} = \frac{1}{2} - \Phi_e \left\{ \sqrt{33}\, \frac{355-V}{\sqrt{355V}} \right\}$
1.0
0.8
0.6
0.4
0.2
0
$\frac{C}{C^o}$
0
200
400
600
Volume throughput (liters)

55514-1 FIG 6

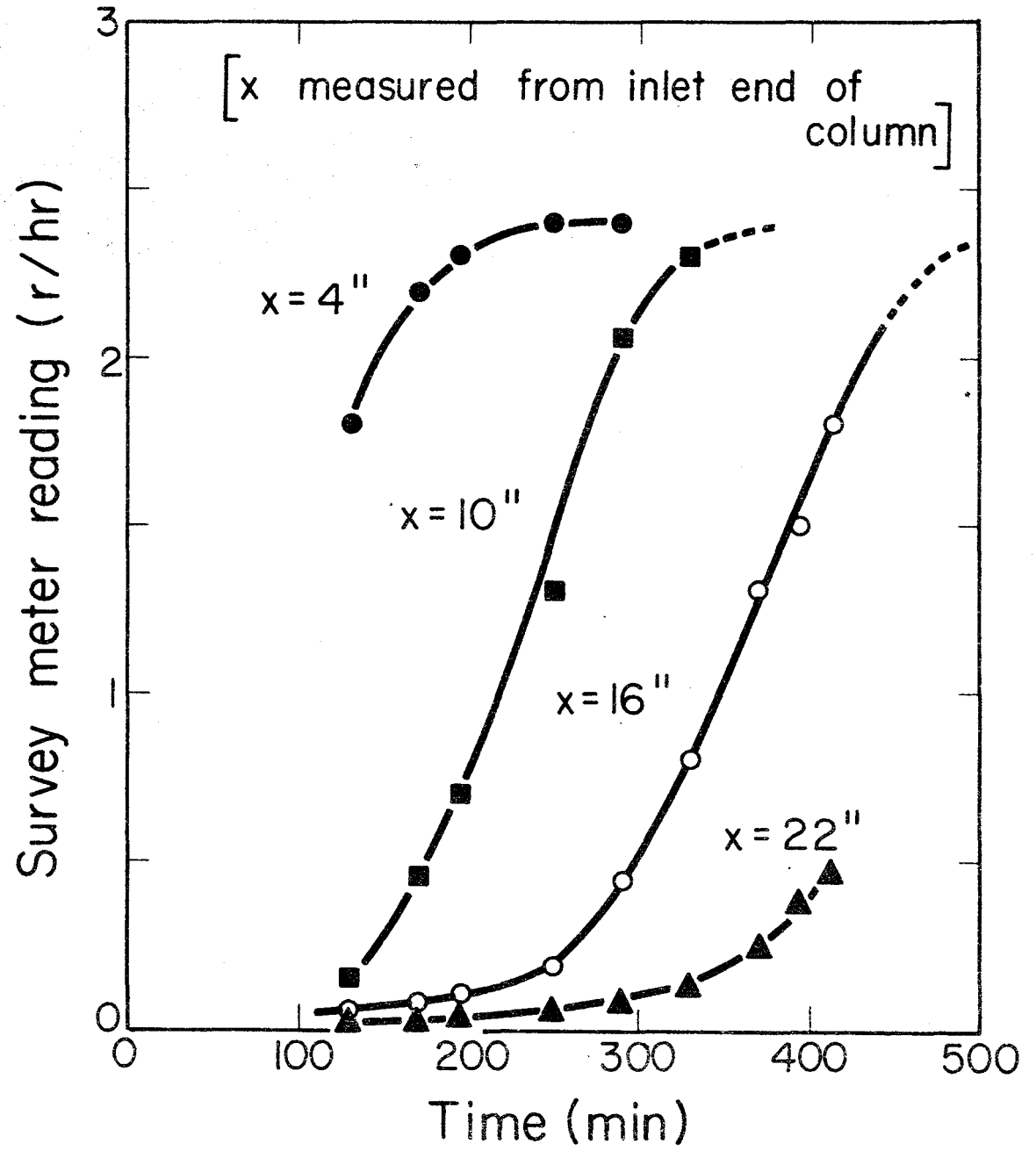

Eq. (2)
Eq. (1)
Cliffchar column
"BC Adsorbite" column
0.995
0.99
0.98
0.90
0.80
0.50
0.20
0.10
0.02
0.01
0.002
C/C0
Experimental points
100
200
300
400
500
Volume (liters)


1000
100
10
1
Ionization chamber readings (arbitrary units)
Feed
Effluent
0
100
200
300
Time (min)


1000
100
10
1
Ionization chamber readings (arbitrary units)
Feed
Effluent
0
100
200
300
400
500
Time (min)


1.0
0.8
0.6
0.4
0.2
0
C/C°
0
100
200
Volume (liters)
Eq. (2)
Eq. (1)
Experimental data

55 512-1 Fig 4


[x measured from inlet end of column]
x = 4"
x = 10"
x = 16"
x = 22"
Survey meter reading (r/hr)
Time (min)
0
1
2
3
0
100
200
300
400
500