Investigations of the Removal of the Toxic Gases, Arsine and Phosgene, from Gas-Air Mixtures by Impregnated Charcoals, using the Radioactive Indicator Method

Thesis by
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The assistance of Dr. E. O. Lawrence and the staff of the Radiation Laboratory together with the hospitality of the Departments of Chemistry and Physics at the University of California at Berkeley was greatly appreciated. The aid of Dr. Martin Kamen in preparing radioactive samples was very helpful.

The work described in this thesis was performed during parts of 1941 and 1942 in collaboration with Dr. R. W. Dodson and directed by Professor Don M. Yost under the National Defense Research Committee Contract B 102, Section B6, OEMsr-28, with the California Institute of Technology. The results have been presented previously in reports to the N.D.R.C. (1, 2, 3). This research was undertaken to study urgent chemical warfare problems which had arisen and actually represents only a small fraction of the intensive work in this country that has been devoted to furnishing satisfactory protection against the toxic chemical agents of battle. The experiments, although fundamental in nature, were planned with the specific practical objective of affording an understanding and a correlation of the processes actually occurring in gas mask absorbents in order that it might be possible to design better canisters.

Possibilities for further interesting research in this field were indicated by the results obtained, but the urgency of other war problems prevented the logical extension of this program.

Since this thesis deals with research and development done in cooperation with the armed services, it must, of course, be classified as "confidential." Because a large portion of the scientific literature dealing with the subjects of interest exists as classified reports which were not available to the author, the bibliography is unfortunately severely limited.

It is earnestly hoped that the work reported has contributed significantly to a satisfactory chemical warfare development program.

INTRODUCTION

The use of chemical agents on a large scale in battle and the spectacular results of the "gas" attacks that occurred in the First World War are well known. Highly effective chemical warfare tactics were devised whereby substances extremely toxic to humans were dispersed over the battle fields to harass, injure, and kill the enemy. According to Prentiss (4) the most extensively used class of agents and the class accounting for the greatest number of fatalities consisted of the nonpersistent "gases." These substances had relatively small molecular weights and low boiling points; so when released, they quickly vaporized and mixed with the air. Even with considerable dilution the quantities that were drawn into the lungs of the personnel with the inspired air and absorbed were capable of producing serious casualties. That these newly invented chemical tactics did not determine the course of the war was due partially, at least, to the development of adequate protective measures.

Protection against the nonpersistent gases was afforded by gas masks in which the inspired gases passed through a canister of suitable absorbents that removed the toxic constituents. Charcoal has been found to be the best practical absorbent for these purposes; all the present day combat gas masks employ a bed of granules of some charcoal material. The original char, which may come from various sources, is usually activated by suitable oxidation processes and may be impregnated with substances which greatly enhance its absorbing powers. Recipes for producing the adsorbents are different in every country and are being constantly modified to yield improved products.

The weight and size of a canister which the troops carry on their person must be kept to an absolute minimum consistent with "adequate protection", and a very thorough and careful design of the gas mask is essential. For proper design the most nearly complete information possible concerning the kinetics of absorption and the processes occurring have proved imperative. Final testing of canisters must, of course, be performed with the war gases at concentrations that can be encountered in the field in actual or simulated breathing tests. For purposes of economy, however, a preliminary development program must be based on a large number of tube tests. In such tube tests the air-gas mixtures may be passed at a constant rate into a bed of the charcoal absorbent supported in a small tube. Either physical or chemical means may be utilized to detect or measure quantitatively the amount of toxic material remaining in the bed or leaving with the effluent gases. The data which can be gained from the tube experiments may then be analyzed to yield information concerning the kinetics of the absorption. The correlation of these kinetics studies to actual canister behavior may follow; although it has been found that considerable care must be exercised in extending the test results to properly account for maximum flow rates and the usual shallow bed thickness in canisters.

If tube tests are analyzed extensively by chemical methods to determine charcoal performance, a large number of quantitative analyses may be involved. The value of physical methods by means of which the concentrations can be measured at frequent intervals,or perhaps be automatically recorded, can be well appreciated.

Yost, Dodson, and Cooley under a previous N.D.R.C. contract (5) developed techniques and constructed instruments for determining the relative intensity of radiation emitted per unit volume by a radioactive substance contained in a flowing gas stream. Counters of the Geiger-Mueller type for measuring essentially the beta radiation were employed in conjunction with ratemeter type electric circuits. The ratemeter produced a current through a milliammeter which was directly proportional to the counting rate of the counter tube. By the use of recording meters a continuous record of the radioactivity could be obtained. After the proper correction for radioactive decay, the activity per unit volume of a gas, in which a single radioelement was present, would be essentially proportional the concentration of that particular element in the gas with an accuracy determined by the inherent statistical fluctuations. It is to be especially noted that the concentration of the tracer element would be obtained, regardless of the various molecular states in which it might exist. The chemical properties and behavior of the compounds containing radioactive isotopes are not different in any important respect from those of the same compounds containing only non-radioactive isotopes.

The use of the above method for determining concentrations was applied in studies of the absorption in tube tests of the two gases, arsine and phosgene, as described in this thesis. The radioactive indicator technique permitted a number of interesting experiments. It was possible to obtain continuous records of concentrations in the effluent gases from the charcoal tubes. The identification of chemical compounds could be accomplished by selective removal of the components from the gas stream and the subsequent measure of the residual activity. Also, it was found feasible to measure the quantity of radioactivity deposited in the charcoal as a function of either time or the position in the bed.

In addition to the naturally occurring radioactivity there have been prepared and identified in recent years a large number of artificial radioactive isotopes, including those of nearly every element. A table of the known radioisotopes has been prepared by Seaborg (6). For charcoal tube tests it was necessary to have available an unstable isotope of at least one of the elements of the toxic compound with a half life sufficiently long so the activity could still be accurately measured at the end of a two or three hour experiment. Rather high activities of these isotopes were required. As small a fraction as 10^{-4} of the original radioactive sample was needed for measurement. If a concentration of 0.1% of the initial concentration was to be detected as 10 counts/min., about one half of a low background, and the efficiency of counting was 5%, which was essentially a geometry factor for energetic beta radiation, then an original activity of at least the order of magnitude of 2×10^9 counts/min. or about a millicurie was required. (One millicurie may be defined as 2.22×10^9 disintegrations per minute.) The larger cyclotrons constitute the only present day source of activities of this magnitude. Beta radiation with energies of at least 1 MEV. was the most convenient for measuring; although activities for β particles with energies as low as 0.1 MEV. could be obtained. An efficient and rapid synthesis, requiring not more than one or two half lives, of the compound to be used from the target materials of the bombardment was essential. It is not possible to prepare an isotope of some elements with a suitable decay constant and in quantities sufficient for tube test experiments; the method is somewhat limited for this reason. In case satisfactory isotopes could be obtained for more than one of the elements of a compound of interest, the behavior of each of these elements could be observed.

Arsine, AsH_3, is a colorless gas with an unpleasant odor and condensing at -55°C. It is a systemic poison, extremely toxic; and the inhalation of small amounts can result in death several days after exposure, according to Henderson and Haggard (7). Its value as a war gas is doubtful in view of the ease of its oxidation and decomposition and its low boiling point. It may, however, be considered as an example of a gas that can be easily oxidized on the catalytic charcoal surface. Arsine may be prepared from radioarsenic; the isotope that can be conveniently utilized is As^{74}. The radiation is β^+, β^-, and γ. The beta radiation is quite energetic, 0.9 MEV. for β^+ and 1.3 MEV. for β^- (6). Its half life, 17 days, is moderately long, so the tube tests may be conveniently carried out. The radiation from radiohydrogen is so feeble, 0.02 MEV. (6), that it could not be used.

Phosgene, $COCl_2$, is a colorless gas with the odor of mouldy hay; it boils at 8°C. It is primarily a lung irritant of high toxicity, and small dosages may result in fatalities as long as 24 hours after exposure (4). In the presence of water it may hydrolyze on the charcoal surface to give the acid products HCl and CO_2. Since it can be cheaply prepared, it has been one of the most widely used and effective of the chemical warfare agents. The carbon isotope C^{11} is available. It emits β^+ radiation, 0.95 MEV. (6), half life 20.5 minutes (8) which is satisfactory for use. Also, radiochlorine, Cl^{38}, β^- radiation of 1.1 and 5.0 MEV. and γ of 1.65 and 2.15 MEV., half life 37 min. (6), can be used. Both its beta and gamma radiation are extremely penetrating. The known unstable isotopes of oxygen, O^{15} and O^{19}, have half lives of 126 sec. and 31 sec. respectively; these are too short to be useful. Indeed, the half life of 20.5 min. for radiocarbon represents very nearly the lower limit that could be utilized for experiments of this sort.

MATHEMATICAL INTRODUCTION

Theoretical considerations have yielded several mathematical equations for describing the results of tube tests. The aim of a theoretical treatment is the definition of a relatively few parameters, such as absorbtion capacity and absorption rate constants , which will characterize the worth of the individual charcoals. The concentration of material in the gas stream or retained on the surface of the charcoal may possibly then be calculated as functions of the time and the position in the bed, these functions containing the assumed parameters. The actual concentrations can then be compared with the calculated values. If the calculations are satisfactory, values of the parameters can be obtained from a small number of experiments. The performance of a charcoal under different conditions or in actual gas mask use may then be calculated. Some mathematical treatment of the problem is essential if any correlation between experiments is to be obtained because of the large number of variables and the complexities involved.

When the absorption studies were started, there were available in N.D.R.C. reports only a few very fragmentary discussions (7,8,9) of the mathematical expressions that pertained. The lack of suitable system for designating reports by the N.D.R.C. at that time prevents satisfactory references to these from being given. The following mathematical treatment, guided by the available information in the reports, was accordingly worked out for the purpose of interpreting the tube tests with radioactive indicators.

Definition of Symbols. The following symbols may be defined.

A = cross-section area of the tube (cm.^{2})

c = concentration of gas in air stream at x and t (mg./l.)

c_0 = influent concentration of gas (mg./l.)

L = length of absorbent bed (cm.)

N = concentration of "gas" absorbed in the bed, mg "gas"/cc. absorbent

t = time (min.)

t' = inlet time for a particular increment of the air stream (min.)

x = distance of a point in the bed from the inlet end (cm.)

v = linear velocity of flow within the bed (cm./min.)

V = volumetric rate of flow (l./min.)

General Considerations for Tube Tests. A cylindrical tube, packed with homogeneous absorbent, through which flows an air stream that carries an absorbable gas was considered. The concentration of gas was assumed to be so small that no appreciable change in the linear velocity occurs because of its removal.

It is possible to set up a general differential equation from a mass balance over an infinitesimal section of the absorbent bed.

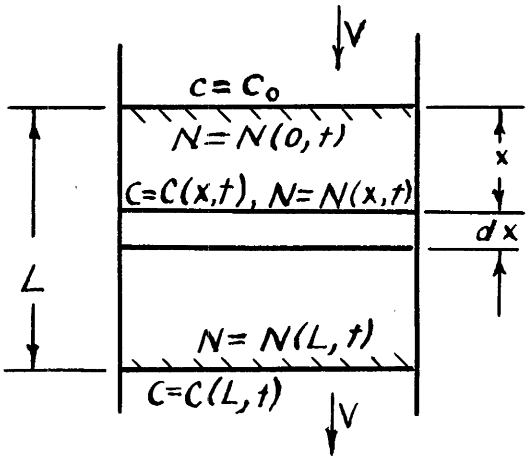

Fig. A

In the portion of the bed between x and x + dx, indicated in Fig. A, the rate of removal of material from the air stream with respect to time would be

$$- V \left[c \left(x + dx, t + \frac{dx}{v} \right) - c \left(x, t \right) \right] .$$

In the expanded form, neglecting differentials of order higher than one, this becomes

$$- V \left[c(x, t) + \left(\frac{\partial c}{\partial x} \right)_t dx + \left(\frac{\partial c}{\partial t} \right)_x \frac{dx}{v} - c(x, t) \right] .$$

The rate at which material appears on the absorbent is

$$A dx \left(\frac{\partial N}{\partial t} \right)_x .$$

Since the rate of removal of gas from the air stream must equal its appearance in the bed, the above expressions are equal; thus

$$A \left(\frac{\partial N}{\partial t} \right)_x = -V \left[\left(\frac{\partial c}{\partial x} \right)_t + \frac{1}{v} \left(\frac{\partial c}{\partial t} \right)_x \right] . \qquad (1)$$

A considerable simplification may be achieved if the independent variables, x and t, are transformed in the following way.

$$x = x \; ; \quad t' = t - \frac{x}{v}$$

By means of this transformation equation 1 is changed to

$$\left(\frac{\partial N}{\partial t'} \right)_x = \frac{-V}{A} \left(\frac{\partial c}{\partial x} \right)_{t'} . \qquad (2)$$

Equation 2 contains no mechanism considerations but is only a statement of the Law of Conservation of Matter. Hence it is general and applies to any tube test experiment.

The quantity, $\frac{x}{v}$, is ordinarily very small, of the order of 0.1 sec. Therefore t' can be treated essentially the same as the variable, t. The statement of the kinetics or mechanism may then comprise a differential equation in which $\left(\frac{\partial N}{\partial t}\right)_x$ is expressed as a function of c and N. Upon solving this equation and equation 2 simultaneously in accord with the boundary conditions, N and c will be obtained as functions of t and x.

Case 1. A useful and convenient solution is obtained in case the charcoal is assumed to have a saturation capacity, N_o; and if the rate of pick-up by the charcoal is assumed to be proportional to the concentration of gas in the air stream and to the unfilled capacity of the charcoal at any point and instant in question. The differential equation applies

$$\left(\frac{\partial N}{\partial t}\right)_x = k_1 c \ (N_o - N) = \left(\frac{\partial N}{\partial t'}\right)_x . \tag{3}$$

(The usual convention has been to call the unfilled capacity of the charcoal N. Equation 3 would then be

$$\left(\frac{\partial N}{\partial t}\right)_x = k_1 cN. \tag{4}$$

However the concept of saturation capacity is definitely a mechanism assumption. By choosing to designate by the symbol, N, the capacity filled with toxic, the generality of equation 2 is enhanced.)

Equations 2 and 3 may be solved for the boundary conditions which correspond to normal tube testing.

At $t' = 0$, $N = 0$ for $0 < x < L$

At $x = 0$, $c = c_o$ for $t' > 0$

From equations 2 and 3 there obtains

$$-\frac{V}{A}\left(\frac{\partial c}{\partial x}\right)_{t'} = k_1 c \ (N_o - N) \quad . \tag{5}$$

Differentiating equation 4 with respect to t' and eliminating (N_o-N) and $\left(\frac{\partial N}{\partial t'}\right)_x$ by means of equations 2 and 5, there results upon rearrangement the second order partial differential equation which does not include N.

$$\frac{1}{c}\,\frac{\partial^2 c}{\partial t'\partial x} - \frac{1}{c^2}\left(\frac{\partial c}{\partial x}\right)_{t'}\left(\frac{\partial c}{\partial t'}\right)_x + k_1\left(\frac{\partial c}{\partial x}\right)_{t'} = 0. \qquad (6)$$

The expression on the left hand side is a perfect differential with respect to x and consequently can be integrated immediately to yield

$$\frac{1}{c}\left(\frac{\partial c}{\partial t'}\right)_x + k_1 c = f(t'). \qquad (7)$$

where $f(t')$ is a function of t' only. From the boundary condition, $c = c_o$ for $t' > 0$ at $x = 0$, it appears that $f(t') = k_1c_o$. Using this value for $f(t')$ and integrating for constant x gives

$$\ln\left(\frac{c_o-c}{c}\right) = k_1c_ot' + g(x) \qquad (8)$$

where $g(x)$ is a function of only x. Rearranging terms to obtain an explicit expression for c gives

$$c = \frac{c_oe^{k_1c_ot'}}{\left[e^{k_1c_ot'} + e^{g(x)}\right]} \qquad (9)$$

But if this value for c is substituted in equation 3 and integrated for constant x from $t' = 0$ to $t' = t'$, the solution involving N is obtained

$$\ln\left(\frac{N_o-N}{N_o}\right) = \ln\left[\frac{1+e^{g(x)}}{e^{k_1c_ot'} + e^{g(x)}}\right] \qquad (10)$$

Thus, solving for N_o-N and N

$$(N_o - N) = N_o \left[\frac{1 + e^{g(x)}}{e^{k_1 c_o t'} + e^{g(x)}}\right], \text{ and } : N = N_o \left[\frac{e^{k_1 c_o t'} - 1}{e^{k_1 c_o t'} + e^{g(x)}}\right] . \quad (11)$$

There remains now only to identify g(x). A differential equation for g(x) is obtained by writing equation 5 in terms of t' and g(x)

$$\left(\frac{\partial c}{\partial x}\right)_{t'} = \frac{-c_o e^{k_1 c_o t'} \frac{dg}{dx} e^{g(x)}}{\left[e^{k_1 c_o t'} + e^{g(x)}\right]^2}$$

$$= \frac{-k_1 A c (N_o - N)}{V} = - \frac{k_1 A}{V} \; \frac{c_o N_o e^{k_1 c_o t'} \left[1 + e^{g(x)}\right]}{\left[e^{k_1 c_o t'} + e^{g(x)}\right]^2} . \quad (12)$$

Solving for g(x) gives

$$g(x) = \ln \left[I_1 e^{\frac{N_o k_1 A x}{V}} - 1 \right] , \quad (13)$$

where I_1 is a constant of the integration. I_1, evaluated from the boundary condition, is 1. The complete solution for Case 1 may now be written

$$\ln\left(\frac{c_o}{c} - 1\right) = -k_1 c_o t' + \ln\left(e^{\frac{N_o k_1 A x}{V}} - 1\right) . \quad (14a)$$

or alternatively

$$c = \frac{c_o e^{k_1 c_o t'}}{\left[e^{k_1 c_o t'} - 1 + e^{\frac{N_o k_1 A x}{V}}\right]} \quad (14b)$$

and

$$N = N_o \frac{e^{k_1 c_o t'} - 1}{\left[e^{k_1 c_o t'} + e^{\frac{N_o k_1 A x}{V}} - 1\right]} . \quad (15)$$

The equation 14a has been especially useful. As far as is known, it was apparently first applied in this war by the British; and it has been given the name, Hinshelwood's equation. The details of Hinshelwood's treatment have not been available; however the equation in the form of 14b was used in the last war. A derivation by Bohart and Adams (9), who assumed equations of the form 4 and 5 in the variables x and t, was published in 1920.

If for a single tube test the toxic concentration in the effluent is measured as a function of time, equation 14a predicts that the function, $\ln\left(\frac{c_o}{c} - 1\right)$, plotted against the time will be a straight line with the slope, $-k_1c_o$. Such a procedure may be used to test experimentally the validity of the original kinetics assumptions and the resulting equations. If approximately a straight line is obtained, then numerical values for k_1 and N_o may be calculated for the particular gas and charcoal from a single experiment. It also appears from Hinshelwood's equation that toxic material penetrates the bed in increasing amounts after the start of the test at $t' = 0$. In practice a break is considered to have occurred when some detectable concentration of gas, c_b, penetrates the bed. If the time, at which this concentration is observed in the effluent, is designated as the life, t'_b, of the bed, then for a bed of length, L, the equation may be written

$$\log_e\left(\frac{c_o}{c_b} - 1\right) = -k_1c_ot'_b + \ln\left(e^{\frac{N_ok_1AL}{V}} - 1\right). \qquad (16)$$

If $\frac{N_ok_1AL}{V}$ is sufficiently large, then

$$\log_e\left(\frac{c_o}{c_b} - 1\right) = -k_1 c_o t_b' + \frac{N_o k_1 AL}{V} . \tag{17}$$

Thus, as L increases, the life-thickness, t_b' - L, curve should approach a straight line. From the slope of this line and from its intercept both k_1 and N_o may be calculated provided the value of c_b is known.

Case 2. In the derivation of Case 1 it was found that N could be eliminated between equations 2 and 3, and the resulting differential equation of second order for c could be integrated immediately. In general, the integration can not be performed so easily. It was found however that a satisfactory solution could be obtained for the case in which the rate of absorption is proportional to only the gas concentration in the air stream for a region where the absorbent is not saturated. Such a condition might be approximated if the rate determining step was the transport of the gas to the charcoal surface. In place of equation 3 in Case 1, the two kinetics equations may be written

$$\left(\frac{\partial N}{\partial t'}\right)_x = k_2 c \text{ for } N < N_o , \tag{18a}$$

$$\left(\frac{\partial N}{\partial t'}\right)_x = 0 \text{ for } N = N_o . \tag{18b}$$

The same boundary conditions as for Case 1 apply, viz.

At $t' = 0$, $N = 0$ for $0 < x < L$.

At $x = 0$, $c = c_o$ for $t' > 0$.

By combining equations 2 and 18a there is obtained

$$\left(\frac{\partial c}{\partial x}\right)_{t'} = -\frac{k_2 Ac}{V} \text{ for } N < N_o . \tag{19}$$

This may be integrated

$$c = f_1(t')\, e^{-\frac{k_2 A}{V}\, x} \quad . \tag{20}$$

From the boundary condition, $c = c_o$ for $t' > 0$ at $x = 0$, it appears that $f(t') = c_o$; so

$$c = c_o e^{-\frac{k_2 A}{V}\, x} \qquad \text{for } N < N_o. \tag{20a}$$

Substituting this value of c in equation 18a and integrating for constant x from $t' = 0$ to $t' = t'$, the expression for N results

$$N = k_2 c_o t' e^{-\frac{k_2 A}{V}\, x} \qquad \text{for } N < N_o\,. \tag{21}$$

Equations 20 and 21 apply during the early portions of the test before any charcoal has been saturated. During this period the gas concentration in the air stream is independent of time; and, consequently, a constant small concentration appears in the effluent. The amount of gas absorbed at any point of the bed increases linearly with time. At $x = 0$, N reaches the saturation value, N_o, in the time t'_o, which is equal to N_o/k_2c_o. This t'_o may be considered as a "theoretical" break time. For at t'_o the top layer of the charcoal has become saturated. A zone of saturation then begins to expand from $x = 0$ through the bed; simultaneously, the effluent concentration begins to increase. Then c is no longer independent of time. If x_o is the thickness of the saturated zone at time t', x_o will be a function of t'. Equation 20a will still be valid if $x - x_o(t')$ is substituted in place of x, since the equation is valid for any region in which $N < N_o$. Thus,

$$c = c_o e^{-\frac{k_2 A}{V}\left[x - x_o(t')\right]} \qquad \text{for } t' > t'_o = \frac{N_o}{K_2 c_o}\ , \tag{22}$$

At $t' = t'_o = \frac{N}{k_2 c_o}$,

$$N = N_o e^{-\frac{k_2 A}{V} x} . \tag{23}$$

The time at which the edge of the saturation zone reaches the point, x, in the bed may be called $\tau'(x)$. The rate at which the boundary of the saturated zone moves through the bed is then $1/\frac{d\tau'}{dx}$. But this is also equal to $\frac{dx_o}{dt'}$. Thus,

$$1/\frac{d\tau'}{dx} = \frac{dx_o}{dt'} . \tag{24}$$

If the quantity, $\left(\frac{\partial N}{\partial t'}\right)_x$, is integrated for constant x from $t' = t'_o$ to $t' = \tau'$, the following results

$$\int_{t'_o}^{\tau'} \left(\frac{\partial N}{\partial t'}\right)_x dt' = N_o \left(1 - e^{-\frac{k_2 A}{V} x}\right) . \tag{25}$$

This equation may be differentiated with respect to x to give

$$\frac{d}{dx} \int_{t'_o}^{\tau'} \left(\frac{\partial N}{\partial t'}\right)_x dt' = \int_{t'_o}^{\tau'} \frac{\partial^2 N}{\partial x \partial t'} dt' + \left[\frac{\partial N}{\partial t'}(\tau', x)\right]_x \frac{d\tau'}{dx}$$

$$= \frac{N_o k_2 A}{V} e^{-\frac{k_2 A}{V} x} . \tag{26}$$

But if the expression for $\left(\frac{\partial N}{\partial t'}\right)_x$ and $\frac{\partial^2 N}{\partial t' \partial x}$ be substituted from equation 2 and 18a respectively and the value of the resulting definite integral taken from equation 25, the above equation becomes

At $t' = t_o' = \frac{N}{k_2 c_o}$,

$$N = N_o e^{-\frac{k_2 A}{V} x} \qquad (23)$$

The time at which the edge of the saturation zone reaches the point, x, in the bed may be called $\tau'(x)$. The rate at which the boundary of the saturated zone moves through the bed is then $1/\frac{d\tau'}{dx}$. But this is also equal to $\frac{dx_o}{dt'}$. Thus,

$$1/\frac{d\tau'}{dx} = \frac{dx_o}{dt} \qquad (24)$$

If the quantity, $\left(\frac{\partial N}{\partial t'}\right)_x$, is integrated for constant x from $t' = t_o'$ to $t' = \tau'$, the following results

$$\int_{t_o}^{\tau'} \left(\frac{\partial N}{\partial t'}\right)_x dt' = N_o \left(1 - e^{-\frac{k_2 A}{V} x}\right). \qquad (25)$$

This equation may be differentiated with respect to x to give

$$\frac{d}{dx} \int_{t_o}^{\tau'} \left(\frac{\partial N}{\partial t'}\right)_x dt' = \int_{t_o'}^{\tau'} \frac{\partial^2 N}{\partial x \partial t'} dt' + \left[\frac{\partial N}{\partial t'}(\tau', x)\right]_x \frac{d\tau'}{dx}$$

$$= \frac{N_o k_2 A}{V} e^{-\frac{k_2 A}{V} x} \qquad (26)$$

But if the expression for $\left(\frac{\partial N}{\partial t'}\right)_x$ and $\frac{\partial^2 N}{\partial t' \partial x}$ be substituted from equation 2 and 18a respectively and the value of the resulting definite integral taken from equation 25, the above equation becomes when combined with equation 24

$$1/\frac{d\tau'}{dx} = \frac{Vc_o}{AN_o} = \frac{dx_o}{dt'} \ . \tag{27}$$

The saturation zone would appear to move through the charcoal bed, its length increasing linearly with time. Equation 27 may therefore be integrated at once to give

$$x_o = \frac{Vc_o}{AN_o}\,(t' - t_o') \ . \tag{28}$$

Placing this value of $x_o(t')$ in equation 22 yields the explicit expression for c

$$c = c_o e^{-\frac{k_2Ax}{V} + \frac{c_ok_2}{N_o}(t' - t_o')} \quad \text{for } t_o' < t' < t_o' + \frac{AN_ox}{Vc_o} \ . \tag{29}$$

The similar expression for N may be obtained by integrating $\left(\frac{\partial N}{\partial t'}\right)_x$, which is equal to k_2c, from $t' = t'$ to $t' = \tau'$, using the value of c given in equation (29). Thus,

$$\int_{t'}^{\tau'} \left(\frac{\partial N}{\partial t'}\right)_x dt' = N_o - N = \int_{t'}^{\tau'} k_2c_oe^{-\frac{k_2Ax}{V} + \frac{c_ok_2}{N_o}(t' - t_o')}\,dt'$$

$$= N_oe^{-\frac{k_2Ax}{V} + \frac{c_ok_2}{N_o}(t' - t_o')}\Bigg]_{t'}^{\tau'} \ . \tag{30}$$

From this it follows

$$N = N_oe^{-\frac{k_2Ax}{V} + \frac{c_ok_2}{N_o}(t' - t_o')} \quad \text{for } t_o' < t' < t_o' + \frac{AN_ox}{Vc_o} \ . \tag{31}$$

The results may now be summarized by the set of six equations

$$\text{For } 0 < t' \leq t_o' = \frac{N_o}{k_2c_o} \ : \quad c = c_oe^{-\frac{k_2A}{V}x} \tag{22}$$

$$\text{For } t'_0 < t' < t'_0 + \frac{AN_0x}{Vc_0} : c = c_0 e^{-\frac{k_2Ax}{V} + \frac{c_0k_2}{N_0}(t' - t'_0)} \tag{29}$$

$$\text{For } t' \geq t'_0 + \frac{AN_0x}{Vc_0} : c = c_0 , \tag{32}$$

$$\text{For } 0 < t' \leq t'_0 = \frac{N_0}{k_2c_0} : N = k_2c_0t' e^{-\frac{k_2Ax}{V}} . \tag{21}$$

$$\text{For } t'_0 < t' < t'_0 + \frac{AN_0x}{Vc_0} : N = N_0 e^{-\frac{k_2Ax}{V} + \frac{c_0k_2}{N_0}(t' - t'_0)} \tag{31}$$

$$\text{For } t' \geq t'_0 + \frac{AN_0x}{Vc_0} : N = N_0 \tag{33}$$

Although some toxic material penetrates the bed immediately, the effluent concentration would remain constant until the "theoretical" break point, t'_0. This behavior is in contrast to Case 1 where the effluent concentration increased continuously. The "theoretical" break point for any one charcoal against any particular gas would be inversely proportional to the influent concentration, c_0, and would be independent of the bed length. It might be, however, that for the early part of the test the effluent concentration in the case of a sufficiently deep bed would escape detection. In which case equation 29 would apply for the practical break time. Equation 29 may be written in the logarithmic form for a bed length of L

$$\ln \frac{c_0}{c} = -\frac{c_0k_2(t' - t'_0)}{N_0} + \frac{k_2AL}{V} \quad \text{for} \quad t' > t'_0 \tag{34}$$

In this case the function $\ln \frac{c_0}{c}$ would be a straight line function of t', and the validity of the mechanism could be tested by plotting the experimentally determined $\ln \frac{c_0}{c}$ against time. As with Hinshelwood's equation the parameters may be determined from such a graph if the results are suitable. It appears also that the life-thickness curve would be a straight line for sufficiently deep beds. The parameters, k_2 and N_o, could be evaluated from a satisfactory life-thickness curve. As the bed length was decreased, the break time, t_b', for some detectable concentration would approach t_o. When by the above equation L was so small that $t_b' \leqq t_o'$, the break time would be zero.

The two theories that have been presented may aid in evaluating charcoals. If the equations are approximately valid, the parameters, k and N_o, offer a convenient means for comparing different charcoals. The best absorbents will have high values for both N_o and k. If a charcoal possesses a high value of N_o and a low value of k, it may provide satisfactory protection in deep beds and fail when used in thin layers. Of the two cases discussed, Case 1, yielding Hinshelwood's equation, is probably the most valid for the present gas mask absorbents.

Other Cases. The case of desorption has not been discussed, although many of the absorption processes are reversible. Kassel (10) considered the rate equation

$$\left(\frac{\partial N}{\partial t}\right)_x = -k_3(N) + k_4 c(N_o - N) . \qquad (35)$$

in which k_3 would be a desorption rate constant. A solution in the form of a complicated series was given for this case. Only incomplete numerical solutions were calculated, and because of its complexity these solutions have not proved useful.

It is apparent that still other mechanism differential equations could be set up. In some instances, at least, the integration for such other cases will be difficult; and simple expressions for c and N as functions of x and t cannot be obtained.

GENERAL EXPERIMENTAL PROCEDURES AND MATERIALS

Charcoal. The absorption studies were made with the gas mask charcoal designated by the Chemical Warfare Service as CWSN19TU8. The unimpregnated or base char for this whetlerite, CWSN19, was also used in a few experiments. The base char, an extruded material, had been made from wood flour by a zinc chloride method, performed by the National Carbon Co. The National Carbon process formed a sizable fraction of the production capacity for charcoal in this country, and subsequent testing has proved it to be undersirable for gas mask use. The base char had been given a cupric ammonia carbonate impregnation followed by a high temperature air drying so that CWSN19TU8 was a whetlerite that would now be classed as type A. It therefore contained copper, about 5 to 7% by weight, in the form of CuO. Its surface would be an active catalyst for many reactions, and its behavior might be expected to be considerably different from an unimpregnated activated charcoal.

All the charcoal used was screened with standard sieves, the fraction passing through 10 mesh (per inch) and over 14 mesh being selected for tube tests. This fraction was dried at least four hours at 150°C. It will be designated as CWSN19TU8 (Dried). Two batches of the dried whetlerite were equilibrated at room temperature with air at 50% and 70% relative humidity (RH) respectively. These portions will be designated CWSN19TU8 (50 RH) and CWSN19TU8 (70 RH). The equilibration was continued until the water pick-up over a period of several hours was negligible as indicated by repeated weighings. The 50 RH material was found to contain 7.0% H_2O, the 70 RH charcoal 27% H_2O, on a wet basis.

Procedures for Tube Tests. For tube tests the charcoal was contained in either aluminum or glass tubes (ca.2cm.1D) and was supported by Witt plates. The aluminum tubes had thin walls (0.04 cm.) and were especially designed for the purpose of permitting the accumulation of activity in the bed to be measured by Geiger-Mueller counter tubes. It was found necessary to coat the inside aluminum walls with shellac to prevent corrosion. Experiments at room temperature were performed with the tubes exposed to the laboratory atmosphere. In other cases, however, the tubes were immersed in liquid baths. Above room temperature a water bath was heated with a hot plate; below room temperature an acetone bath was cooled with dry ice.

In each experiment a weighed amount of charcoal was introduced into a tube; and the bed depth was adjusted to a predetermined value so the apparent density of dried whetlerite was a constant, and in the experiments equal to 0.50 gm./cc. In the case of an equilibrated charcoal the weight of absorbent used was made equal to the weight of dried charcoal in the adjusted bed depth plus the weight of water absorbed by this amount of dried material in the equilibration process.

The tubes were always mounted with their axes in a vertical position, and the air-gas stream was passed down through the bed. The effluent stream was frequently passed through chemical indicator solutions in test tubes for the detection of the toxic constituent and to determine standard chemical break points.

Preparation of Air-Gas Mixtures. Ordinary steel oxygen cylinders (Volume $\approx$ 23L) were prepared. Their interiors were carefully cleaned, dried, given a coat of shellac, and finally dried again with a current of hot air for several hours. To fill a tank, it was first evacuated by a mechanical pump. A glass bulb (about 1 to 2L capacity) filled with a sample of the radioactive gas was attached to the evacuated cylinder. The sample of gas was drawn into the cylinder; then dried air was flushed through the bulb into the still partially evacuated tank. If necessary, a sample of inactive gas from another bulb could also be introduced in the same manner. Finally, compressed air from another steel cylinder was admitted until the pressure of the air-gas sample was 500-600lbs/in^2, gage. The cylinder from which compressed air was drawn had not been initially dried. Subsequent examination revealed that it contained a small quantity of liquid water. In use, the pressure of these tanks was always greater than 1000lbs/in^2. Air, saturated with water at these pressures, would have a relative humidity of less than 2% when expanded to one atmosphere. This figure may be considered an upper limit to the relative humidity of the gas-air mixtures.

The cylinder containing the sample was provided with a regulator and a needle valve, these valves being used to control the flow from the tanks. Conventional flow meters of various ranges were employed to measure the rates of flow, and barostats were used to secure uniform air velocities. If needed, air from a compressed air line could be mixed at a controlled rate with the gas from the cylinder to provide further dilution. Desorption was studied by passing air through a charcoal after the air-gas mixture. A portion of every sample in the cylinder was withdrawn for quantitative chemical analyses.

<u>Temperature Measurements</u>. In early tests it was noted that the removal of the gas was accompanied by thermal effects. Therefore in later

studies thermocouple junctions, made from silk covered fine copper and constantan wire, were inserted in the charcoal at various distances along the bed so temperatures might be measured. The potentials were measured with a Leeds and Northrup portable precision potentiometer.

Radioactivity Measurements. The counter tubes and ratemeter circuits, that were used for measuring radioactivities, were constructed under a previous N.D.R.C. contract and have been described in a formal report by Yost, Dodson and Cooley (5). The counters were bell-shaped and of the Geiger-Mueller type. The flat end of each tube was covered with a window of thin mica, the area density of which was 2 to 5 mg/cm^2. The counters had plateaus of 200 to 300v. in the neighborhood of 1200v. and backgrounds of 20 cts./min. when shielded with 2 in. of lead. Their excellent counting characteristics appeared to be stable for long periods of time. As stated previously, the counter tubes were operated in conjunction with ratemeter circuits and milliammeters which automatically recorded a current proportional to the counting rate of the tubes. The ratemeters had seven ranges, the full scale counting rates extending from 200 cts./min. for low activities up to 20,000 cts./min., the maximum range of the instruments.

Gas samples were contained in cylindrical glass pots for the measurement of their activities. These pots, about 5 cm. in diameter had a volume of approximately 50 ml. Over one end of each had been placed either a mica window similar to those for the counter tubes or else an aluminum foil window, one mil thick. With phosgene it was necessary to coat the inside of the aluminum foil with shellac to prevent the corrosion of the metal and the formation of a film containing active chlorine. The pots were mounted directly under the counters and both units enclosed in a shield of cast lead whose walls were 2 in. thick. The windows of counter and pot were placed adjacent and very nearly in contact. The mounting was so arranged that the position of the pot with respect to the counter was quickly and easily reproduced. Energetic beta radiation from the gas could easily penetrate both windows. For such an arrangement it was estimated that about 5% of the beta particles from the gas contained in the pot would enter the counter and be recorded. The pots were constructed with delivery tubes so that a stream of gas could be swept through them, in practice usually at a rate of 2 L./min. In this way there was measured effectively the activity per unit volume of the flowing gas stream. For each gas-air mixture the activity of a sample taken directly from the steel cylinder was determined. With this value and with the chemical analysis of the tank mixture, the concentration, c, of the radioelement in the gas stream could be calculated from its measured activity, I, by the simple relation

$$c \text{ (gm. atom/unit vol.)} = \frac{I}{I_o} \, nc_o \text{ (mols/unit vol)} \qquad (36)$$

where c_o is the concentration of toxic material in the mixture from the cylinder, I_o the activity measured for the cylinder mixture, and n is the number of atoms of the tracer element per molecule of the toxic compound.

To measure the relative activity in the charcoal itself, two methods were used. In the first, the bed was made up in 0.5 cm. sections separated by fine brass screens. After passage of the gas stream, either short of or beyond the break, the sections were removed and their separate activities recorded with the counters. The measured activity was an average over the length of the section and was taken as representing the activity of the midpoint of its section. This method could not be used with the radiocarbon and radiochlorine because of their rapid decay. In the second more convenient method, the thin walled glass or aluminum charcoal tube was mounted immediately adjacent to a horizontal slit. The slit was formed by two lead bricks both 10 cm. thick separated by 3 mm. Behind the bricks, its window pointed toward the slit, was placed a shielded counter. The counting rate so determined was an indication of the activity in the charcoal section directly before the slit; but a correction for the scattering of the beta particles by the walls of the slit was necessary.

In order to investigate the effects of electron scattering on the measurements with the slit, beds of varying thickness of charcoal containing active arsenic were set up and scanned; ie, the activity was measured with various sections of the charcoal bed in front of the slit. For a given specific activity it was found that the measured activity at the center of a section increased appreciably as the section width was increased beyond 3 mm., this effect being attributed to scattering of oblique radiation by the lead walls of the slit. To arrive at a representation of the average activity of a given 0.5 cm. section of charcoal, the activity of such a section was observed with the slit center in line with the section center. Then, additional 0.5 cm. sections of charcoal containing the same specific arsenic activity were placed adjacent to the first section. After each addition the activity at the midpoint of the first section was redetermined; also the entire bed was scanned. The effect of sections added after the second 0.5 cm. increment was slight. The results of these measurements were represented by the following relation:

$$I^{o}_{j} = I_{j} - \left[0.1\,(I^{o}_{j+1} + I_{j-1}) + 0.04\,(I^{o}_{j+2} + I^{o}_{j-2})\right], \qquad (37)$$

where j is a running index along the bed, I_j^o is the activity of a 0.5 cm. section alone, and I_j is the activity measured in the presence of adjacent active 0.5 cm. sections.

This relation was used to correct measurements made with the lead slit system. I_j^o was taken as representing the concentration of active arsenic at the center of the j^{th} 0.5 cm. section. Because of the short half lives the scattering corrections for carbon and chlorine were not obtained.

With the aid of the above scattering correction it was possible to quickly scan a charcoal bed and obtain the distribution of activity therein. It was also possible to determine the accumulation of activity at any one section during a tube test as a function of time. In this case the correction for scattering was less certain, but estimates of the correction were made where possible.

Corrections and Errors. In addition to the instrumental and observational errors ordinarily encountered in physical measurements, the accuracy of the data was also dependent on the statistical fluctuations inherent in radioactive decay. This statistical error would vary with the activity of the sample and would be magnified at low counting rates. It would amount to perhaps 25% at the lowest rates during the detection of minimum concentrations but would be reduced to less than 3% at the highest counting rates.

Flow rates, chemical analyses, and other measurements were subject to errors of about 3%, an accuracy considered consistent with the needs of the studies.

For each experiment the background for the counter was determined, and this value was subtracted from the recorded counting rates. A complication to the background corrections was introduced in the experiments with radiocarbon and radiochlorine. The activities of these elements were initially so high that the radiation, penetrating the steel cylinder and scattered through openings of the lead counter shield, was able to raise the normal background several fold. The magnitude of this contribution at times of interest was estimated by interpolation; however when this effect was large, the activity measured was also great so the percentage correction was small. In certain experiments when activities greater than the maximum range of the ratemeters were encountered, metal absorbers were placed between the pot and counter; the absorption factors were later estimated and applied to the observed rates. These factors might have been in error by 5%.

Because of the rapid decay of carbon and chlorine activities it was necessary to calculate all their activities to some reference instant of time; the start of gas flow through the charcoal was selected for this point. Since in many cases the correction to time zero was made over several (as many as ten) half lives, a slight error in the half life would be magnified in the activity calculated for time zero. In correcting the carbon activities, the half life was taken to be 20.5 ± 0.1 min., as determined by Yost, Ridenour, and Shinohara (13) and as confirmed by Solomon (8). The value of 37.0 ± 0.4 min., given by Van Voorhis (14), was used for the half life of Cl^{38}. Because of the conveniently long half life of As^{74}, no decay correction was needed for tests of two to three hours duration.

The ratemeters were calibrated with a pulse generator and readjusted once a week during the course of the experiments; in general the calibration of each scale was found to have changed by less than 5% during this time. The small drifts in calibration were erratic and seemed to be temperature dependent.

An additional factor contributing to errors in the counting measurements was high frequency "hash" occasionally picked up from the power line. This caused apparent counting rates to increase markedly during short time intervals. The disturbance was minimized by placing a filter across the line; in the few cases when otherwise unaccountable humps appeared in the milliammeter trace, they were disregarded.

The records of the milliammeters were corrected for the time lag inherent in the ratemeter circuit. A tank circuit in the ratemeter contained a large condenser, C, and a parallel resistor, R. A current, I_T, in the form of small pulses for each discharge of the counter tube, was fed into the tank condenser. Since the milliammeter recorded effectively the current, I_R, flowing through the resistor, the current, I_T, would be given to a good approximation by the expression:

$$I_T = I_R + \tau \frac{d I_R}{d t} \tag{38}$$

where τ is the time constant of the tank circuit and equal to RC. This relation is a generalization of an early step in the analysis presented by Shiff and Evans (15). The value of τ ranged from about 1/3 min. for the highest counting scale to one min. for the lowest ranges. I_T was the true measure of radioactivity; and the activities were computed from its values that were calculated by the above expression from the milliammeter currents, I_R, which varied with time.

Preparation of Graphs. In analyzing the results, graphs for each experiment were prepared from the data that were collected. In some cases the concentrations in the effluent stream were plotted against time, in other cases the function, $\log\left(\frac{c_o}{c} - 1\right)$, appearing in Hinshelwood's equation was drawn, and on occasions both curves were prepared for comparison purposes. Also, when they were determined, the distribution of the activity residing in the bed, according to the scanning or sectioning method, and the accumulation of activity on the charcoal as a function of time were graphed. It was found that these graphs gave a complete representation of the experimental data in a form from which it could be quickly and conveniently comprehended. There were only a limited number of experiments performed, and each represented a considerable expenditure of radioactive material. Since however with the use of the radioactive indicator technique a very considerable knowledge of the charcoal performance could be obtained from each test, a complete set of prints for the experimental graphs has been included in the Appendixes of this thesis.

Appendix I	Graphs for Experiments with Arsine Containing Radioarsenic
Appendix II	Graphs for Experiments with Phosgene Containing Radiocarbon
Appendix III	Graphs for Experiments with Phosgene Containing Radiochlorine
Appendix IV	Graphs for Temperature Measurements in Phosgene Tube Tests

The graphs for each test have been grouped together and arranged in the order of experiment number.

EXPERIMENTS WITH RADIOARSINE

Preparation and Separation of Radioarsenic and Synthesis of Arsine. As^{74} was prepared in the 60 in. cyclotron of the University of California at Berkeley by the bombardment of GeO_2 with 16 MEV. deuterons. It resulted from a d-n reaction with Ge^{73}. Two products of such bombardment, in the form of finely powdered germanium dioxide bearing the arsenic activity, were received from Berkeley. It was first necessary to separate the arsenic activity from the target material and then to synthesize arsine from this unstable arsenic. Because of the striking similarity of many corresponding germanium and arsenic compounds the separation of the elements presented some difficulties; however the following procedure proved satisfactory.

The target material, about one gram of GeO_2, was placed in a 75 ml. long-necked distilling flask, filled with an inlet tube through a ground glass stopper in the top. 50 mg. of arsenic for carrier in the form of sodium arsenate and 25 ml. of aqua regia were added to the flask and the mixture distilled to dryness. Another 25 ml. of aqua regia was added and the distillation repeated to assure the removal of all the germanium. The distillate contained all the germanium, which was then recovered, but none of the arsenic. In aqua regia arsenic remains in the pentavalent state; and as such it does not, like trivalent arsenic, form volatile halides. The residue in the flask was then treated with 20 ml. of 12N. HCl and 2 ml. of 42% HBr and the resulting mixture distilled, the distillate being collected in a 100 ml. volumetric flask cooled in ice water. A further 20 ml. portion of HCl was added to the flask and the distillation repeated. The distillate contained nearly all the arsenic as $AsCl_3$ and $AsBr_3$, the recovery amounting to over 90%. The HBr served to reduce the arsenate to trivalent arsenic.

A small aliquot portion of each sample was precipitated with H_2S as AsS_3. From the activities of these precipitates the original activities of the samples were estimated to be 3 and 10 millicuries respectively. A decay curve of the sulphide precipitate, followed for two weeks, indicated that the samples consisted mainly, if not entirely, of the As^{74} isotope with a half life of 17 days.

The HCl solution of radioarsenic of about 50 ml. volume was mixed with about 50 ml. of 16N. H_2SO_4 containing 0.5 gm. of $CdSO_4$, a catalyst. The solution was allowed to drop through a funnel onto a large excess of granulated zinc (10-12 mesh) in a flask equipped with a side delivery tube. The trivalent arsenic was reduced by the zinc to form AsH_3, which was carried out of the reaction vessel with the current of hydrogen formed simultaneously. The gases passed through a drying tube and into a liquid air trap where the AsH_3 condensed. The efficiency of this synthesis was better than 95%. About 2 liters (STP) of inactive arsine was prepared by the same reaction using larger quantities of zinc and a 10N. H_2SO_4 solution saturated with As_2O_3 and containing a little $CdSO_4$. With the higher concentrations of arsenic only about a 50% yield was achieved. The inactive arsine was condensed in the same trap with the radioactive material. After evacuating the trap at liquid air temperatures, the arsine was allowed to expand at room temperature into the glass bulb from which the steel cylinder was filled.

Analyses. In the cylinder the concentration of arsine slowly decreased, about 5% per day, the loss being due to the slow oxidation of arsine by oxygen. Even flasks of arsine at atmospheric pressure containing a little air showed gradually increasing deposits of arsenic mirrors on the walls. Because of this decrease in concentration analyses of the air-arsine mixtures were made at frequent intervals. The method of analysis, recommended by the Chemical Warfare Service at the time, proved to be unsatisfactory. According to directions the air-arsine mixture was passed through two absorption bottles containing standard iodine solution and a third bottle with standard sodium thiosulfate solution to retain the iodine vapor. Titration of the contents of the three bottles with either standard iodine or thiosulfate followed. But the radioactive tracer method indicated that the absorption of AsH_3 was incomplete even at prohibitatively slow flow rates. The method of analysis finally adopted was still dependent upon the action of iodine according to the reaction

$$4H_2O + 4I_3^- + AsH_3 = 12I^- + H_3AsO_4 + 8H^+.$$

A 500 ml. flask of measured volume was equipped with a short stoppered burette and openings through which a gas sample could be drawn and about 20 ml. of a $NaHCO_3$ and fresh starch solution admitted. Standard iodine was added from the burette to the bicarbonate-starch solution until the blue starch iodine color persisted even after vigorous shaking to assure absorption of the arsine. Unless specifically stated otherwise, all concentrations, volumetric flow rates, and rate constants reported in this thesis have been calculated for the temperature and pressure conditions of the laboratory, consistent with their use in the theoretical equations.

Two radioactive arsine-air mixtures, SA-2 and SA-3, were prepared from the first, 3 millicurie sample, and one, SA-4, from the 10 millicurie sample. The initial arsine concentrations, c_o, and the initial activity, I_o, for these concentrations in the pot under the counter have been given in Table I for the three mixtures.

Table I

CONCENTRATIONS AND ACTIVITIES FOR ARSINE-AIR MIXTURES

Air-Arsine Mixture	c_o (initial) mg./L.	I_o (initial) counts/min.
SA-2	7.0	4,300
SA-3	6.2	2,900
SA-4	5.6	19,600

Tube Tests. Several tube tests were performed with each of the three gas mixtures. CWSN19TU8 was used exclusively together with dry air-arsine mixtures ($<$ 2%RH). All tests were made at room temperature. The concentration of the inlet stream taken directly from the cylinder varied from test to test because of the gradual oxidation of the arsine in the tank. The gas stream from the pot under the counter was passed through a test tube containing dilute aqueous $AgNO_3$ solution. The presence of arsine was indicated in the solution by the formation of a colloidal precipitate of metallic silver, according to the reaction:

$$AsH_3 + 6Ag^+ + 3H_2O = 6Ag + H_3AsO_3 + 6H^+.$$

Such a chemical test provided an integrated indication of arsine concentration over the period that gas bubbled through the solution. With the radioactivity measurements it was possible to detect 0.02 to 0.03 mg./L. of AsH_3. The break times for these concentrations were recorded. It is apparent that the definition of break time must include the concentration of gas detected or an equivalent statement. The conditions of the various tests, together with the silver nitrate and the radioactivity break times have been collected in Table II. Bed depths ranging from 2.5 to 5.0 cm. were tested; the flow rates were about 9.1 ml/cm^{2}sec., except in test SA2-4 when a flow of 4.6 ml/cm^{2}sec. was used. The silver nitrate break times were considerably shorter than those determined by radioactivity. The gas mixture, SA4, possessing a higher specific activity than the other mixtures, permitted the determination of smaller concentrations of arsenic. In the SA4 series, accordingly, it was found that the silver nitrate break occurred with arsine concentrations of about 0.004 mg./L. Table II illustrates very clearly that break times were not reproducible with any degree of precision, especially when the bed depth of the absorbent was 3 cm. or less.

The graphical representation of the radioactivity measurements has been included in Appendix I. The concentrations given on the graphs for arsine experiments were all calculated for (STP) conditions. To test the validity of Hinshelwood's equation, number 14a, the values of log $\left(\frac{c_o}{c} - 1\right)$ for each test were plotted against time. In no case were these curves straight; but for most cases appreciable portions of the graphs were moderately straight. The values of k_1 for Hinshel-

Table II

ARSINE TUBE TESTS.

CWSN19TU8 (Dried)

Expt. No.	Flow $\frac{ml.}{cm^2 sec.}$	c_0 Influent AsH_3 Conc. mg./L.	Bed Depth cm.	Break Time (at 0.02 to) (0.03 mg./L.) min.	Break Time $AgNO_3$ min.	k_1 $\frac{L}{mol.\ min.}$
SA2-2	9.12	7.0	5.0	52	38	1065
SA3-1	9.15	6.2	4.7	71	49	1100
SA4-2	9.34	5.6	5.0	49	34	1590
SA3-2	9.15	6.2	4.0	52.5	30	1200
SA4-4	9.34	4.1	4.0	43	26.7	1520
SA3-3	9.15	5.6	3.0	37.5	21	1590
SA4-3	9.34	4.7	3.0	24.2	12	2840
SA2-5	8.94	6.8	2.5	8	2	1700
SA2-6	9.20	6.8	2.5	12	5	2100
SA2-4	4.60	6.8	5.0	136	95	350

wood's equation were calculated from the slope of nearly linear portions of the curves, and they also have been included in Table II. The values so calculated were surprisingly constant for uniform flow rates and variable bed depths from 5 down to 3 cm.; when the bed depth reached 3 cm. or less, k_1 increased rapidly. An increase in c_0 seemed to cause a small decrease of k_1. The value of k_1 for experiment SA2-4, with about one half the flow rate of the other tests, was only one third the value for the comparable tests. These variations of k_1 were not predicted by the simple kinetics considerations of Case 1. It is to be noted that the curvature of the $\log\left(\frac{c_o}{c} - 1\right)$ curves was always positive; therefore the plot of the function, $\log \frac{c_o}{c}$, which appeared in equation 34, would be less satisfactory. If k_1, calculated from effluent concentrations of tube tests, is to furnish a satisfactory measure of the effectiveness of a charcoal, a correlation of these variations will be necessary.

When air was passed through charcoal which had been run even well past its break point, no active arsenic could be detected in the effluent stream.

Accumulation and Distribution Experiments. In the SA4 series the 3 mm. slit arrangement was set up to measure the accumulation of activity in the uppermost layer of the bed as a function of time during the absorption of arsine. At the top layer the concentration of the gas stream was constant and equal to c_o; therefore the complication of variation in c was avoided. Thus the dependence of the rate of arsenic pick-up on N, the concentration of absorbed arsenic in the charcoal, was determined to test directly the validity of kinetics equations 3 and 25a-b, which were assumed in Case 1 and Case 2 of the mathematical treatment. Since the correction for scattering for this type of experiment was somewhat uncertain, both the corrected and uncorrected activities were plotted in the graphs. It was apparent from the curves that the top layer of charcoal had not reached the saturation of its effectiveness in removing arsine, even for a long time after the break point; but the rate of removal did decrease rapidly with time in the initial stages of the tests. Thus the results were contrary to the assumptions involved in both Case 1 and Case 2.

In Case 1 equation 15 would give for the activity at $x = 0$

$$\text{Activity} = K_1\left(1 - e^{-k_1 c_0 t'}\right), \quad K_1 \text{ a constant.} \tag{39}$$

According to equations 29 and 43 of Case 2

$$\text{Activity} = K_2 t' \quad \text{for } t' < t'_0, \; K_2 \text{ a constant.} \tag{40a}$$

and

$$\text{Activity} = K_2 t'_0 \text{ for } t' > t'_0 \tag{40b}$$

As a matter of fact the experimental curves were represented very closely by an equation of the form

$$\text{Activity} = k_3\left(1 - e^{-k_4 t'}\right) + k_5 t' \tag{41}$$

where k_3, k_4, and k_5 are constants. Thus when the first term in equation 41 had reached a nearly constant value, after 40 to 60 minutes of gas flow, the top layer still continued to remove arsine at a constant rate for the remainder of the tests periods. A theoretical treatment, based on this equation, might lead to interesting results; at present it has not been attempted.

It may be pointed out that the value of k_1 calculated from the slope of the $\log\left(\frac{c_0}{c} - 1\right)$ curves and one point from the curve might be combined in Hinshelwood's equation to yield a value for N_0, the saturation capacity of the charcoal. In light of equation 41, however, such a calculation would have little significance.

When air was passed through the charcoal after the air-arsine mixture, no detectable decrease in the activity of the top layer occurred. Because of the absence of any observed desorption and because a considerable evolution of heat accompanied the removal process, it was believed that the arsenic was completely oxidized on the charcoal surface to form nonvolatile arsenic or oxides of arsenic.

After most of the tube tests the distribution of activity in the bed was determined. In experiments SA3-1 and 3-2 both the sectioning and the slit scanning techniques were employed. When the results of the sectioning were corrected to give the same numerical activity for the top 0.5 cm. increment of the bed as the scanning, identical curves were obtained for the two procedures. For experiment 3-3 only the sectioning technique was used while the more convenient scanning method was employed in the remaining experiments. In every case the scanning activities were corrected for scattering according to equation 37, discussed previously. The points in all experiments fell closely along smooth curves that were drawn to represent the distribution functions. In test SA2-3 the gas flow was stopped at approximately one half the break time. In this bed no activity was detected in the bottom layer, and an estimated 85% of the activity remained in the first two cm. of the 5 cm. bed. Thus the lower 3 cm. constituted an unused or "dead" layer. With beds for which gas flow had proceeded well past the break, the bottom layer frequently possessed an appreciable quantity of arsenic activity. The direct comparison of the distribution curves with the theoretical equation 15 of Case 1 and equations 29, 41, and 43 of Case 2 for N did not appear practicable. However a useful correlation was suggested from the results of Case 1. Equations 14b and 15 were combined to give

$$\frac{N(L,t')}{N_o} = \frac{c(L,t')}{c_o} + \frac{1}{\left(e^{k_1 c_o t'} + e^{\frac{N_o k_1 A x}{V}} - 1\right)} \qquad (42)$$

and

$$\frac{N(0,t')}{N_o} = \left(1-e^{-k_1 c_o t'}\right). \qquad (43)$$

If N_o is eliminated between these equations, there obtains

$$\frac{N(L,t')}{N(0,t')} = \left(1-e^{-k_1 c_o t'}\right)\left[\frac{c(L,t)}{c_o} + \frac{1}{e^{k_1 c_o t'} + e^{N_o k_1 Ax/V} - 1}\right] \qquad (44)$$

When t' becomes sufficiently large, the following simple expression results

$$\frac{N(L,t')}{N(0,t')} = \frac{c(L,t')}{c_o} \qquad (45)$$

But $N(L,t')/N(0,t')$ would be given by the ratio of the activities on the charcoal in the bottom and the top sections; and $c(L,t')/c_o$ would be the final effluent concentration divided by the influent concentration. The experimental values for these quantities appear in Table III.

Table III

DISTRIBUTION OF ACTIVE ARSENIC

Expt. No.	L Bed Depth cm.	t' Time of Gas Flow Min.	t'_b Break Time (0.02 to 0.03) (mg./L. AsH_3) Min.	$\frac{N(L,t')}{N(0,t')}$	$\frac{c(L,t')}{c_o}$
SA3-3	3.0	93	37.5	0.4	0.40
SA4-3	3.0	80	24.2	0.5	0.36
SA3-2	4.0	122	52.5	0.5	0.35
SA4-4	4.0	214	43	0.6	0.80
SA2-3	5.0	17.5	ca. 35	0.0	$<$0.003
SA2-1	5.0	72	52	0.1	0.05
SA4-2	5.0	110	49	0.2	0.20
SA3-1	5.0	170	71	0.6	0.59

The correlation predicted by equation 45 seemed remarkably good in many instances.

Although N_o could not be obtained, the concentration of arsenic in the bed could be calculated from the data. Such a calculation was made for experiment SA4-4, the longest run, from the known arsine input and from the loss of arsenic determined by a graphical integration of the effluent concentrations for the test. Then with the aid of the experimental distribution function it was calculated that the concentration of arsenic, expressed as the element, in the top layer of the charcoal amounted to 118 mg./cc.

The data accumulated with radioarsenic have been by necessity very limited. For this reason it appears unwise at present to draw further conclusions. The experimental results and the conclusions which were reached,however, have in themselves proved useful in partially describing the phenomenon of arsine removal. Limitations in the correlations of charcoal performance by present methods have appeared; and certainly the desirability of a more satisfying theoretical treatment to predict the experimental behavior has been clearly shown. It is very probable that a more extensive investigation, especially if it included the radioactive tracer methods, would lead to a clearer understanding of the mechanisms involved.

EXPERIMENTS WITH RADIOPHOSGENE (C*, Cl*)

Because of the short half lives of radiocarbon and radiochlorine the work with phosgene was performed mostly in the laboratories of the University of California at Berkeley so that experiments with the radioactive materials could proceed immediately following the cyclotron bombardments.

Preparation of Inactive Phosgene. About 400 g. of phosgene was prepared from CO and Cl_2 by passing an approximately equimolar mixture of the dried gases through two beds, each about 5 cm. long, of dried CWSN19, which acted as a catalyst. Cylinder Cl_2 was used, and CO was generated by the reaction of concentrated H_2SO_4 with formic acid. The product gases were passed through a bed of crushed antimony which combined with the free chlorine and condensed in a flask cooled in a dry ice bath. The phosgene was further purified by refluxing the liquid in the presence of metallic antimony for a period of several hours, the reflux condenser being cooled by a dry ice bath. All but a trace of yellow color due to dissolved Cl_2 was removed. The liquid phosgene was stored in a small steel cylinder .

Preparation of Phosgene Containing Active Carbon. C^{11} was prepared by a d-n reaction from B^{10}. The target, in the form of boric oxide fused on a copper plate, was bombarded with 80-100 μa. of 16 MEV. deuterons for 30 to 60 min. in the 60 in. Berkeley cyclotron. Active carbon prepared in this way existed largely as CO. The target was enclosed in a gas tight brass box with two ports. To each port was attached a 2 L. bulb; one bulb was evacuated and one contained dry

CO at one atm. Shortly after bombardment the radioactive CO was flushed into the evacuated bulb with CO from the other bulb. The previously evacuated bulb, containing CO at 0.5 atm. and bearing all the active CO, was filled to one atm. with dry Cl_2. Illumination of this mixture for 10 min. with light from two 500 w. incandescent lamps placed very close to the glass bulb, resulted in the synthesis of phosgene with a yield of 80-90%. (This photochemical reaction was the method by which Davy (16), using sunlight, first prepared phosgene). The phosgene from the reaction bulb was passed over metallic antimony to remove Cl_2 and was condensed by liquid air; the trap was then evacuated to remove any CO. The resulting purified phosgene was distilled from the trap directly into the evacuated steel cylinder, dry air being used to flush out the trap. When desired, inactive phosgene was also introduced before compressed air from another cylinder was added. The synthesis required about 40 min., or two carbon half lives, after the cessation of bombardment.

The total activity of the carbon, calculated for the end of the bombardment, amounted to about 100 millicuries.

<u>Preparation of Phosgene from Radioactive Chlorine</u>. Cl^{38}, resulting from a d-p reaction with chloride, was formed by the direct deuteron bombardment of LiCl, fused on a copper target plate, with 16 MEV. deuterons at 80 to 100 μa. for about one hour. Shortly after bombardment the target plate was removed from the cyclotron and the LiCl washed from the plate with distilled water into a distilling flask. The active chloride was converted into chlorine by direct exchange, making use of the fortunate circumstance that this exchange is practically instantaneous (17, 18).

To accomplish the exchange, one L. of Cl_2 at 1 atm. was bubbled through the LiCl solution, passed through a $Mg(ClO_4)_2$ drying agent, and then condensed with liquid air. The Cl_2 was distilled from the trap into a 2 L. bulb that contained dry CO at 0.5 atm. The chlorine, which passed through the LiCl solution, removed at least 90% of the chlorine activity. The photochemical preparation of phosgene from the $CO-Cl_2$ mixtures was carried out as with the radiocarbon. The synthesis required about 50 min. or slightly more than one chlorine half life.

The radiochlorine samples were intensely active; and in a condensed phase, they glowed brightly in the dark. The measured total chlorine activity at the end of bombardment was about 100 millicuries.

Chemical Analysis and Tests for Phosgene. The concentrations of phosgene in the cylinders were determined by bubbling the mixture at a known rate, about 250 ml./min. as indicated by a flowmeter, through two absorption bottles connected in series and each containing 50 ml. of 3N. NaOH solution. The chloride content of the NaOH solutions was then determined by the Volhard method.

A saturated aqueous solution of aniline and N,N′- diphenylurea was used for the chemical detection of phosgene. The formation of the white precipitate of diphenylurea (solubility in H_2O 0.015 g./100 ml.H_2O at 25° C.) gave a less sensitive but more reproducible test than did p-dimethylaminobenzaldehyde-diphenylamine paper or solution, which were used occasionally. The sensitivity of the aniline test was estimated by passing known concentrations of phosgene through the solution and noting the time required for the formation of a visible precipitate. This was made the basis of a rough chemical estimation of minute concentrations of phosgene. Subsequent experiments have not given quantitative reproducible results, and the concentrations obtained by this method were considered to be lower limits of the phosgene concentration. The method was useful however since it indicated only phosgene while the radioactive method recorded total chloride concentration. The sensitivity of the test as used in the experiments varied from 0.15 to 0.40 mg. of phosgene, depending on the concentration present. These results were obtained under the following conditions: flow rate 2 L./min., room temperature 18.5° C., 5 ml. of aqueous solution saturated with aniline and diphenylurea. Aqueous $AgNO_3$ solutions proved useful indicators also since with the concentrations involved a precipitate of AgCl was formed only slowly when phosgene-air mixtures were passed through them. On the other hand, low concentrations of HCl produced an immediate copious precipitate. The presence of phosgene was frequently detected by smell.

Tests with Radiocarbon. In the first tube test with phosgene containing labeled carbon it was evident that large amounts of a substance containing the radiocarbon were transmitted almost without delay. To further study this rapid penetration by some carbon containing material, several experiments were performed at reduced flow rates (about 0.5 and 1.0 ml./cm^2 sec.) utilizing a 5.0 cm. bed of CWSN19TU8 (Dried), (50 RH), and (70 RH) at room temperature. The conditions of these tests have been included in Table IVA. Desorption was studied in experiments CG5-1C and CG_6-2C by passing an air stream through the bed after the air-phosgene mixture. In experiment CG4-C the flow rate was increased from

Table IV A

CONDITIONS OF RADIOCARBON TESTS AT LOW FLOW RATES

(Bed Depth = 5.0 cm.)

Expt. No.	Charcoal	Temp. °C.	c_o Phosgene mg./L. $\left(\frac{\text{mmols.}}{\text{m}^2}\right)$	Flow Rate ml./cm.^{2} sec.	Duration Flow Min.	Duration Desorption Min.
CG2-C	CWSN19TU8 (Dried)	20.5	9.22 (93.3)	0.54	65	
CG5-2C	CWSN19TU8 (Dried)	20.6	9.62 (97.4)	0.53	34	
CG6-1C	CWSN19TU8 (Dried)	20.0	10.6 (107.1)	1.06	50	
CG6-2C	CWSN19TU8 (Dried)	20.0	10.6 (107.1)	1.06	35	44 to 62
CG5-1C	CWSN19TU8 (50 RH)	20.6	9.62 (97.4)	0.55	70	82 to 102
CG4-C	CWSN19TU8 (70 RH)	19.8	6.94 (70.1)	(0.53 ((10.0	(71 ((75 to 105	

Table IV B

RESULTS OF RADIOCARBON TESTS AT LOW FLOW RATES

(Bed Depth = 5 cm.)

Expt. No.	Total Phosgene Input mmols.	C^* Absorbed mmols.	C^* Desorbed mmols.	Remarks
CG2-C	0.64	0.36		No marked accumulation of activity in entrant layer.
CG5-2C	0.34	0.27		
CG6-1C	1.11	0.48		Activity in effluent completely removed by soda lime.
CG6-2C	0.78	0.29	0.14	Activity in effluent completely removed by soda lime.
CG5-1C	0.73	0.60	0.12	
CG-4C	(0.51 ((4.2 (Additional)	(0.47 ((0.5 (Additional)		

0.51 to 10.0 ml./cm.^{2} min. after 71 min. and maintained at that value for 30 min. The penetration of the bed by active carbon has been illustrated in the figures for experiments: CG2-C, CG4-C, CG5-1C, CG5-2C, CG6-1C, and CG6-2C, which are contained in Appendix II. The figures show the carbon concentrations that appeared in the effluent streams. None of the experiments were run sufficiently long to obtain a phosgene break as indicated by the aniline test. The amounts of active carbon retained and transmitted by the bed as well as the quantities later desorbed were calculated by graphical integration of the effluent concentration curves. These results have been listed in Table IVB.

The results from the low flow rate experiments were noted:

1. The carbon activity appearing in the effluent was partially removed by a single liquid air trap and completely by a soda lime absorption tube. It possessed no detectable odor and later experiments proved that no chlorine was associated with it. Upon these observations and the nature of its origin it was concluded that the active substance was probably CO_2.

2. For low flows the CO_2 did not appear immediately in the effluent, there was a finite CO_2 break time.

3. For comparable conditions the presence of water in the charcoal markedly increased the retention of CO_2. The CO_2 break times increased and the slope the effluent CO_2 concentration-time curves decreased with increasing water content.

4. The charcoal retained from 0.3 to 1.0 millimols of the active carbon; and of this, a sizable fraction, 0.2 to 0.5, was readily desorbed

by an air stream.

Tube tests were then performed at normal flow rates (ca. 10 ml./cm.^{2}sec.) with dry air-phosgene mixtures and with 5 cm. beds of the CWSN19TU8 (Dried), (50 RH), (70 RH) and CWSN19 (Dried). These experiments were all run well past the phosgene break indicated by the chemical indicators. In some instances desorption with an air flow at the same rate as for the toxic stream was studied. The conditions of the tests have been presented in Table VA. The graphs of the radioactivity results for these experiments also appear in Appendix II (Experiments CG7-C, CG8-C, CG9-C, CG10-C, CG11-C, CG12-C and CG14-C). The figures show the plots of the active carbon concentration in the effluent. The total phosgene input and the chemically indicated break time for each experiment have been included in Table VB together with the amount of carbon retained during absorption and the amount later desorbed, which were obtained by the graphical integration of the graphs.

The following results were noted:

1. A substance containing radiocarbon, completely removed by soda lime, penetrated the bed from the start of gas flow; it was concluded that this substance was again CO_2.

2. The concentration of CO_2 in the effluent in a very few minutes attained a constant value which was equal to that for the influent radiocarbon. The total carbon concentration did not change later in the experiment when phosgene penetrated the bed.

3. Unexplained discrepancies appeared in the results of experiments CG10-C and CG12-C which were performed under almost identical

Table V A

CONDITIONS OF RADIOCARBON TESTS AT HIGH FLOW RATES

(Bed Depth = 5.0 cm.)

Expt. No.	Charcoal	Temp. °C.	c_o Phosgene mg./L. $\left(\frac{\text{mmols.}}{m^3}\right)$	Flow Rate ml./cm.^{2} sec.	Duration Flow Min.	Duration Desorption Min.
CG7-C	CWSN19TU8 (Dried)	18	9.00 (91.0)	10.4	80	110 to 118
CG8-C	CWSN19TU8 (Dried)	18	7.47 (75.6)	10.1	105	112 to 122
CG11-C	CWSN19TU8 (Dried)	17.5	7.86 (79.6)	10.3	90	111 to 171
CG9-C	CWSN19TU8 (70 RH)	18	8.90 (90.0)	10.1	100	110 to 142
CG10-C	CWSN19 (Dried)	18	7.86 (79.6)	10.1	65	-
CG12-C	CWSN19 (Dried)	16	7.51 (76.0)	10.3	90	109 to 127
CG14-C	CWSN19TU8 (70 RH)	-25	22.2 (224)	8.0	50	(69 to 86 ((88 to 138) (at 19°C.)

Table V B

RESULTS OF RADIOCARBON TESTS AT HIGH FLOW RATES

(Bed Depth = 5 cm.)

Expt. No.	Phosgene Input mmols.	C^* Absorbed mmols.	C^* Desorbed mmols.	Phosgene Desorbed mmols.	Remarks
CG7-C	14.9	0.5	ca.0.1		C* completely removed from effluent by soda lime. Ca. 3 min. after desn. started, Phosgene conc. was 7 x the C* conc.
CG8-C	15.7	0.5	0.17		C* completely removed from effluent by soda lime. Continued strong phosgene test by aniline after initial burst of activity during desn.
CG11-C	14.4	0.4	0.13	0.55	Aniline break, 60 min.
CG9-C	17.8	1.2	0.09	ca.0.05	Large desorption of HCl
CG10-C	10.4				AgCl break 18 min. Aniline break 50 min.
CG12-C	13.7	0.2	0.25	0.74	AgCl break, 10 min. Aniline break, 57 min.
CG14-C	20.5	1.2	0.2	0.05	Bed and influent stream cooled to -25°C. Aniline break 20 min. No phosgene detected in desorption. Bed warmed to rm. temp. during second desn.

conditions with CWSN19 (Freshly dried). In CG10-C the active carbon in the effluent stream rose to only 70-80% of that in the influent. At the aniline break the active carbon concentration may have started to rise, although the test was not continued long enough for this to have been determined with certainty. In CG12-C, however, the effluent concentration rose quickly to the influent value and remained constant thereafter. HCl appeared in each test in the effluent in 10 to 20 min.; but phosgene did not appear until 50 to 60 min., the phosgene break time being somewhat shorter than for the dry whetlerite.

4. The quantity of active carbon retained by the whetlerite and and the quantity that could later be desorbed were of the same order of magnitude as the corresponding values at the low flow rates when the total phosgene input was approximately only 5% as great.

5. A surprising result was that in the desorption experiments with dried CWSN19TU8, phosgene continued to be desorbed, as indicated by the estimates with the chemical tests, after the carbon activity had fallen to a negligible amount. A lower limit to the quantity of phosgene desorbed was given by the precipitation of diphenylurea from aniline solutions. These results indicated that three to four times the amount of phosgene was desorbed than was to be inferred from the radioactivity.

<u>Experiments with Radiochlorine</u>. The preceding experiments, although informative, proved that radiocarbon could not be used successfully to evaluate the protection of the charcoals against phosgene. Accordingly, phosgene labeled with Cl^{38} was prepared and used for tube tests with

dried and equilibrated whetlerites in a 5.0 cm. bed at room temperature, -25°C. and 40°C. Again dry air-phosgene mixtures ($<2\%$ RH) were used exclusively. The radiochlorine, in contrast to the active carbon, exhibited normal behavior. The conditions for the tests, together with the aniline break points and the 1% chlorine penetration times, have been listed in Table VI A. The graphs for the experiments, CG16-Cl, CG17-Cl, CG18-2Cl, CG20-1, 2, 3Cl, CG21-1, 2, 3Cl and CG22-Cl, have been included in Appendix III. Active chlorine concentration vs. time curves were prepared for comparison with the radiocarbon tests. Also the $\log\left(\frac{c_o}{c} - 1\right)$ function was plotted to test the theoretical equations. In the few cases where it was measured, CG17-Cl, CG18-2Cl, and CG22-Cl, the accumulation of activity in the entrant layer was plotted. On the graphs the aniline break points have been indicated by the symbol, A.

For determining the accumulation of activity, the slit technique was employed. A 1 or 3 mm. slit was used; and because of the intensity of the radiation the slits were 200 mm. deep, the top of the slit being in line with the top of the bed. The correction for scattering was not determined with radiochlorine; therefore the activities were plotted uncorrected. The correction for scattering should not have changed the general form of the curves however. It appeared that the concentration of chlorine on the entrant layer of charcoal during absorption did increase with time with a rapidly decreasing rate. It did seem to approach a limiting value which was nearly reached at the break time (effluent chlorine = 1% influent). Thus it agreed fairly well with the equation resulting from Case 1

Table VI A

RADIOCHLORINE TESTS

(Bed Depth = 5 cm.)

Expt. No. (Temp.)	Charcoal	c_o Phosgene mg./L. (mmols.Cl*/m^3)	Flow Rate ml./cm.^{2}sec. Duration Flow (min.)	Break Time Cl* 1% of Influent min.	Break Time Aniline min.
CG15-Cl (19°C.)	CWSN19TU8 (Dried)	7.81 (151.8)	10.3 (100)	60	62
CG16-Cl (19°C.)	CWSN19TU8 (Dried)	9.38 (189.8)	10.2 (80)	44	44
CG22-Cl (21°C.)	CWSN19TU8 (Dried)	22.3 (451)	10.3 (71.8)	26	27
CG18-2Cl (20°C.)	CWSN19TU8 (50 RH)	7.36 (149)	10.3 (95)	42	45
CG17-Cl (19°C.)	CWSN19TU8 (70 RH)	10.6 (214)	10.3 (110)	47	-
CG20-3Cl (-25°C.)	CWSN19TU8 (Dried)	23.9 (484)	8.0 (109.5)	74	80
CG20-2Cl (-25°C.)	CWSN19TU8 (50 RH)	23.9 (484)	8.0 (60)	25	39
CG20-1Cl (-25°C.)	CWSN19TU8 (70 RH)	23.9 (484)	8.0 (45)	15	<21
CG21-3Cl (40°C.)	CWSN19TU8 (Dried)	20.4 (413)	10.0 (58)	25	<37
CG21-1Cl (40°C.)	CWSN19TU8 (50 RH)	20.4 (413)	10.0 (50)	27	<33
CG21-2Cl (40°C.)	CWSN19TU8 (70 RH)	20.4 (413)	10.0 (56)	28	<35

Table VI B

RESULTS OF RADIO CHLORINE TESTS

(Bed Depth = 5 cm.)

Expt. No.	Phosgene Retained Before Break mmols.	Total Cl^* Absorbed mmols.	Cl^* Desorbed Time Interval of Desorption (min.)	Fraction Cl^* Desorbed	Remarks
CG15-Cl	9.57				
CG16-Cl	8.39	29.2	3.80 (135 to 164) (165 to 186)	0.12	Desorbed first with N_2, then with air. Aniline test + during desorp.
CG22-Cl	11.83	51.0	17.0 (74 to 130)	0.33	Aniline test ++ during desorp.
CG18-2Cl	6.31	26.8	1.41 (110 to 139)	0.05	Aniline test faint $AgNO_3$ test + during desn.
CG17-Cl	9.81	41.5	4.05 (191 to 216)	0.10	Aniline test very faint. $AgNO_3$ test + during desorp.
CG20-3Cl	32.5	83.3	11.1 (111 to 127)	0.13	Aniline test ++ during desorp.
CG20-2Cl	10.97	48.5	2.62 (61 to 75)	0.54	Aniline test + $AgNO_3$ test ++ during desorp.
CG20-1Cl	6.60	36.2	0 (58 to 65)	0	Aniline test negative during desorp.
CG21-3Cl	11.89	42.0	11.3 (68 to 83)	0.28	Aniline test ++ during desorp.
CG21-1Cl	12.80	43.7	5.37 (53 to 68)	0.13	Aniline test ++ during desorp.
CG21-2Cl	13.20	-	-	-	Aniline test + during desorp.

NOTE + and ++ indicate positive and strongly positive test.

$$\text{Activity} = K\left(1 - e^{-k_1 c_0 t}\right), \; K \text{ a constant.} \tag{39}$$

The steeper rise for CG22-Cl may have been due to the greater slit width (3 mm. as compared with 1mm.). The dependence of the rate of absorption on N would therefore be in agreement with the assumption for Case 1. The resulting equations for Case 1 then would or would not be valid according to the dependence of the rate of absorption on c.

It was noteworthy that one third to one half of the chlorine in the entrant layer could be desorbed; the remainder was not removed by continued air flow.

From the plots of $\log\left(\frac{c_0}{c} - 1\right)$ it can be seen that a small fraction of the entrant chlorine appeared in the effluent and remained roughly constant at about 0.1% of the influent until the break. This was noted whether the thermocouples were or were not inserted in the bed. To exclude the possibility that this effect was caused by radiation from the charcoal scattered through openings of the counter shield, a liquid air trap and a soda lime tube were inserted in the influent line before the pot and counter assembly. Each of these removed a large fraction, although not all, of the activity from the stream. It was therefore concluded that some chloride containing substance penetrated the charcoal in small quantities immediately. Further investigations would be required for its identification.

The radioactivity break times for 1% penetration of chlorine proved to be nearly identical with the aniline breaks. The values obtained by both methods have been given in Table VI A. The break times for comparable tests were not strongly dependent on the moisture content of the charcoal at either 20 or 40°C. although possibly the higher water content contributed to slightly better protection. No difference in protection between 20 and 40°C. was apparent. The differences in moisture content however resulted in striking differences of protection at low temperatures. At -25°C. the dry charcoal had three times the life, the (50 RH) sample nearly the same life, and the (70 RH) sample roughly only 0.6 the life of the absorbents tested at room temperature.

The quantities of phosgene retained by the charcoal before the break together with the amount of active chlorine absorbed by and desorbed from the bed, as calculated by means of graphical integrations of the effluent concentration curves, have been given in Table VI B. The molecular state of the chlorine was not indicated, of course, by the radioactivity measurements. However a comparison of the aniline and silver nitrate indicator tests showed that with dried whetlerite only very minute traces of HCl compared to phosgene could have been present in the effluent during either gas flow or desorption. The concentrations of chlorine during desorption were of the same order of magnitude as the concentrations penetrating the bed in the later period of absorption, and usually they decreased fairly rapidly as desorption progressed. The value of 3.80 mmols. of active Cl desorbed as phosgene for test CG16-C1 can be compared with the value, 0.13 mmols. of active carbon, for experiment CG11-C. The dried whetlerite from one of the tube tests still retained the odor of phosgene several days after the test. When it was placed in water, both cupric and chloride ions were identified in the solution. With the equilibrated charcoals at 20 and 40°C., on the other hand, although the chlorine concentration curves were similar to those for the dry whetlerite, it was evident from the chemical indicators that the effluent contained both phosgene and HCl. HCl, and CO_2 are, of course, the hydrolysis products of phosgene. During the last periods of gas flow and during the desorption probably the larger fraction of the chlorine was present as HCl. In general, there was less chlorine desorbed from equilibrated chars. At -25°C. a surprising result was that no detectable chlorine was desorbed from the (70 RH) whetlerite either at the low temperature or after the charcoal had been warmed to room temperature, although the break time had been only 15 min., and HCl had appeared in the effluent.

It was found from the $\log\left(\frac{c_o}{c} - 1\right)$ graphs that, as was the case with arsine, straight lines were not obtained for this function, but that appreciable portions of the curves were nearly linear. By means of the approximate Hinshelwood equation,

$$\ln\left(\frac{c_o}{c} - 1\right) = -k_1 c_o t' + \frac{k_1 N_o A x}{V} , \qquad (17)$$

the values for the rate constant, k_1, and for the capacity factor, N_o, were calculated. These parameters were computed for the point at which $c_o/c = 100$ since this point corresponded closely to the chemical break point, and because the logarithmic plots had only slight curvature in this region. The calculated values appear in Table VII.

Although the number of experiments was too small to permit satisfactory generalizations, some interesting observations concerning the Hinshelwood constants may be made. The value of k_1 for dried CWSN19TU8 at room temperature in the two comparable experiments decreased slightly, from 880 to 730 $cm.^3(mmols.\ Cl)^{-1}min.^{-1}$ with a two fold increase of c_o. This difference may not have been significant. However the values

Table VII

PARAMETERS OF APPROXIMATE HINSHELWOOD EQUATION, NUMBER 17, CALCULATED FOR RADIOCHLORINE

$$\ln\left(\frac{c_o}{c} - 1\right) = -k_1 c_o t' + \frac{k_1 A N_o x}{V}$$

Expt. No.	Charcoal CWSN19TU8	Temp. $^oC.$	$\frac{V}{A}$ $\frac{cm.}{min.}$	c_o $\frac{mmols.\ Cl}{m^3}$	k_1 $\frac{cm.^3}{(mmols.\ Cl)min.}$	N_o $\frac{mmols.\ Cl}{cm.^3}$
CG16-Cl	(Dried)	19	618	189	880	1.68
CG22-Cl	(Dried)	21	618	451	730	2.20
CG18-2Cl	(50 RH)	20	618	149	540	1.84
CG17-Cl	(70 RH)	19	618	214	310	3.06
CG21-3Cl	(Dried)	40	600	413	1150	1.72
CG21-1Cl	(50 RH)	40	600	413	1000	1.96
CG20-3Cl	(Dried)	-25	480	484	570	4.20
CG20-2Cl	(50 RH)	-25	480	484	480	2.18
CG20-3Cl	(70 RH)	-25	480	484	440	1.70

decreased considerably with increased water content, being 540 for CWSN19TU8 (50 RH) and 310 $cm.^3 (mmols.\ Cl)^{-1} min.^{-1}$ for (70 RH). The rate constants were markedly higher at 40°C. than at room temperature, amounting to 1150 and 1000 $cm.^3 (mmols.\ Cl)^{-1} min.^{-1}$ for the dried and (50 RH) whetlerite. The capacity figures, N_o, on the other hand, showed a rather large increase with increasing concentration, increase with increasing water content, and a significant decrease, as would be expected, when the temperature was increased from 20 to 40°C. Thus, the variations of these parameters indicated considerable differences in charcoal behavior under the different conditions tested. However in the tube tests performed, the variations of k_1 so balanced the changes in N_o that for equal concentrations nearly equal break times were obtained in most cases at 20 to 40°C. At -25°C. the values of k_1 were nearly independent of moisture and were about equal to the value for the (50 RH) material at room temperature. The striking differences in the protection occurred at the low temperatures because N_o varied from the low value of 1.70 $mmols.\ Cl/cm.^3$ with CWSN19TU8 (70 RH) to the extremely high value of 4.20 $mmols.\ Cl/cm.^3$ for the dried whetlerite.

The desorption of chlorine which occurs with phosgene was not in agreement with the assumptions involved in Case 1 for the derivation of Hinshelwood's equation. However it might result that the overall differential equation, including desorption as well as absorption, might approximate the assumed equation 3 for a constant concentration of toxic material entering the bed. From the limited number of data the use of the results from Case 1 to evaluate a charcoal's phosgene protection shows some promise. The dependence of k_1 and N_o on the test conditions should however be determined.

The values of k_1 and N_o were calculated on the basis of chlorine. When the values of k_1 were changed to a phosgene basis and expressed with the same units as for the case of arsine, very similar values were obtained for a pair of comparable experiments: for arsine, experiment SA4-2, k_1 = 1590 L.(mols. AsH_3)$^{-1}$min.$^{-1}$; for phosgene, experiment CG16-Cl, k_1 = 1760 L.(mols $COCl_2$)$^{-1}$min.$^{-1}$. Both these experiments were with 5.0 cm. beds of dried CWSN19TU8 and at nearly the same temperature and flow rate. The value of N_o, expressed on a phosgene basis for experiment CG16-Cl was 0.84 (mmols. $COCl_2$)/cm.^{3} The maximum concentration of arsenic in the charcoal was found to be 1.57 (mmols. AsH_3)/cm.^{3}

Thermocouple Measurements. Temperatures at the top, in the middle, and at the bottom of the absorbent beds were measured by means of thermocouples whose junctions were inserted in the charcoal 0.5 cm., 2.5 cm., and 4.5 cm. above the bottom of the bed. Curves of the temperatures determined by these thermocouples have been included in Appendix IV. At low flow rates the temperature change in the bed was small; but at high flows a temperature rise of several degrees accompanied the removal. The entrant layer showed little temperature change; this was attributed to the removal of heat by the incoming stream. With this qualification it was seen that a warm zone moved down the bed. The chlorine break occurred close to the time when the peak of the temperature wave reached the bottom (exit) of the charcoal. Quantitative interpretations of the temperature measurements would be difficult because of the heat loss to the room; therefore no estimate of ΔH for the removal process was attempted. The maximum rise in dry beds was about 6°C.; for moist beds it was 1-2°C. since probably H_2O was desorbed by the gas stream.

In the early tests desorption was carried out with air from a compressed air line; these desorptions were accompanied by a rise in temperature. In experiment CG12 and subsequently, a calcium chloride tube was inserted in the line; thereafter no marked temperature effect was noted.

Discussion of Results. The removal of phosgene by whetlerite would appear to be more involved than proposed by the present theories of adsorption and of hydrolysis by water present either in the charcoal or in the gas stream (19). Two major features of the experimental results must be explained; they are:

1. The carbon dioxide transmitted was equivalent to nearly all the phosgene which had entered the dried charcoal up to the time a chloride compound penetrated the bed.

2. Greater amounts of phosgene than corresponded to the labeled carbon were desorbed from a dry bed by an air stream after absorption.

The first hypothesis which suggests itself to account for the evolution of CO_2 from the dried whetlerite is that the copper oxide existing in the charcoal played an important role in reacting with the phosgene, according to the overall reaction

$$CuO + C^{*}OCl_2 = C^{*}O_2 + CuCl_2.$$

It may be pointed out that actually this reaction may have occurred in two steps in which the phosgene was first hydrolyzed and then in which the HCl formed was neutralized by the CuO. Thus,

$$C^{*}OCl_2 + H_2O = C^{*}O_2 + 2HCl$$
$$2HCl + CuO = CuCl_2 + H_2O.$$

The water formed in the second step would therefore be released to hydrolyze a second phosgene molecule, and so on. In this way a trace of water, which was not removed at 150° C. or which might have entered the charcoal in handling, could contribute to the hydrolysis of a significant quantity of phosgene. The maximum possible water content of the air used, 2% RH, would itself have accounted for the hydrolysis of about 2 mg. phosgene /L. according to the first step of the above reaction pair; and with the formation of water in the second step it would also have been able to remove additional phosgene.

If it were assumed that the charcoal adsorbed the HCl as such, however, without the formation of copper chloride, then to account for the CO_2 formation by hydrolysis in experiment CG22-Cl would require that the charcoal must have contained 5.4% H_2O, a value that seemed unreasonably high. It is worthwhile to note that the charcoal was stored in tightly sealed screw cap bottles, and that, further, samples which were redried at 150°C. and used the same day or a few days later gave the same results as the older samples from the storage bottles. The absence of appreciable HCl in the effluent stream at any time after the Cl^* break or during desorption indicated that if any acid were formed, it must have been retained very firmly by the charcoal. Indeed, if the phosgene had hydrolyzed, and the HCl had not been neutralized, then HCl would have greatly predominated over the phosgene in the bed, since nearly all the phosgene until the break had reacted to form CO_2. Then HCl, contrary to experiment, would have been expected to appear in the effluent. In experiment CG16-Cl it was calculated that 16.8 milliequivalents of chlorine had been retained by the bed before the Cl^* break; assuming the whetlerite to have been 7% copper, the amount of copper present was 17 milliequivalents, that is, just about enough to account for all the phosgene or HCl which might have formed.

The behavior of the CWSN19 base char would appear somewhat surprising therefore since with it, also, large quantities of active carbon dioxide appeared immediately in the effluent gases. Because the unimpregnated char contained no copper oxide, it might be supposed that the hydrolysis resulting in the formation of CO_2 would also have produced HCl which would have appeared in the effluent. This was in agreement with the observation that for experiments CG10-C and CG12-C HCl was detected in the effluent after 10 to 20 min., about 40 min. sooner than the penetration of phosgene was indicated. A 2.5% moisture content would have been required to supply the water for this hydrolysis in CG12-C.

The reaction of phosgene with CuO or water does not explain the fact that during desorption more phosgene appeared in the effluent stream than could be inferred from the carbon activity. This was indicated qualitatively by the chemical indicator solutions; however it can be demonstrated quantitatively by the comparison of experiment CG11-C with radiocarbon and experiment CG16-Cl with radiochlorine, for which closely similar conditions prevailed. It should be noted however that nitrogen was used for a portion of the desorption in CG16-Cl. According to an integration of the effluent concentration curves for these experiments, 0.13 mmols. of C^* was desorbed in CG11-C and 3.80 mmols. of Cl^* in CG16-Cl. Thus a ratio of 15 to 1, based on the phosgene equivalents of chlorine and carbon, existed. This represented a lower limit to the actual ratio since probably a portion of the carbon was present as CO_2, and the desorption in CG16-Cl was stopped while the effluent concentration was greater than 30 mmols./m.^{3} It is to be reemphasized that with the dried whetlerites only phosgene, and no HCl, was detected in the effluent stream.

A second hypothesis that could account for the evolution of C^*O_2 is that phosgene combined directly with oxygen on the charcoal to produce C^*O_2, the two chlorine atoms being left momentarily adsorbed on the charcoal. The chlorine might then have reacted with "surface oxides" present on the charcoal to form inactive phosgene.

$$C^*OCl_2 = C^*OCl_2 \text{ (adsorbed)}$$

$$C^*OCl_2 \text{ (ads)} + O = C^*O_2 + 2Cl \text{ (ads)}$$

$$2Cl \text{ (ads)} + C{=}O \text{ (surface)} = COCl_2$$

The inactive $COCl_2$ produced by the third step might be expected to have undergone these same reactions, leading to a chain which would have produced large quantities of inactive CO_2. Chemical estimations of the CO_2 have subsequently shown that such was not the case. Therefore if this mechanism is to be considered, a restriction must be placed on either the reactivity or the rate of formation of the phosgene molecule formed in the third step. It can be seen that this mechanism would account for both the production of C^*O_2 and for the exchange reaction observed. It does not account for HCl formation; however a limited amount of hydrolysis might have proceeded simultaneously.

An alternative mechanism, leading to exchange alone, would be the dissociation of C^*OCl_2 on the charcoal surface, followed by recombination of chlorine with the "surface oxides" to regenerate $COCl_2$.

This process would have caused an accumulation of active carbon in the bed, which was found not to occur to any appreciable extent.

The following additional experiments might be of value in clarifying the removal processes for phosgene:

1. Determination of the amount of water actually in CWSN19TU8 and CWSN19, dried for several hours at 150°C.

2. Further experiments similar to the ones reported, but using thoroughly dried air and charcoal dried at 150°C. or higher for prolonged periods of time.

3. Accurate measurement of both HCl and phosgene concentrations in the effluent streams. This might be done by a combination of photometric and radioactive methods.

4. A thorough study of phosgene tube tests using standard chemical methods.

The phosgene experiments, as the ones with arsine, have been limited in number; but they have yielded some unexpected results and given considerable information about the processes studied. They have indicated that the removal process for phosgene, which had been considered well known and fairly simple, may possess unexpected complications. Certainly, the results have again pointed out many additional experiments that might be performed to gain a clearer understanding of the mechanisms involved.

The method of radioactive indicators has required considerable expenditure for the instruments required for the studies and for nuclear bombardments. But as in its many other applications it has again proved a valuable tool for fundamental studies. Although the method is subject to limitations and must certainly be accompanied by other investigations, the techniques have proved practicable for studying gas mask absorbents. It is believed that the efforts have been justified.

SUMMARY

1. The method of radioactive indicators, using separately As^{74}, C^{11}, and Cl^{38}, has been applied in tube test studies of the removal of arsine and phosgene from air-gas mixtures by the gas mask absorbent, CWSN19TU8, a type A army whetlerite. Experiments were performed in which the concentration of the indicator element in the effluent stream was measured continuously, in which the accumulation of activity in the entrant layer of the charcoal was followed, and in which the distribution of activity throughout the charcoal was ascertained.

2. A mathematical treatment for tube test absorption has been included, containing the derivation of Hinshelwood's equation.

3. The deviation of the behavior in the case of arsine from that predicted by the theories was demonstrated, particularly the action of the charcoal to continue the absorption of arsine for a long time at a low constant rate. Arsine desorption was found to be negligible.

4. With phosgene it was found that nearly all the carbon in the gas penetrated the bed immediately as CO_2, both with the whetlerite and its base char.

5. From the experimental $\log\left(\frac{c_o}{c} - 1\right)$ functions obtained with active chlorine, the parameters of Hinshelwood's equation were calculated for tube tests with varying moisture contents at -25°C., 20°C. and 40°C.

6. In studies of the desorption of phosgene following tube tests it was found that significant quantities of phosgene were desorbed in

which the carbon had been exchanged.

7. The temperature changes accompanying phosgene removal were measured.

8. Possible mechanisms to account for the results of the phosgene absorption were discussed.

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APPENDIX I

GRAPHS FOR ARSINE EXPERIMENTS.

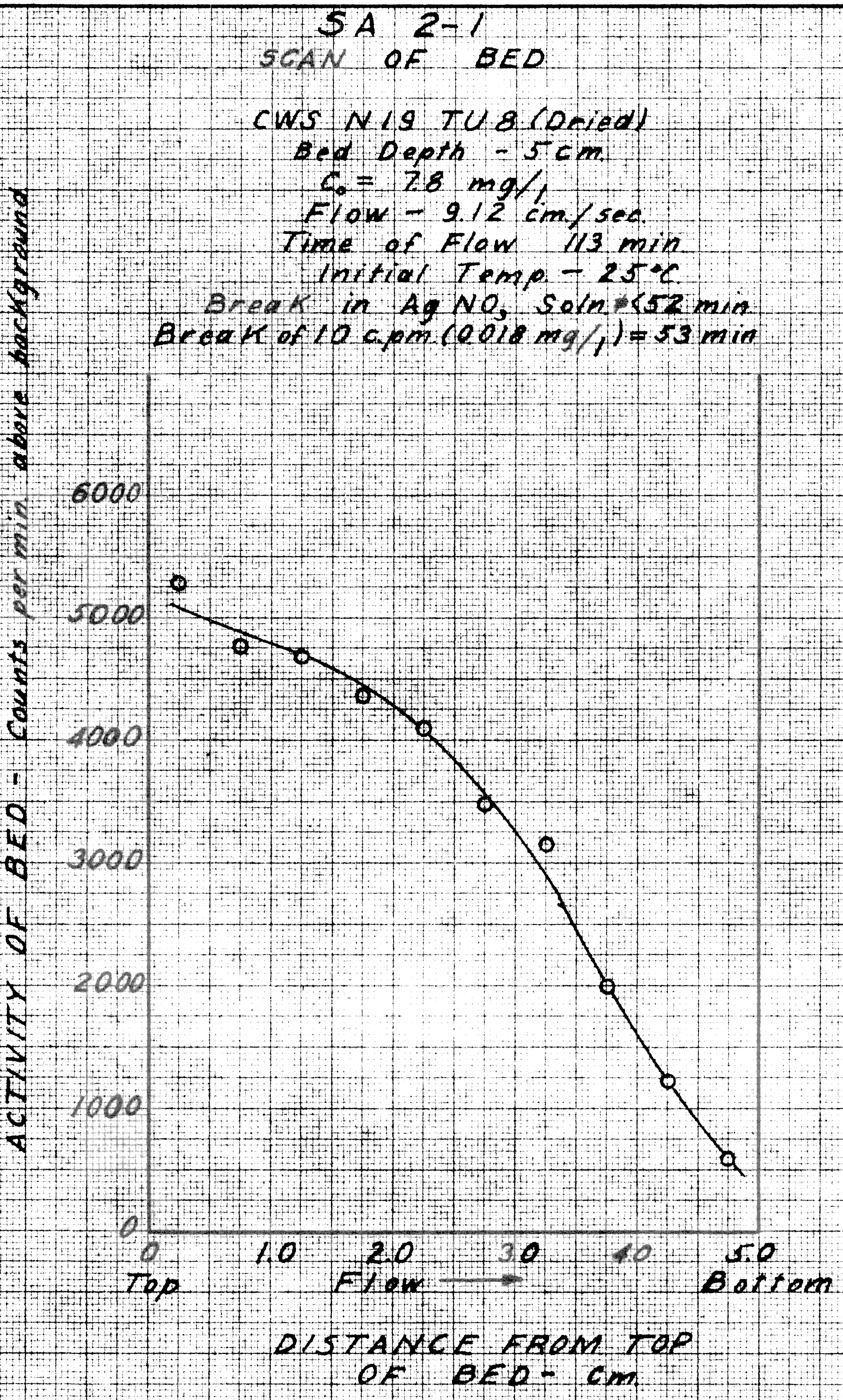
Expt. No.	Function Plotted	Expt. No.	Function Plotted
SA2-1	D	SA4-2,3,4	C
SA2-2	L	SA4-2	L
SA2-3	D		A
SA2-4	L		D
SA2-5	L	SA4-3	L
SA2-6	L		A
SA3-1	L		D
	D	SA4-4	L
SA3-2	L		A
	D		D
SA3-3	L		
	D		

Note: A = Accumulation of activity in entrant layer vs. time

C = Concentration in effluent vs. time

D = Distribution of activity in charcoal

L = $\log\left(\frac{c_o}{c} - 1\right)$ vs. time



SA 2-1
SCAN OF BED

CWS N19 TU8 (Dried)
Bed Depth - 5 cm.
C_0 = 7.8 mg/l
Flow - 9.12 cm./sec.
Time of Flow 113 min
Initial Temp. - 25°C
Break in $AgNO_3$ Soln. <52 min
Break of 10 c.p.m. (0.018 mg/l) = 53 min

KEUFFEL & ESSER CO., N. Y. NO. 359-14
Millimeters, 10th lines heavy.
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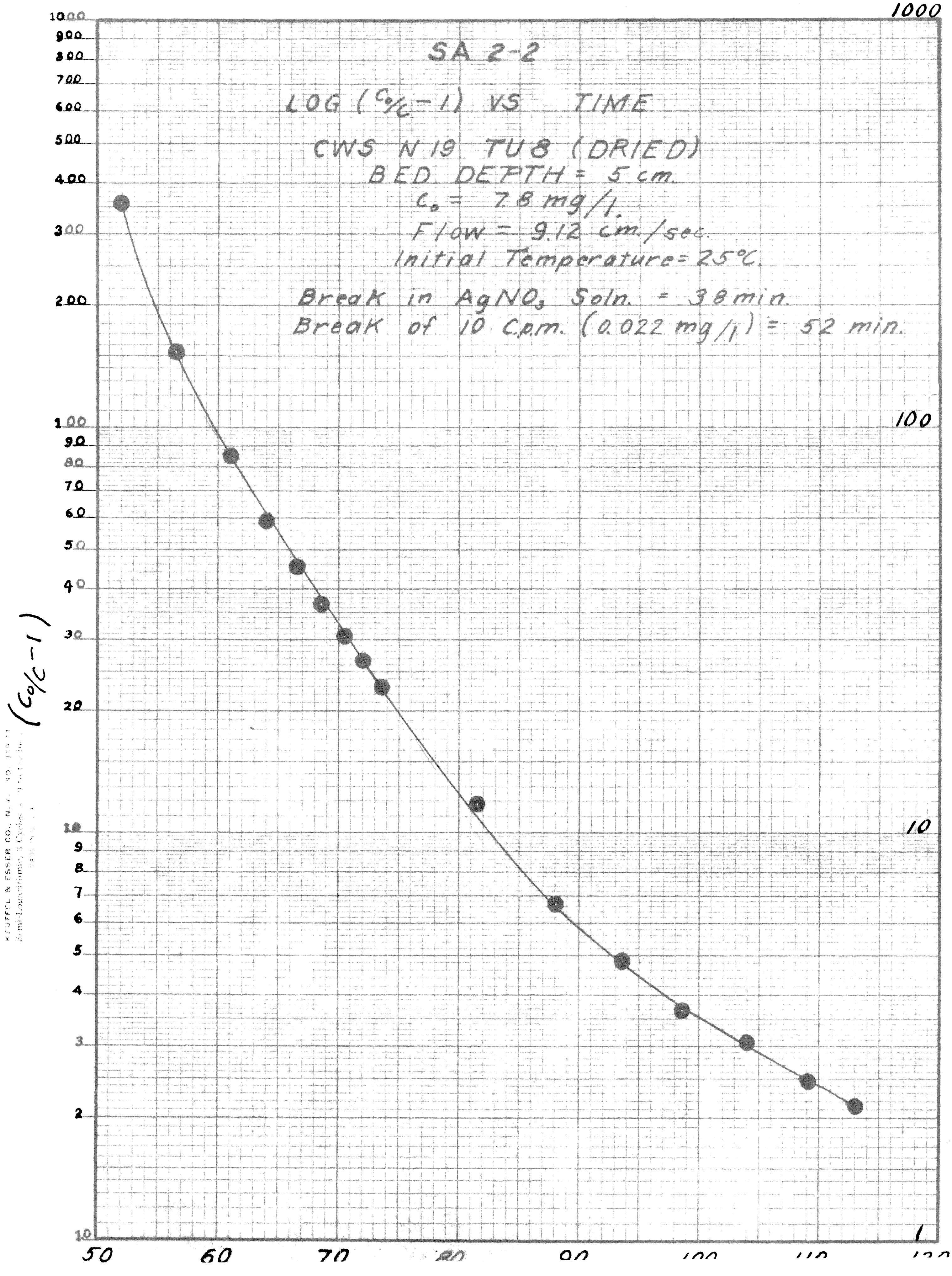


SA 2-2

LOG (C_0/C - 1) VS TIME

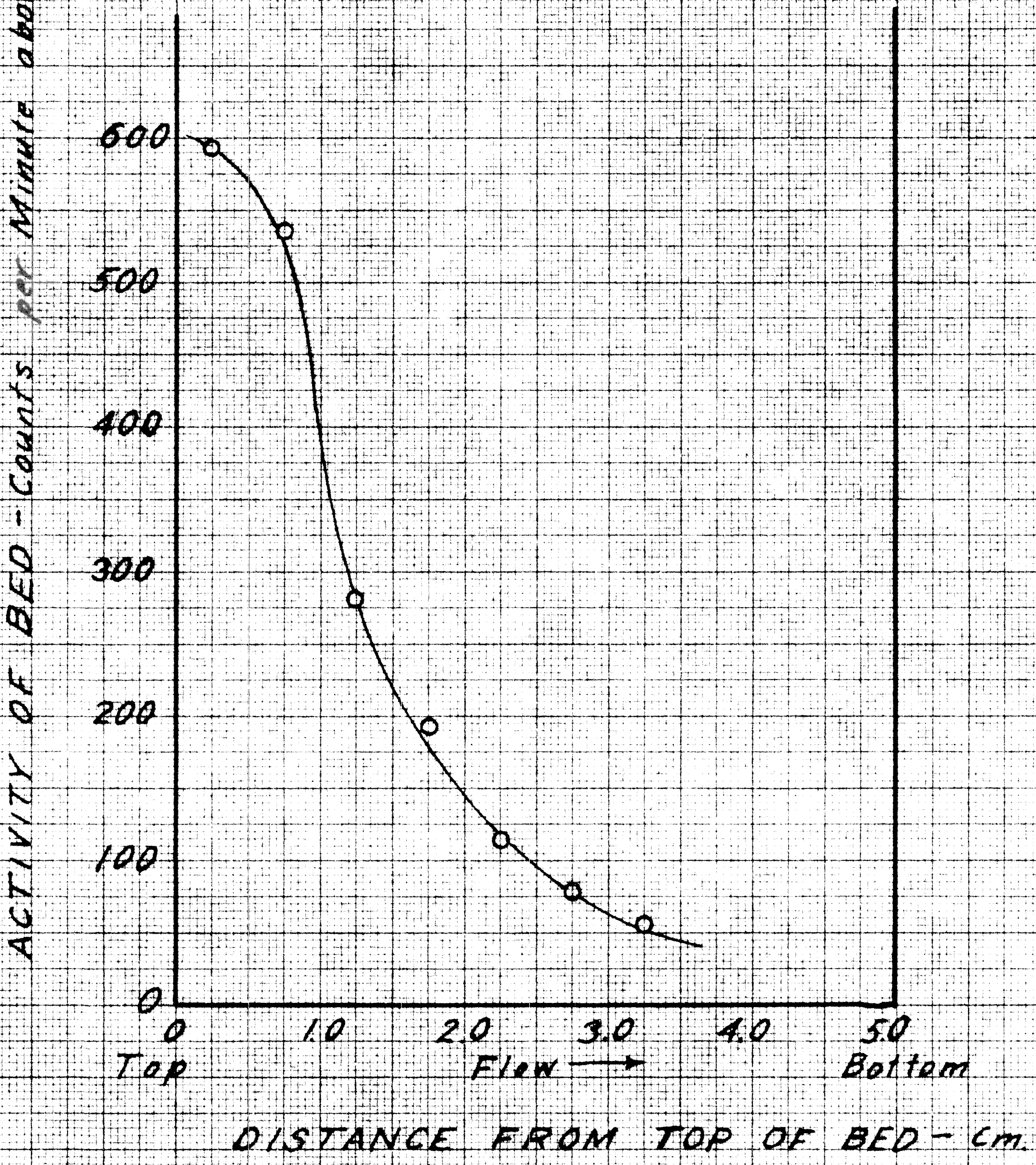
CWS N 19 TU 8 (DRIED)
BED DEPTH = 5 cm.
C_0 = 7.8 mg/l.
Flow = 9.12 cm./sec.
Initial Temperature = 25°C.

Break in $AgNO_3$ Soln. = 38 min.
Break of 10 C.p.m. (0.022 mg/l) = 52 min.

SA 2-3

SCAN OF BED

CWS N 19 TU 8 (DRIED)
BED DEPTH – 5 CM.
C_0 = 7.8 mg/l
FLOW 9.12 cm/sec.
TIME OF FLOW = 17½ MIN
(Approx. ½ Break Time)



KEUFFEL & ESSER CO., N. Y. NO. 359-14
Millimeters, 10th lines heavy
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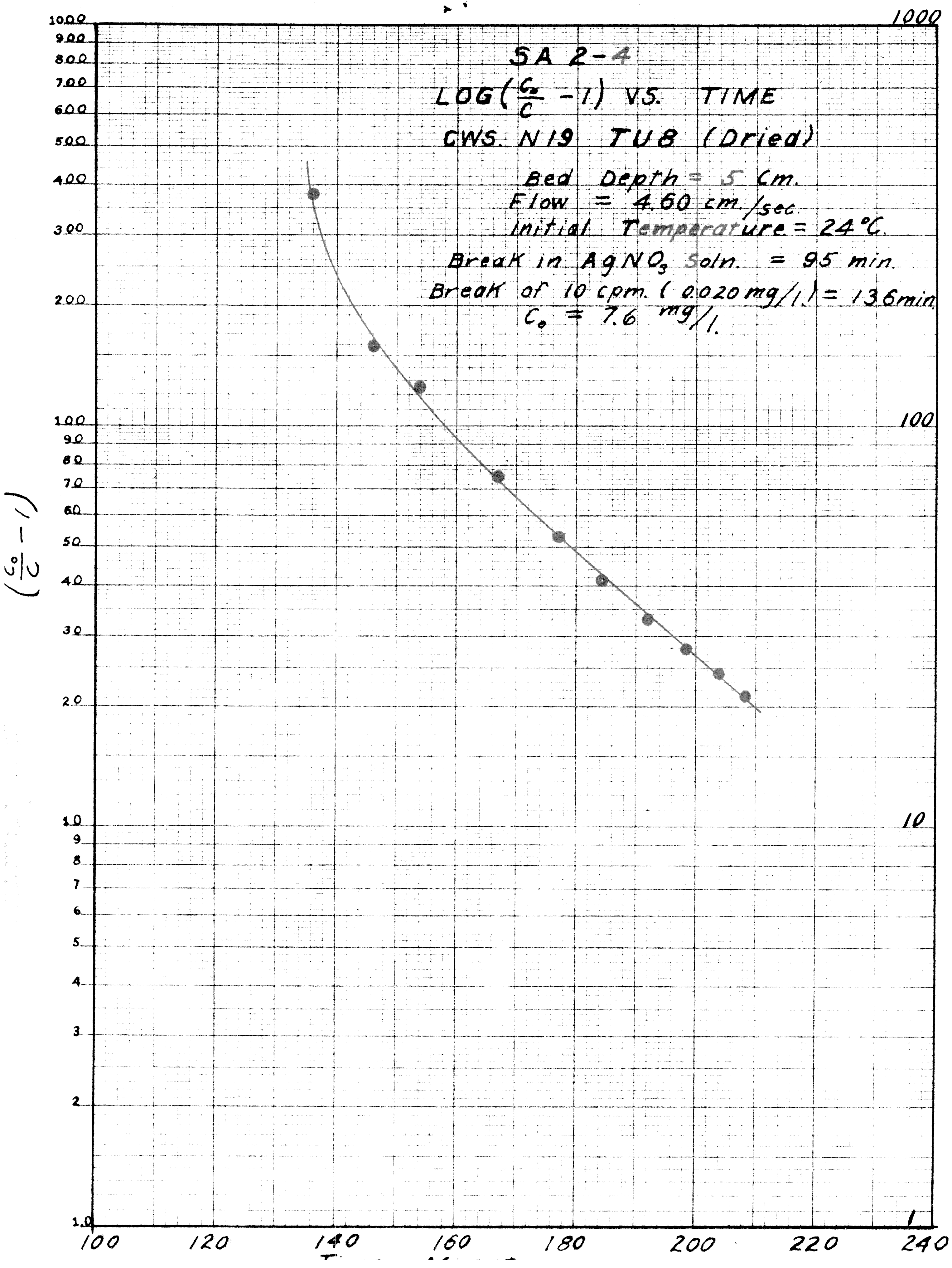
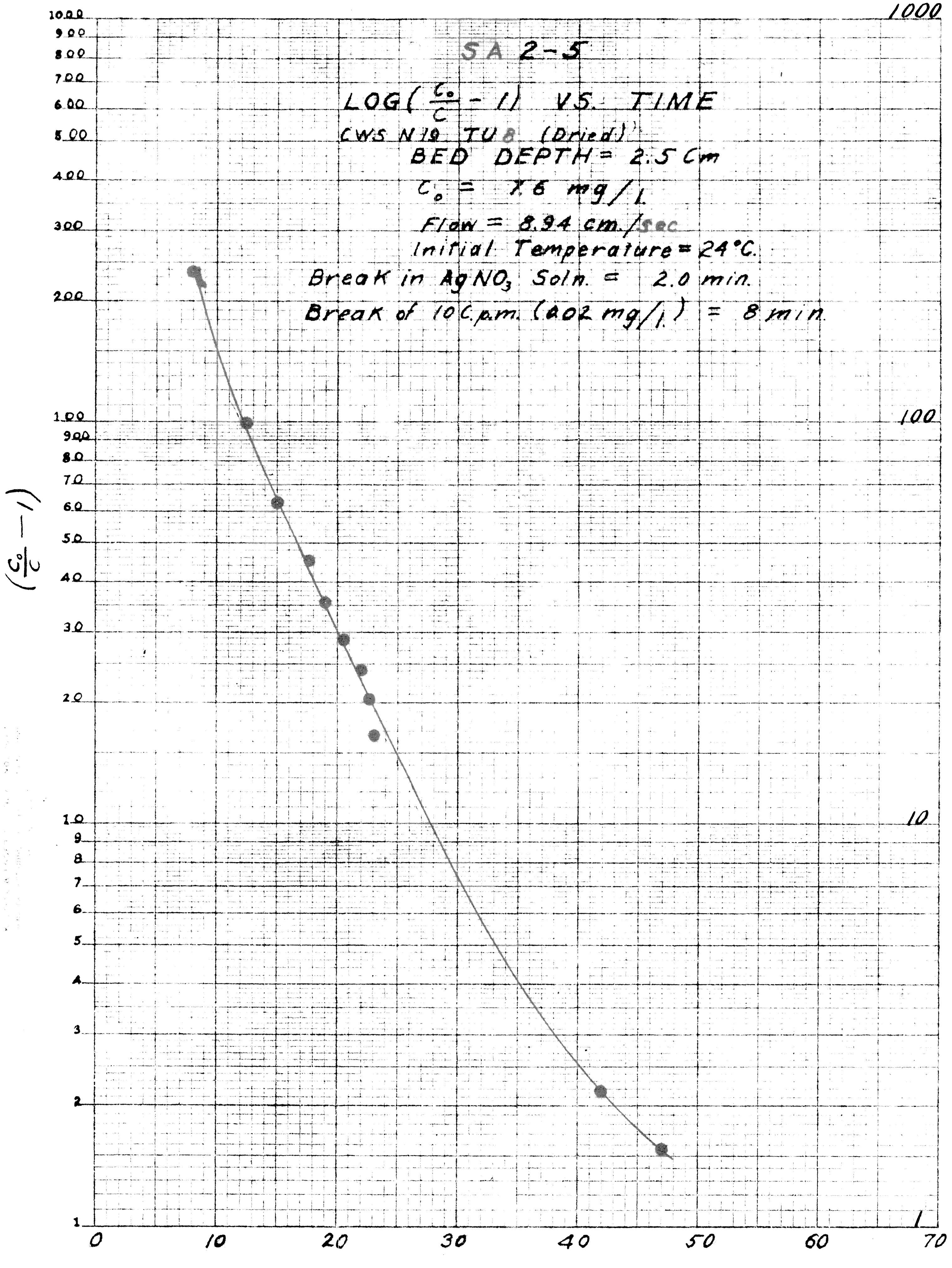


SA 2-4

LOG$\left(\frac{C_o}{C}-1\right)$ VS. TIME

CWS. N19 TU8 (Dried)

Bed Depth = 5 Cm.
Flow = 4.60 cm./sec.
Initial Temperature = 24°C.
Break in $AgNO_3$ Soln. = 95 min.
Break of 10 cpm. (0.020 mg/l.) = 136 min.
C_o = 7.6 mg/l.



SA 2-5

LOG($\frac{C_0}{C}$ - 1) VS. TIME

CWS N19 TU8 (Dried)

BED DEPTH = 2.5 Cm

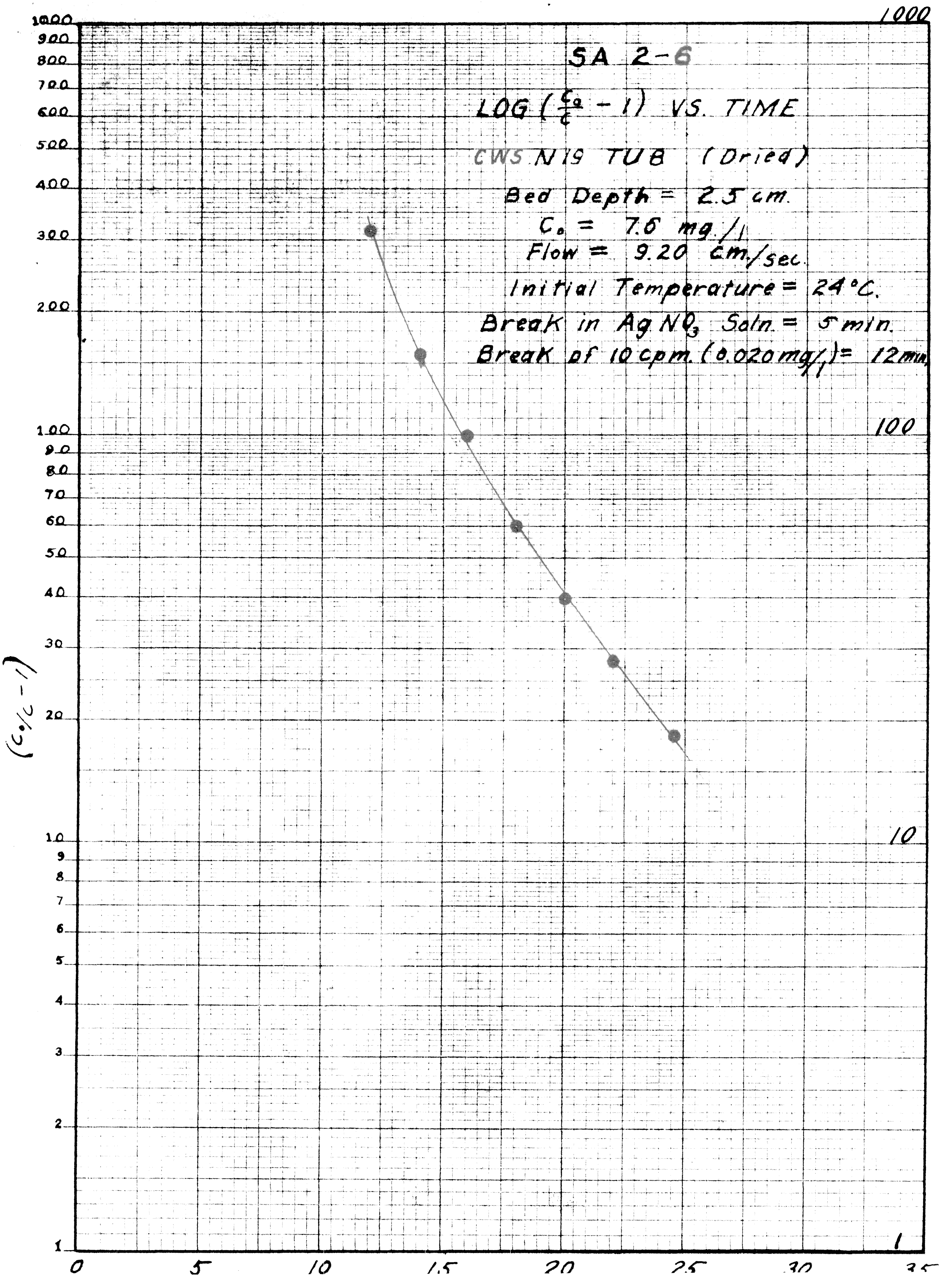
C_0 = 7.6 mg/l.

Flow = 8.94 cm./sec

Initial Temperature = 24°C.

Break in $AgNO_3$ Soln. = 2.0 min.

Break of 10 C.p.m. (0.02 mg/l.) = 8 min.



SA 2-6

LOG ($\frac{C_o}{C}$ - 1) VS. TIME

CWS N19 TUB (Dried)

Bed Depth = 2.5 cm.

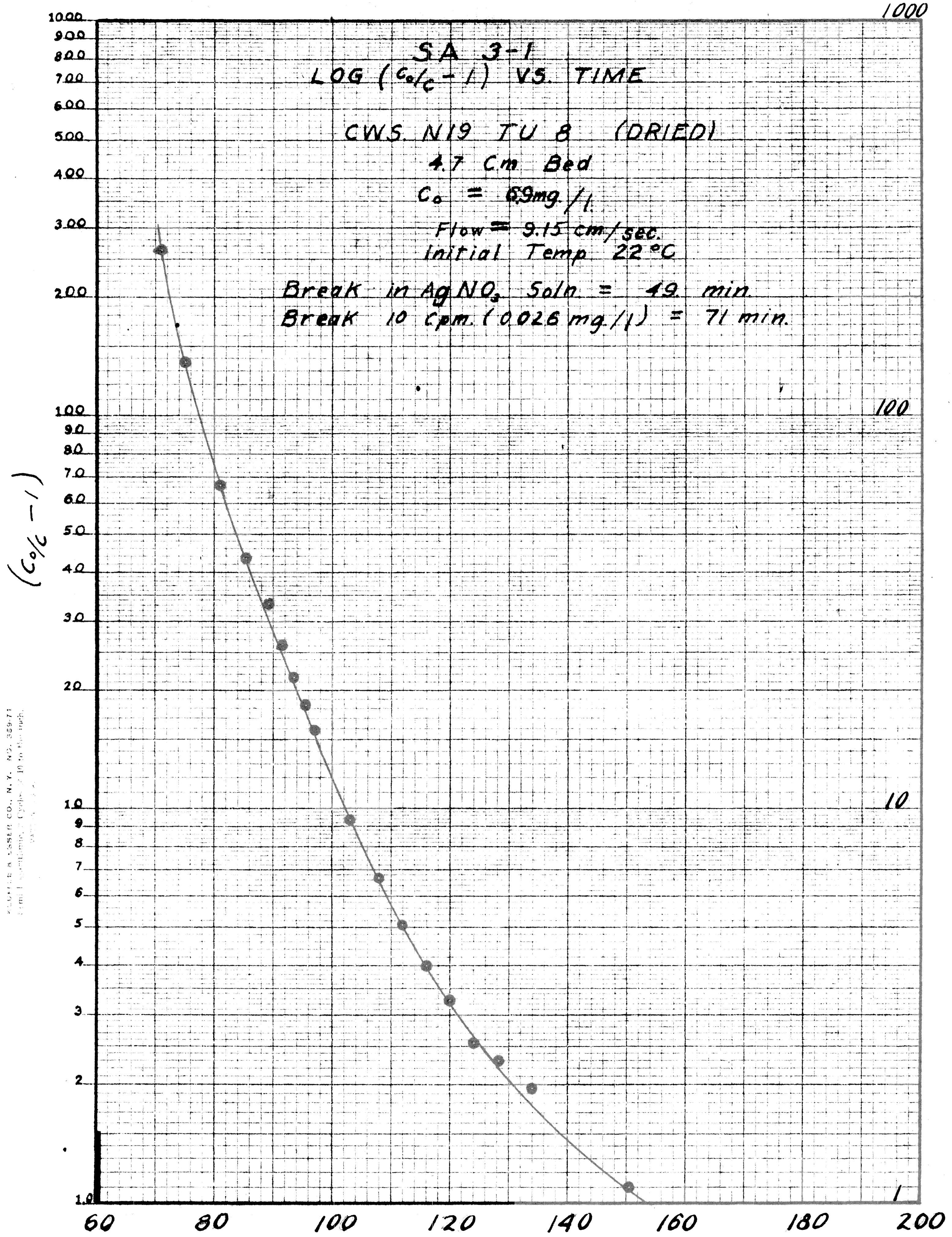
C_o = 7.6 mg./l

Flow = 9.20 cm./sec.

Initial Temperature = 24°C.

Break in $AgNO_3$ Soln. = 5 min.

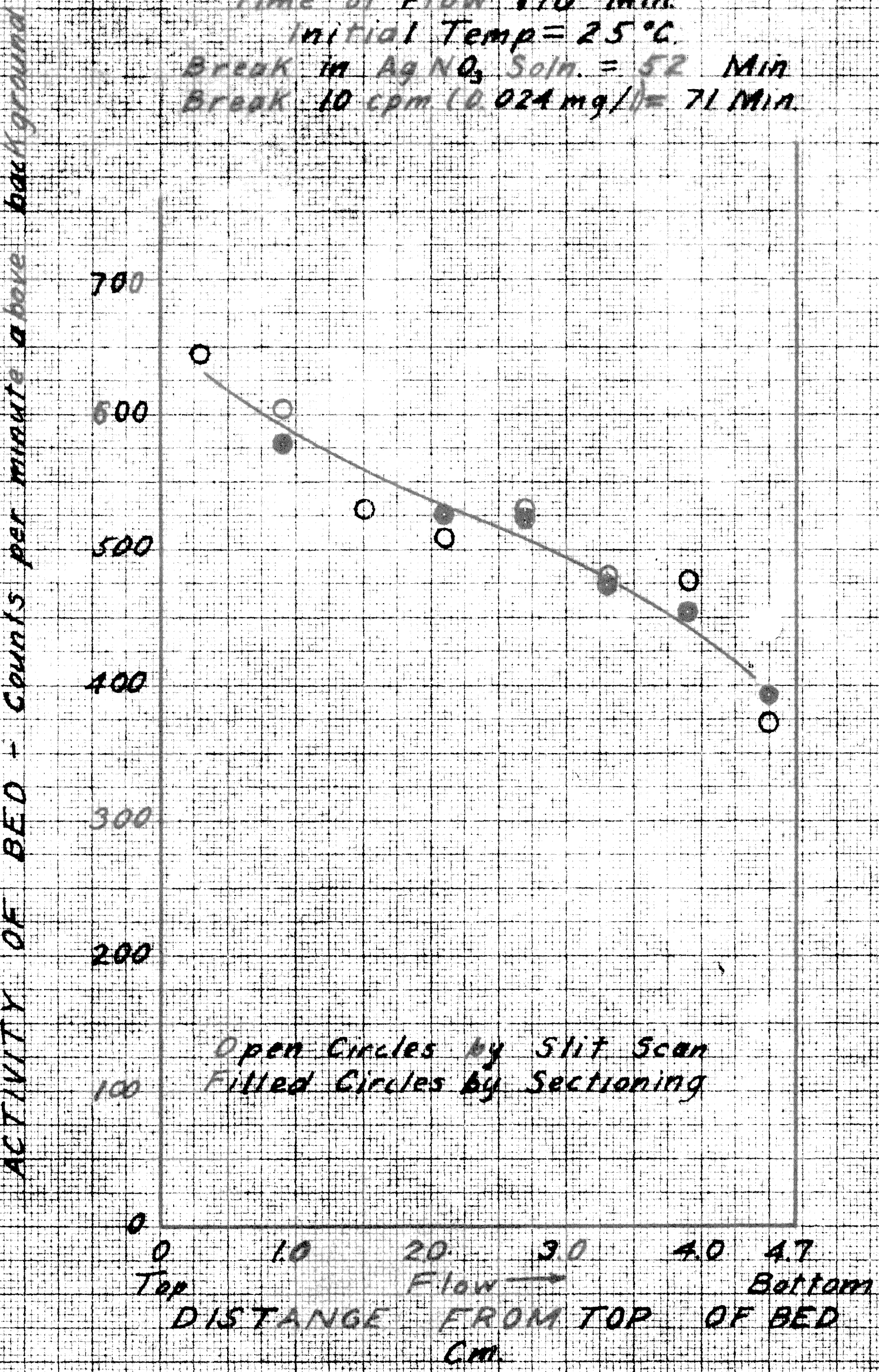
Break of 10 cpm. (0.020 mg/l) = 12 min.



KEUFFEL & ESSER CO., N.Y. NO. 359-71
3 Cycles × 10 to the inch.

SA 3-1
SCAN OF BED

CWS N19TU B (Dried)
Bed Depth - 4.7 Cm.
C_0 = 6.9 mg/l.
Flow 9.15 cm./sec.
Time of Flow 170 Min.
Initial Temp = 25°C.
Break in $AgNO_3$ Soln. = 52 Min
Break 10 cpm (0.024 mg/l) = 71 Min.



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Millimeters, 10th lines heavy.
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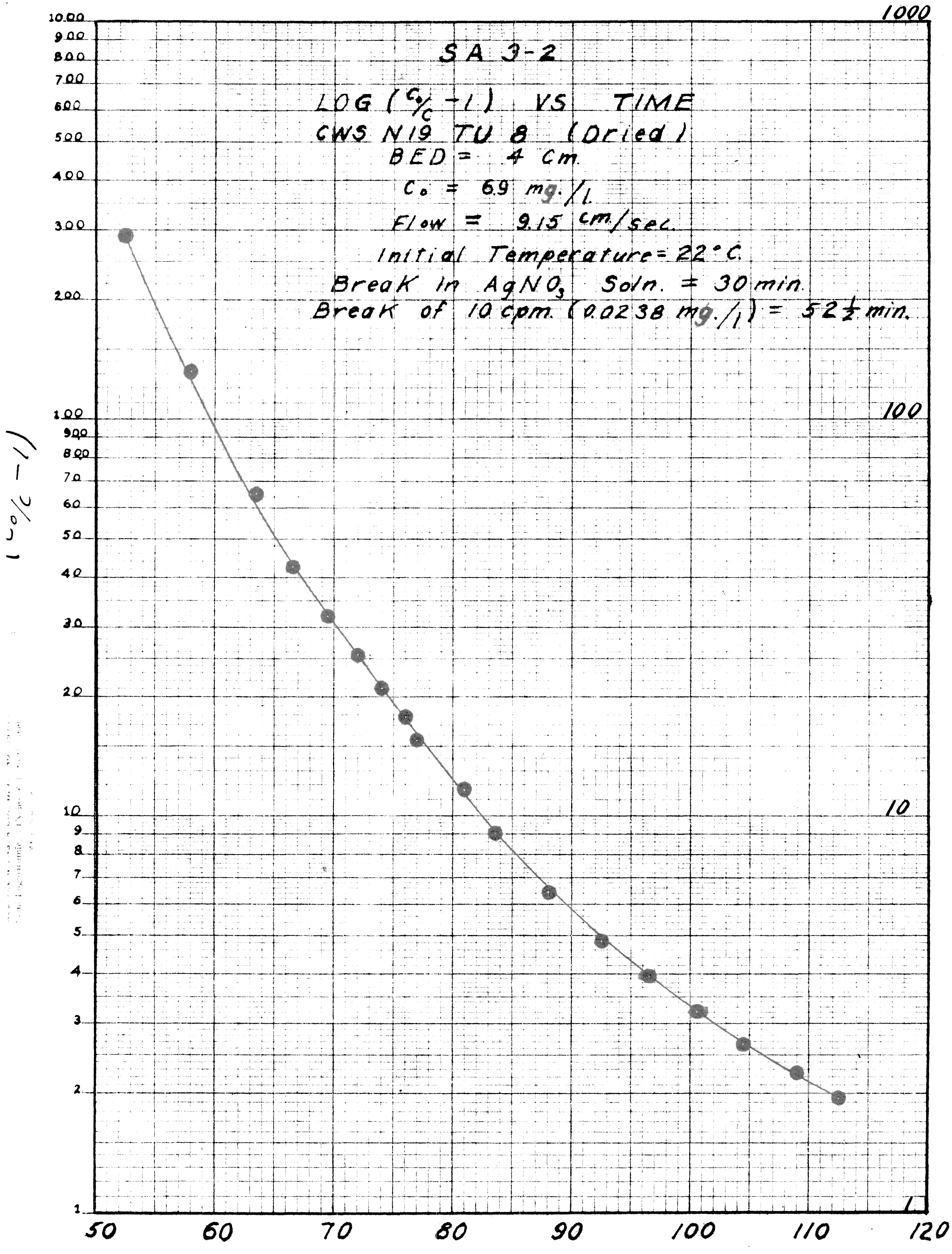


SA 3-2

LOG (C_o/C - 1) VS TIME

CWS N19 TU 8 (Dried)

BED = 4 Cm.

C_o = 6.9 mg./l.

Flow = 9.15 cm/sec.

Initial Temperature = 22 °C.

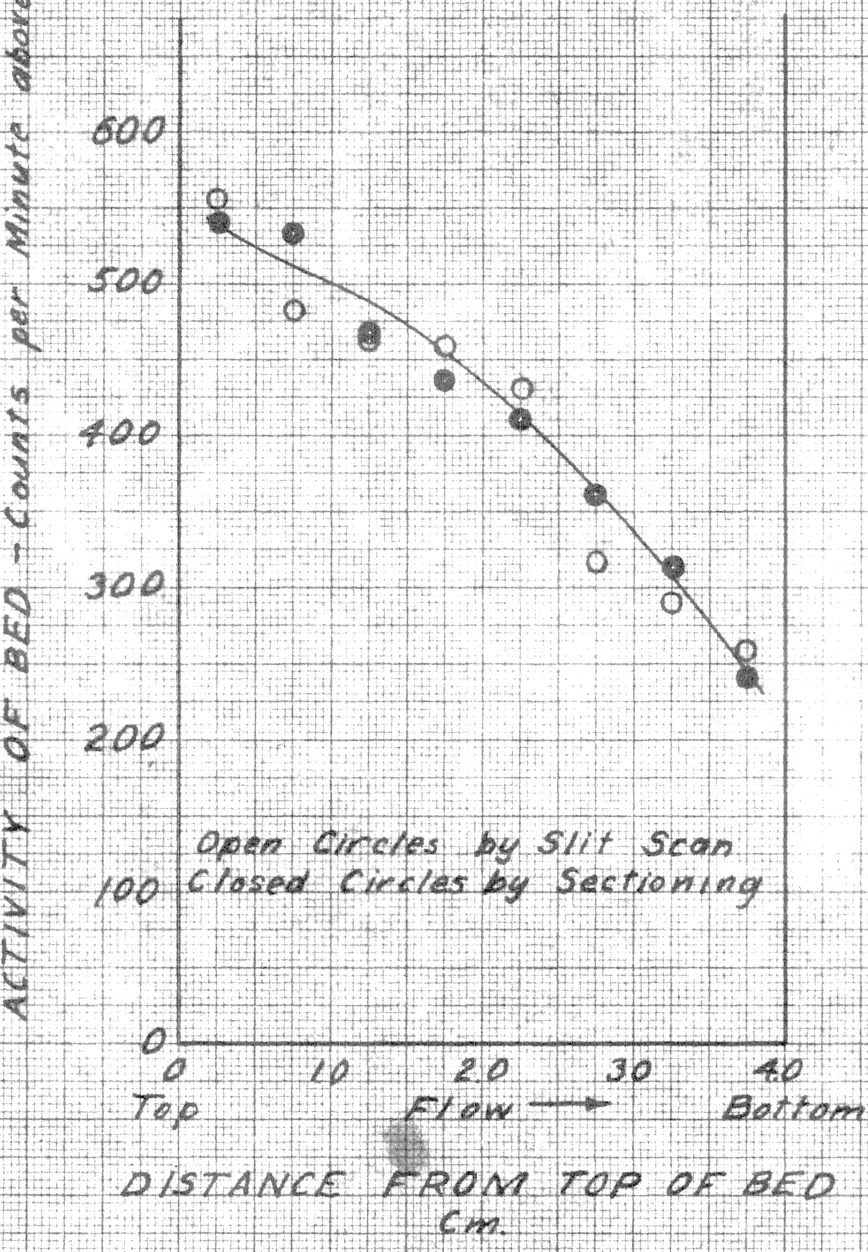
Break in $AgNO_3$ Soln. = 30 min.

Break of 10 cpm. (0.0238 mg./l) = 52½ min.

SA 3-2

SCAN OF BED

CWS N19 TU 8 (Dried)
Bed Depth 4 Cm.
C_0 = 6.9 mg/l.
Flow = 9.15 Cm./sec.
Time of Flow = 122 Min.
Initial Temp. = 24°C.
Break in $AgNO_3$ Soln. - 30 Min
Break of 10 C.p.m. (0.024 mg/l) - 52½ Min.



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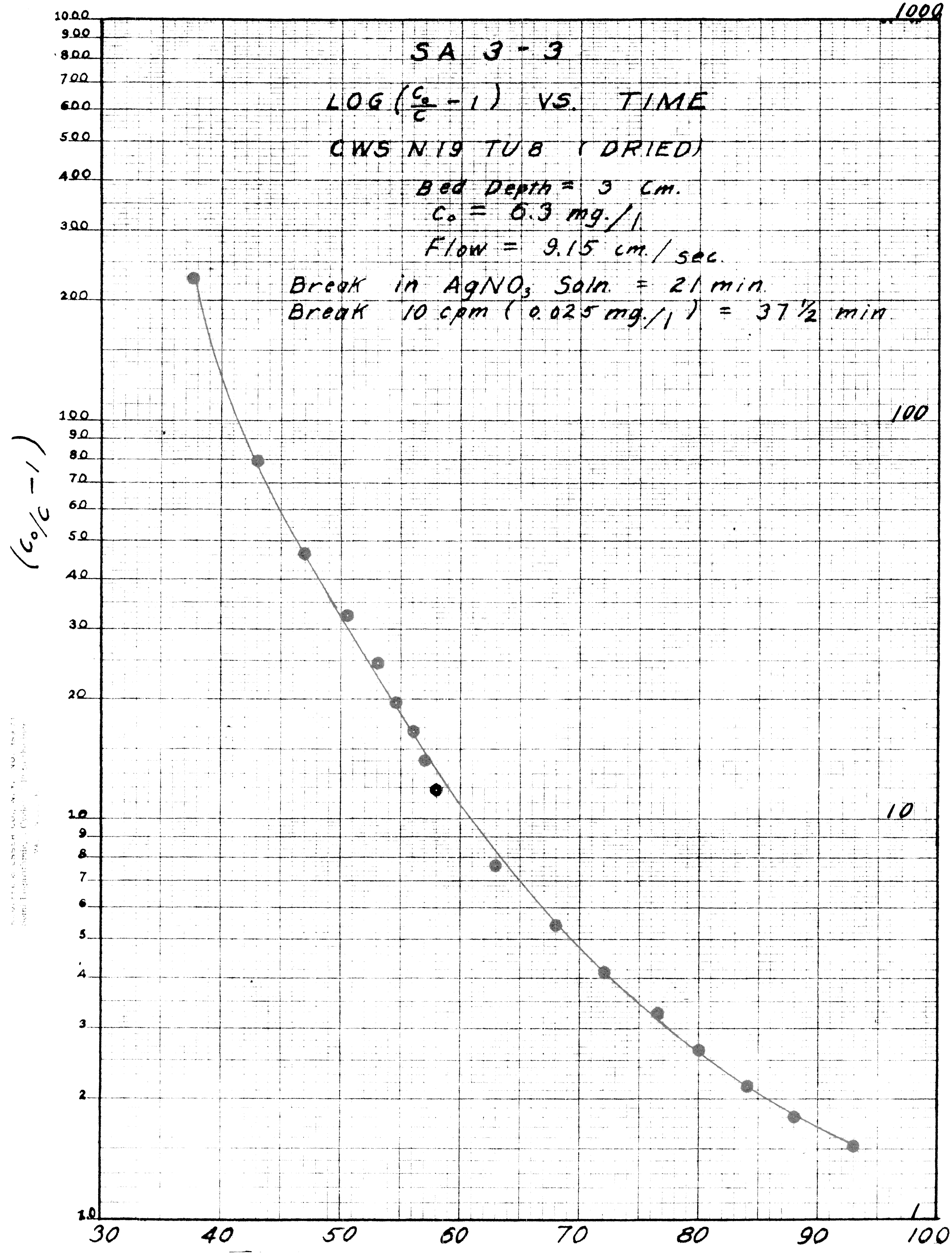
Millimeter, 10th lines heavy.
MADE IN U.S.A.



SA 3 - 3

LOG $(\frac{C_o}{C} - 1)$ VS. TIME

CWS N 19 TU 8 (DRIED)

Bed Depth = 3 Cm.

C_o = 6.3 mg./l

Flow = 9.15 cm./sec.

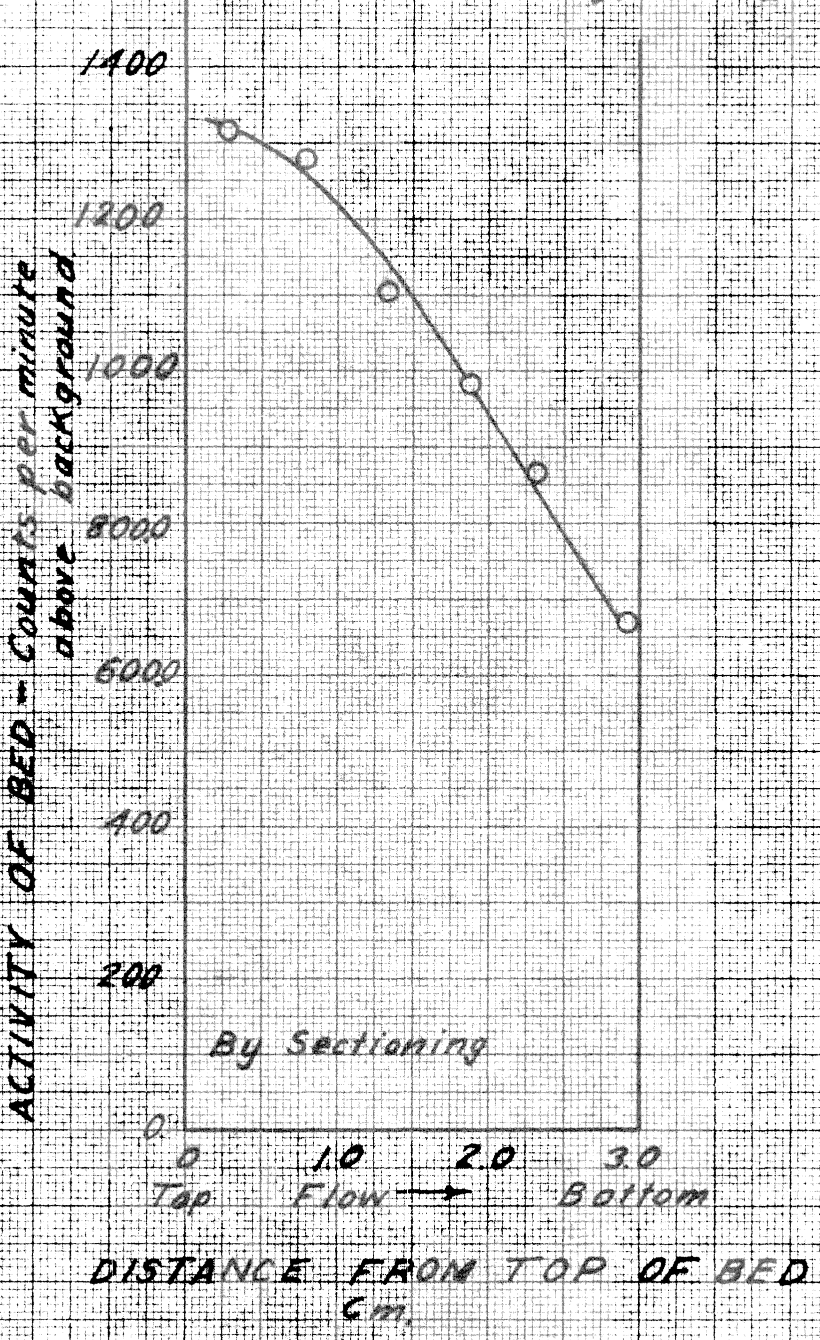
Break in $AgNO_3$ Soln. = 21 min.

Break 10 cpm (0.025 mg./l) = 37½ min

SA 3-3
SCAN OF BED

CWS N19 TUB (Dried)
Bed Depth 3 cm.
C_o = 6.3 mg/l.
Flow - 9.15 Cm/sec.
Time of Flow - 93 Min.
Initial Temperature 25°C.
Break in $AgNO_3$ Soln. = 25 min.

Break of 10 Cpm (0025 mg/l.) = 37½ min.



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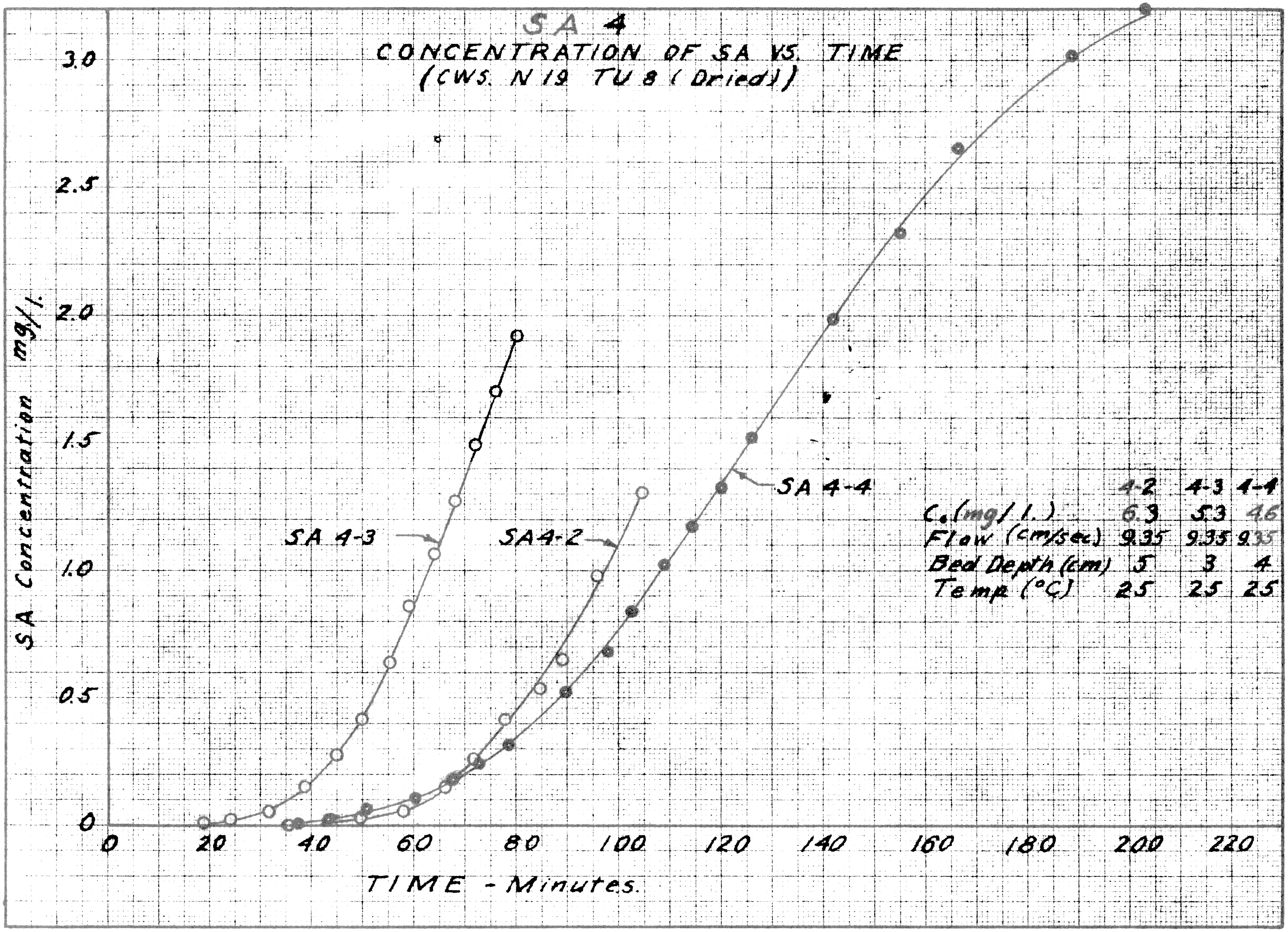
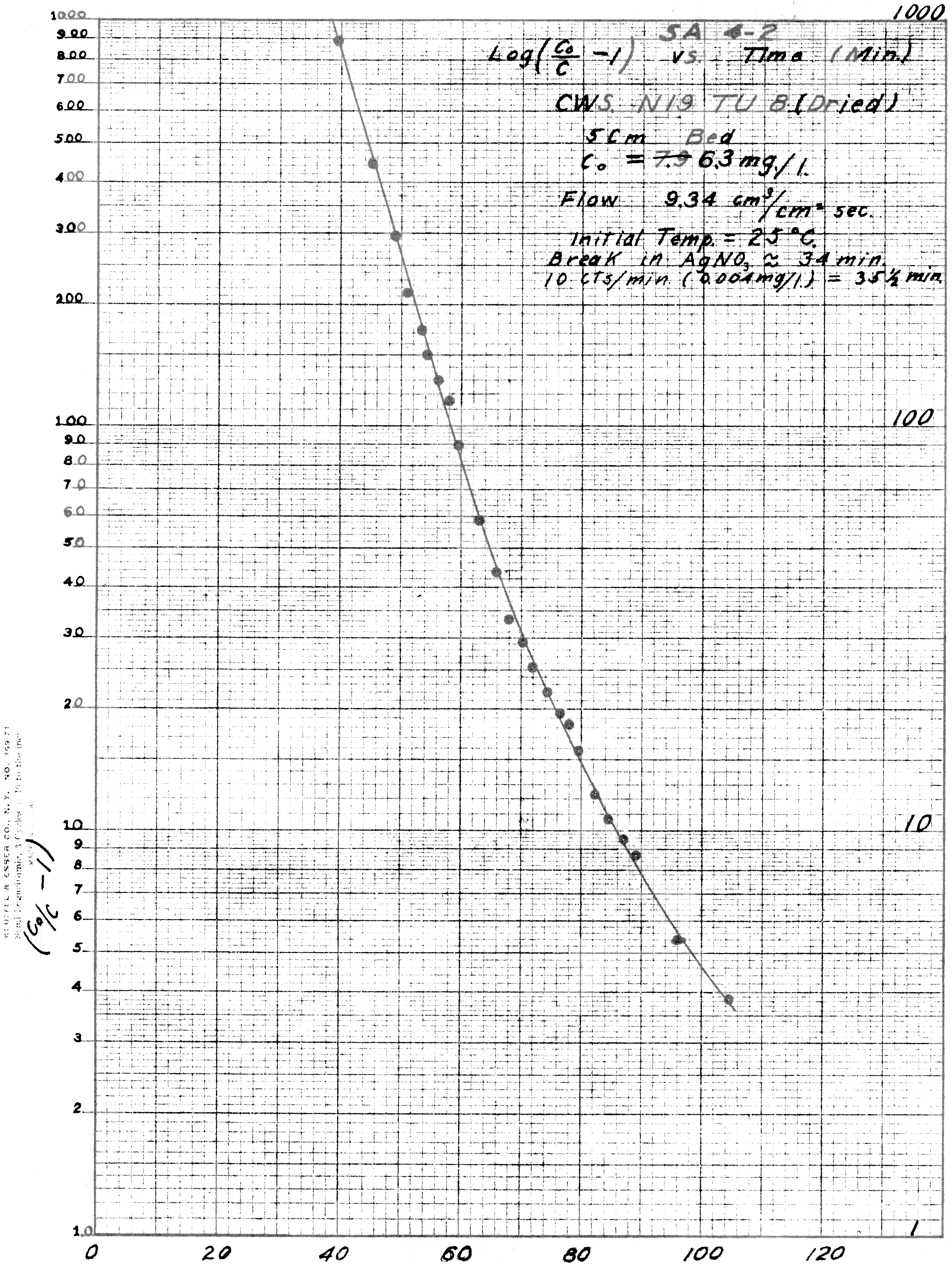


SA 4

CONCENTRATION OF SA VS. TIME
(CWS. N19 TU 8 (Dried))



SA 4-2

$\text{Log}\left(\frac{C_0}{C} - 1\right)$ vs. Time (Min.)

CWS. N19 TU 8 (Dried)

5 Cm Bed

C_0 = ~~7.9~~ 6.3 mg/l.

Flow 9.34 cm^3/cm^2 sec.

Initial Temp. = 25 °C.

Break in $AgNO_3$ ≃ 34 min.

10 CTs/min. (0.004 mg/l.) = 35½ min.

KEUFFEL & ESSER CO., N. Y. NO. 359-71
Semi-Logarithmic, 3 Cycles × 10 to the inch.
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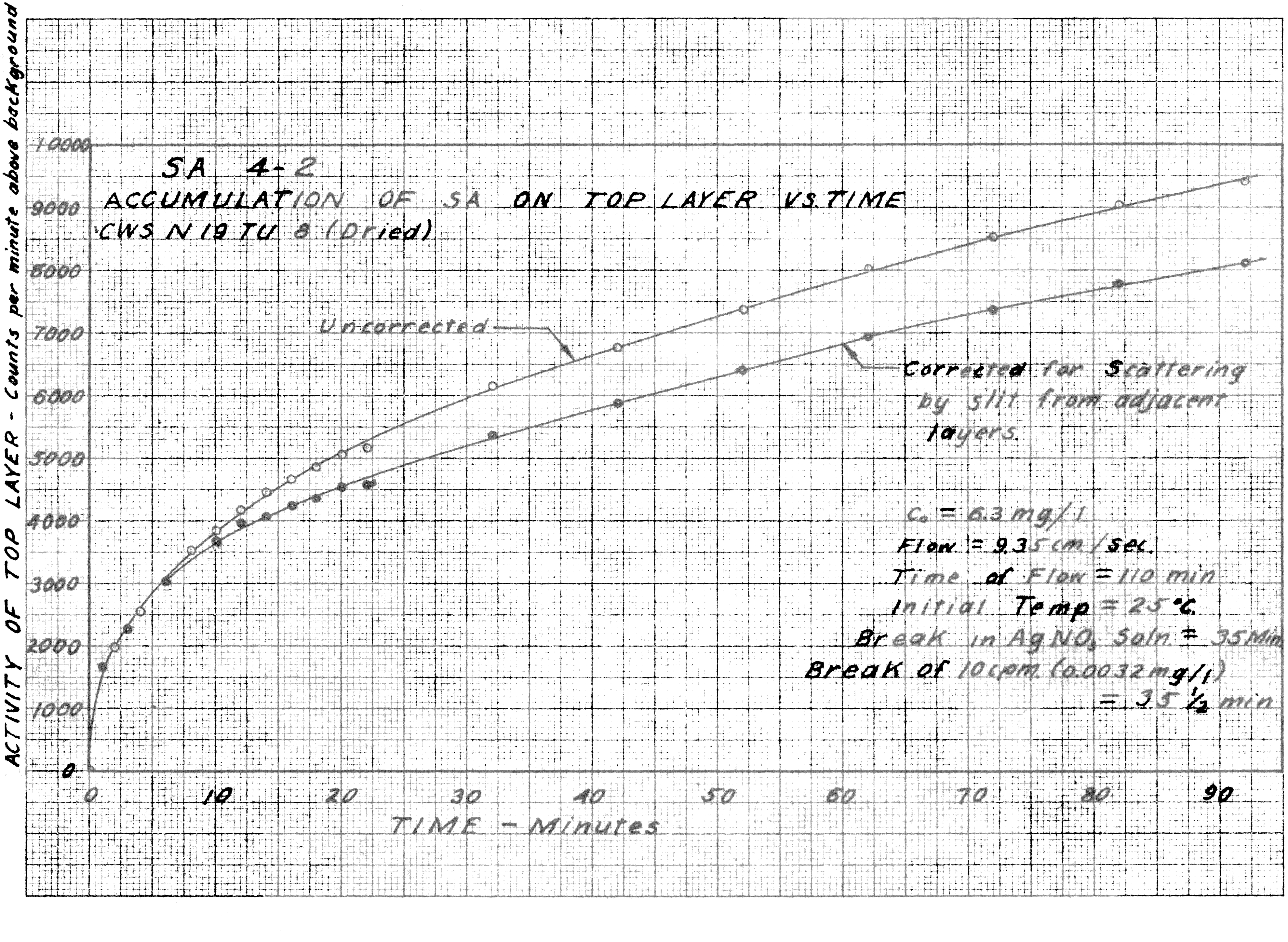
[illegible]
20 × 20 to the inch, 10th lines heavy.
MADE IN U.S.A.



SA 4-2

ACCUMULATION OF SA ON TOP LAYER VS. TIME

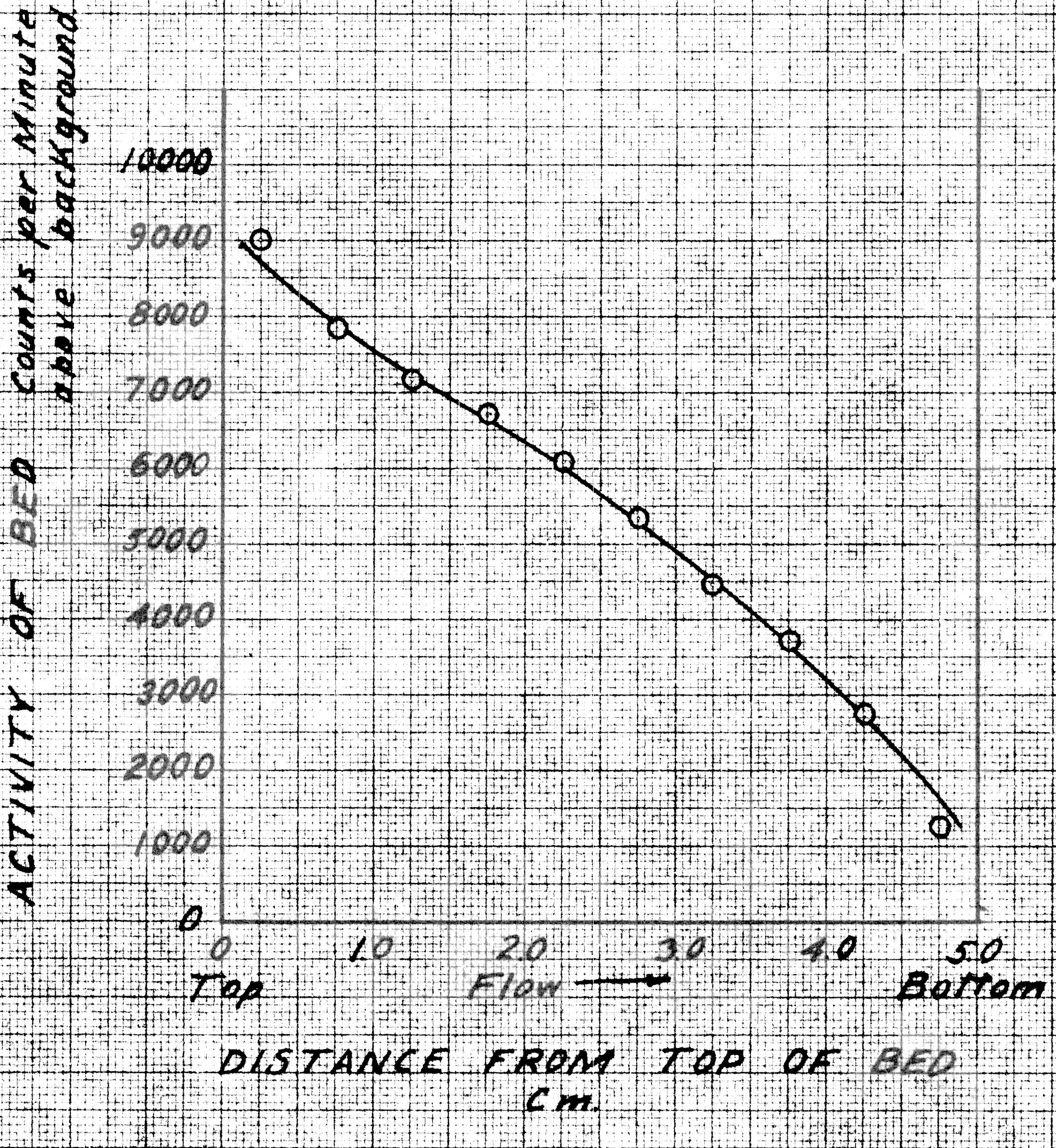
CWS N 19 TU 8 (Dried)

C_0 = 6.3 mg/l
Flow = 9.35 cm/sec.
Time of Flow = 110 min
Initial Temp = 25 °C
Break in $AgNO_3$ Soln = 35 Min
Break of 10 ccm (0.0032 mg/l)
= 35½ min

SA 4-2

SCAN OF BED

CWS N 19 TU 8 (Dried)
Bed Depth 5 Cm.
$C_0 = 6.3$ mg/l.
Flow = 9.35 cm./sec.
Time of Flow 110 Min
Initial Temperature 25 °C.
Break in $AgNO_3$ Soln. — 35 Min.
Break of 10 Cpm. (0.0032 mg/l) = $35\frac{1}{2}$ Min.



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Millimeters, 10th lines heavy.
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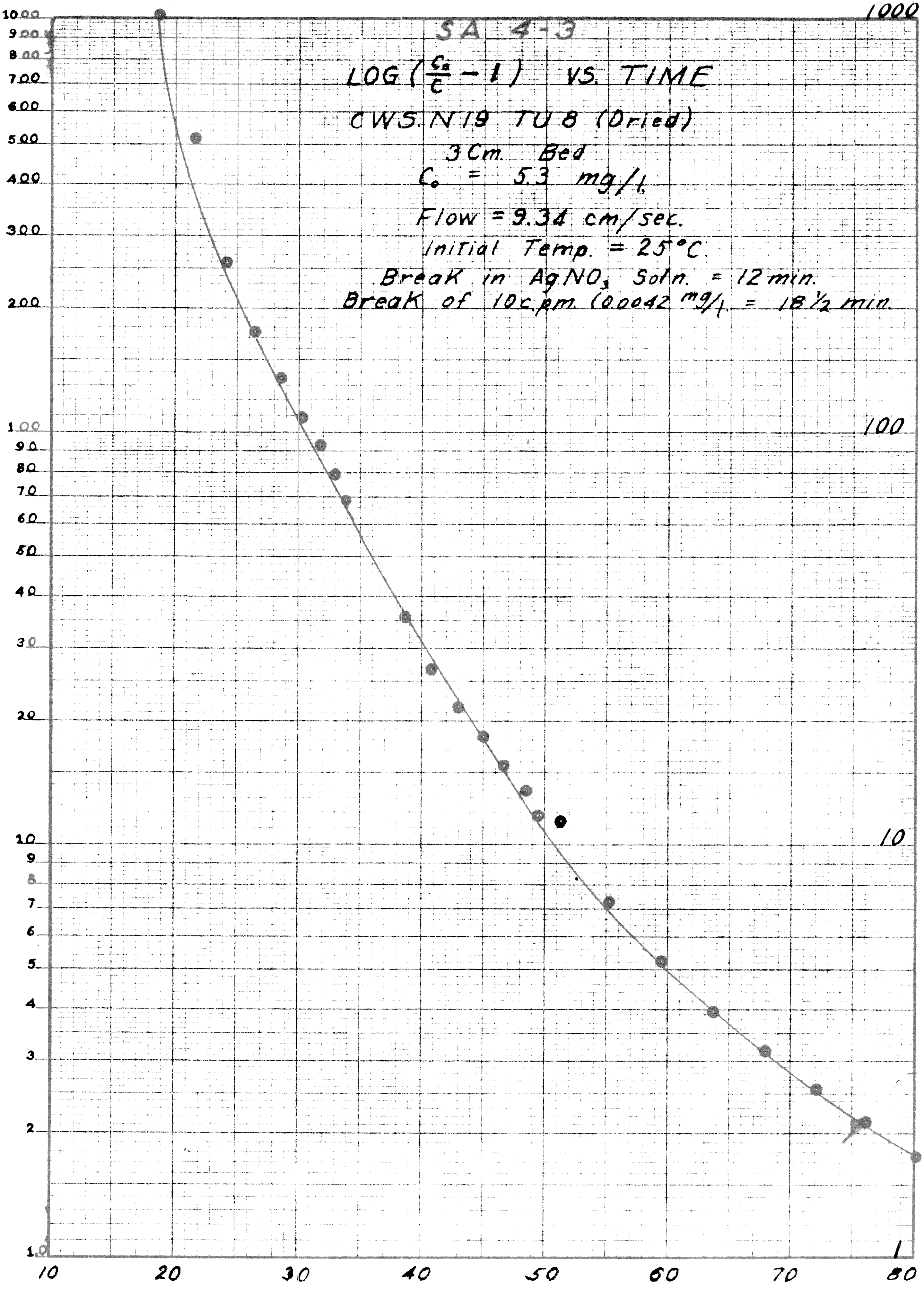
SA 4-3



LOG ($\frac{C_0}{C} - 1$) VS. TIME

CWS. N19 TU 8 (Dried)

3 Cm. Bed

C_0 = 5.3 mg/l.

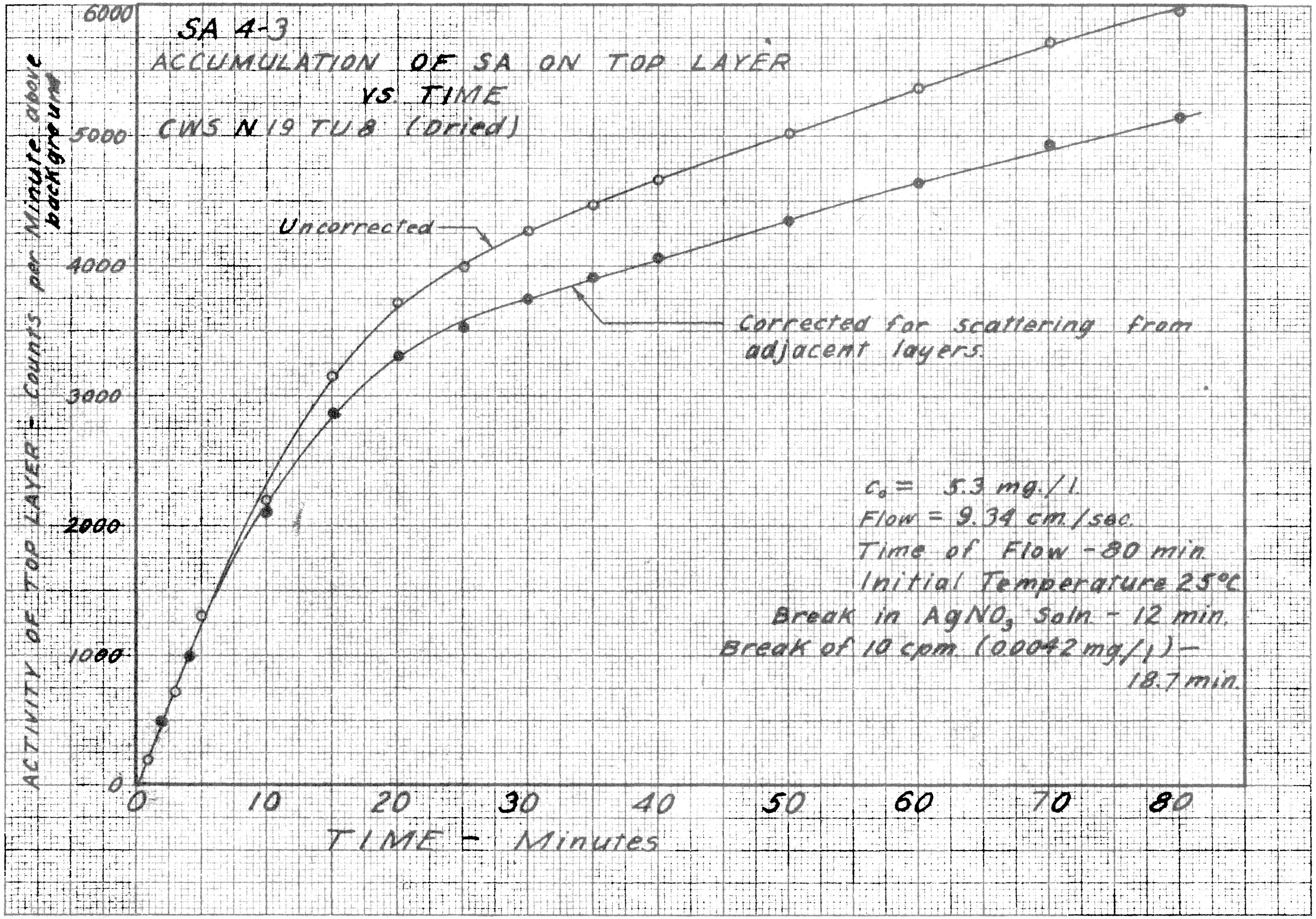
Flow = 9.34 cm/sec.

Initial Temp. = 25°C.

Break in $AgNO_3$ Soln. = 12 min.

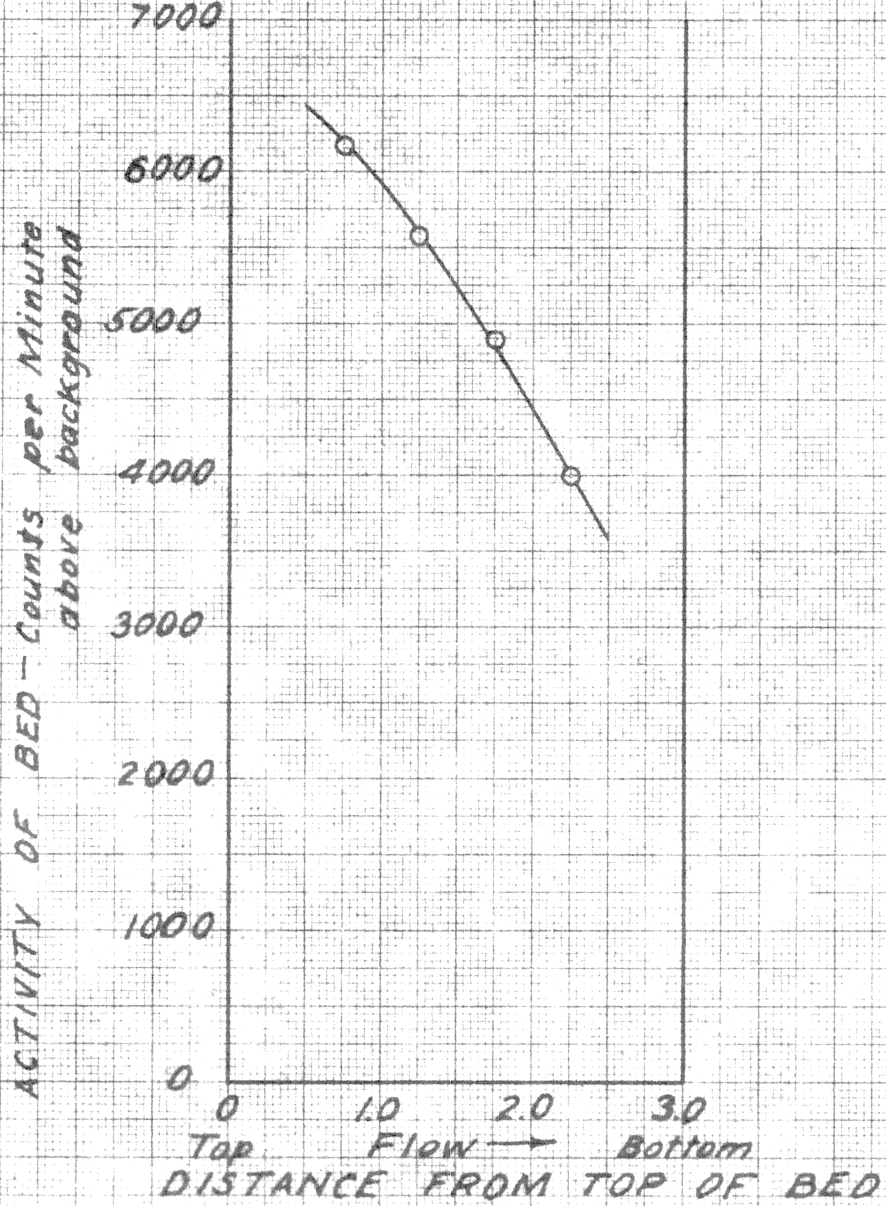
Break of 10c.pm. (0.0042 mg/l = 18½ min.

20 × 20 to the inch, 10th lines heavy.
MADE IN U.S.A.

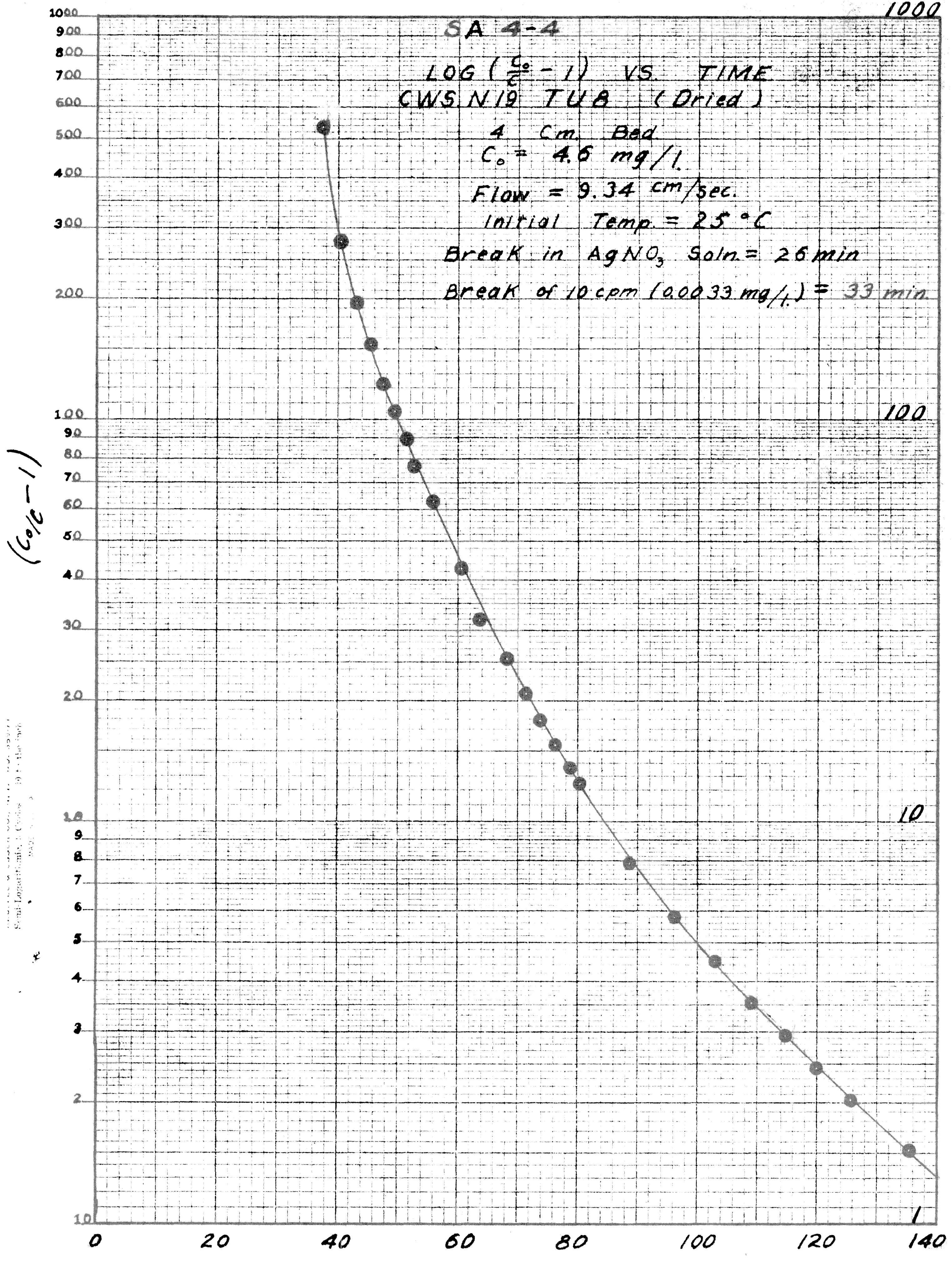


SA 4-3
SCAN OF BED

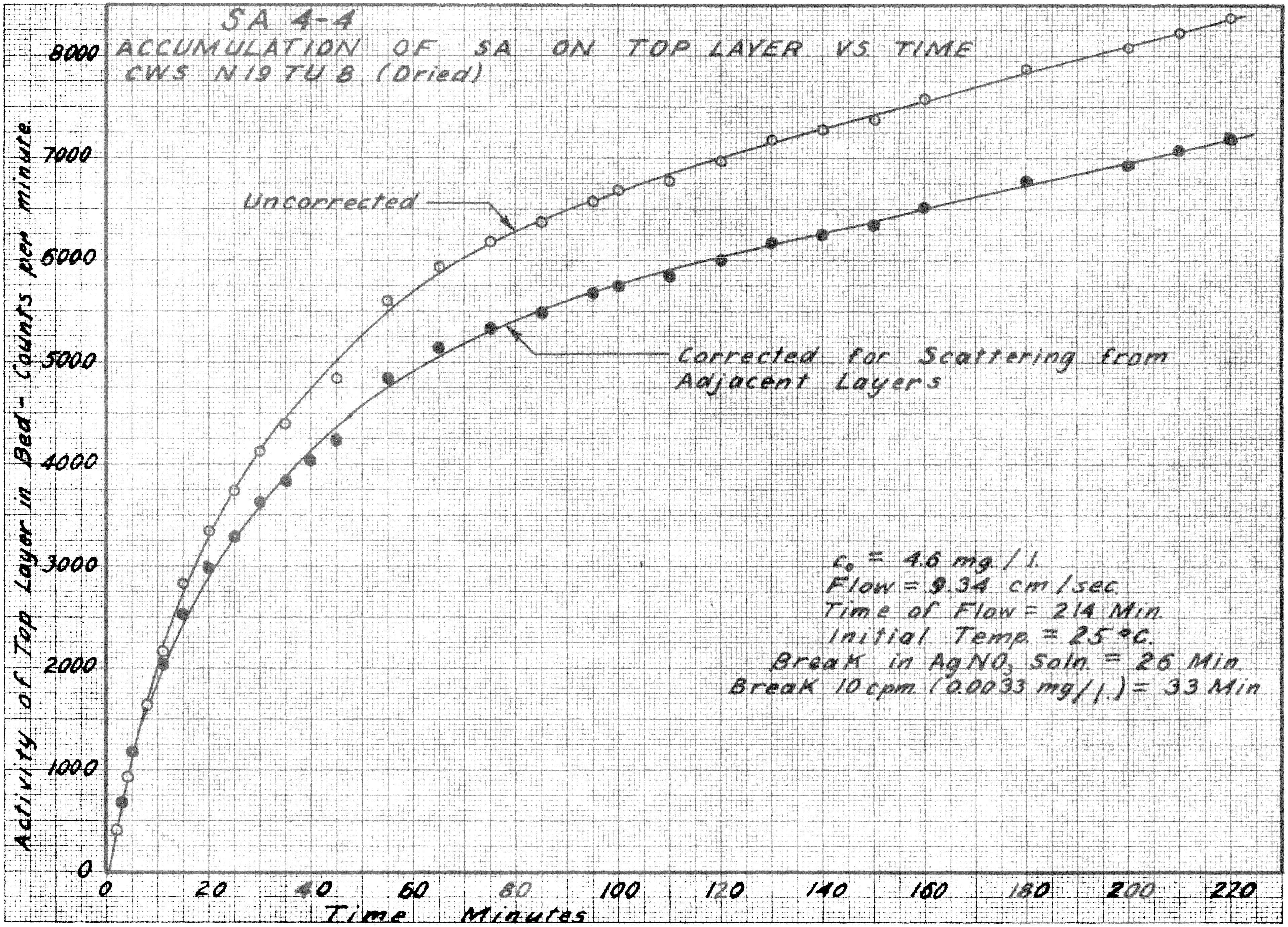
CWS N19 TUB (Dried)
C_o = 5.3 mg./l.
Flow = 9.34 cm./sec.
Time of Flow - 80 min.
Initial Temperature - 25°C.
Break in $AgNO_3$ Soln. - 12 Min.
Break 10 Cpm. (0.0042 mg/l) - 187 Min.



KEUFFEL & ESSER CO. N.Y. NO. 359-14
Millimeters, 10th lines heavy.
Made in U.S.A.

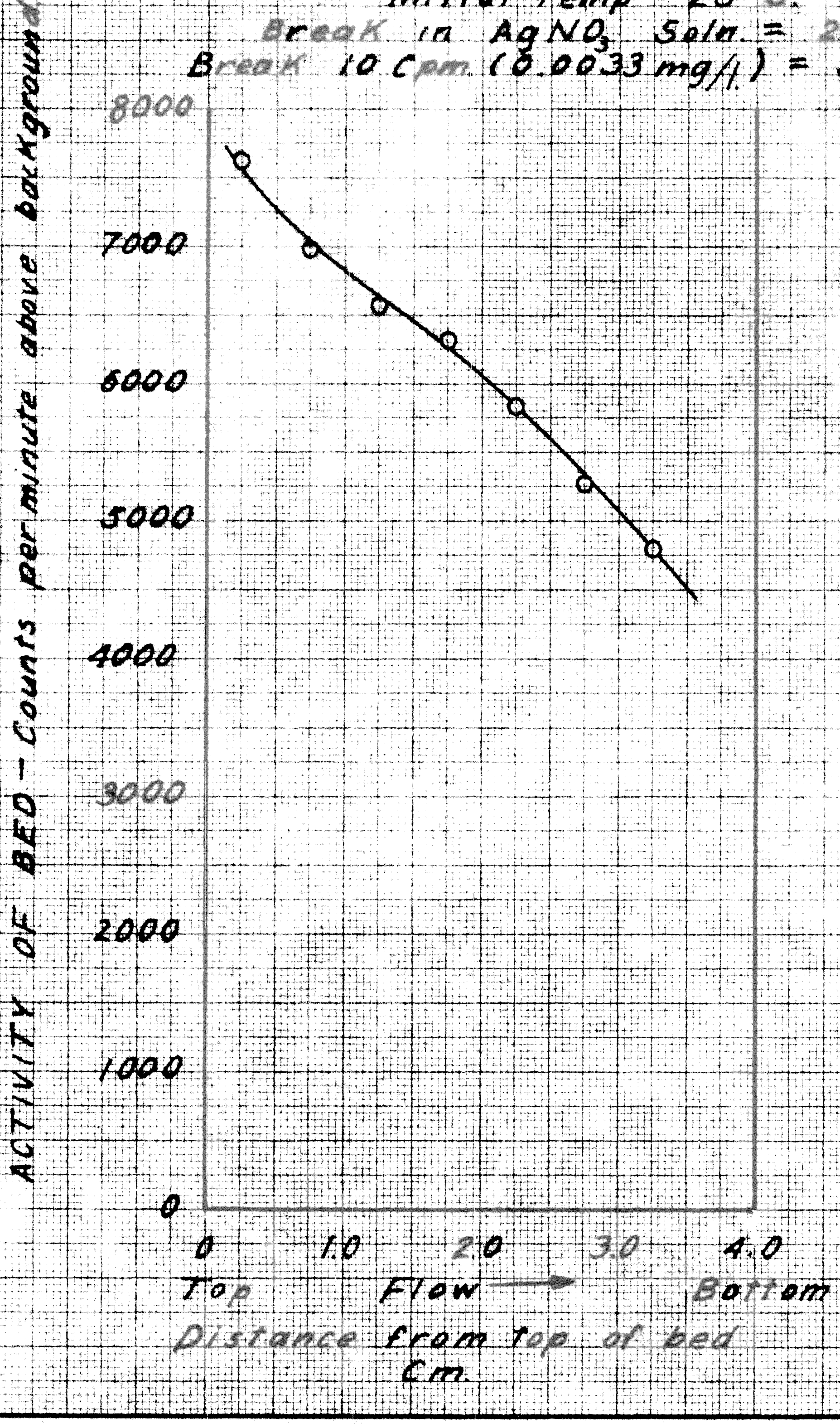

SA 4-4
LOG ($\frac{C_o}{C}$ - 1) VS. TIME
CWS N19 TUB (Dried)
4 Cm. Bed
C_o = 4.6 mg/l.
Flow = 9.34 cm/sec.
Initial Temp. = 25 °C
Break in $AgNO_3$ Soln. = 26 min
Break of 10 cpm (0.0033 mg/l.) = 33 min.
(C_o/C − 1)
1000
900
800
700
600
500
400
300
200
100
90
80
70
60
50
40
30
20
10
9
8
7
6
5
4
3
2
1
1000
100
10
1
0
20
40
60
80
100
120
140

KEUFFEL & ESSER CO., N. Y. NO. 359-14
Millimeters, 10th lines heavy
MADE IN U.S.A.



SA 4-4
SCAN OF BED

CWS N 19 TU 8 (Dried)
Bed Depth - 4 Cm.
C_0 = 4.6 mg/l.
Flow = 9.34 cm/sec.
Time of Flow 214 Min.
Initial Temp = 25°C.
Break in $AgNO_3$ Soln. = 26 Min.
Break 10 Cpm. (0.0033 mg/l.) = 33 Min.



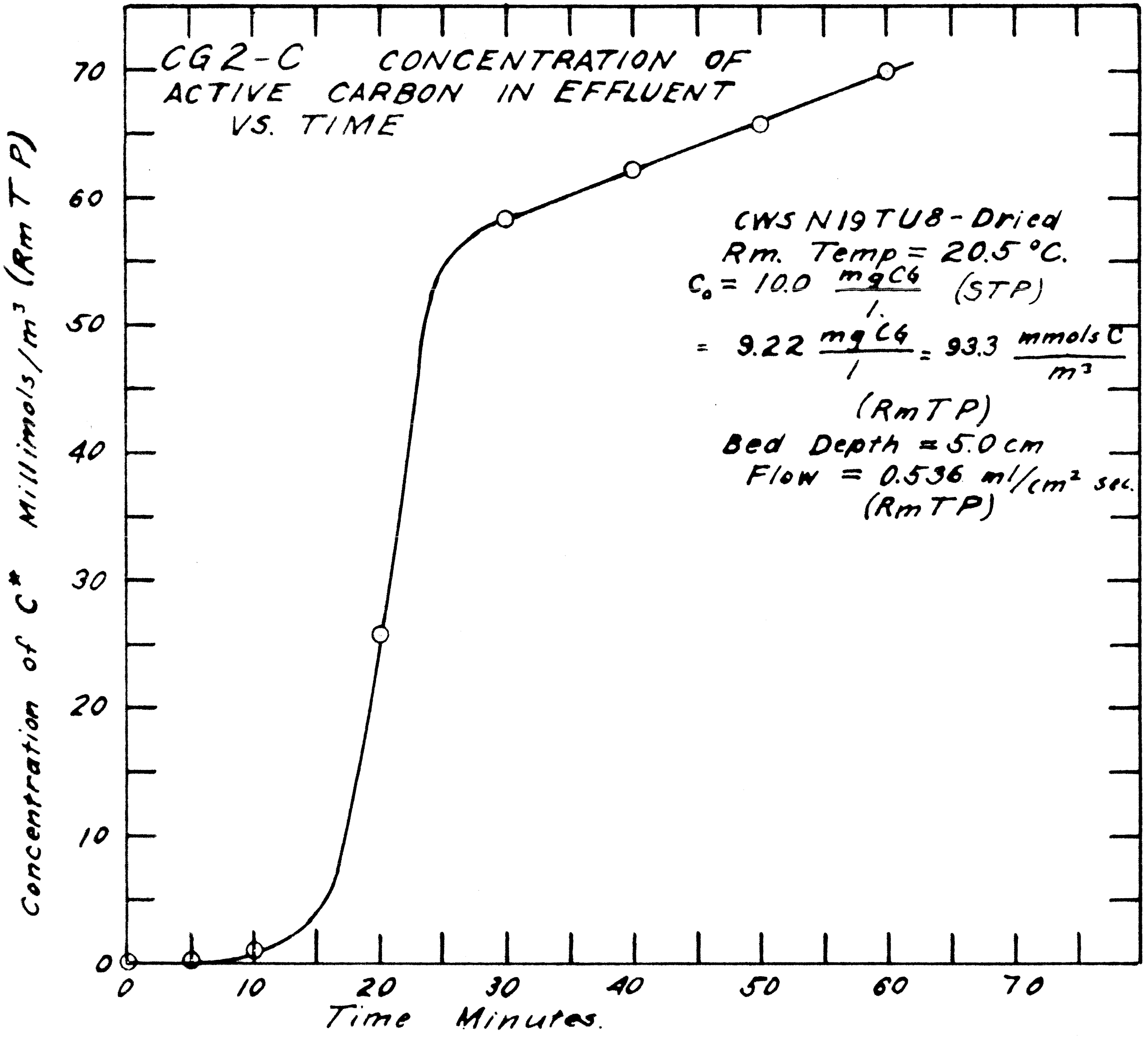
KEUFFEL & ESSER CO., N. Y. NO. 359-14
Millimeters, 10th lines heavy.
Made in U.S.A.

APPENDIX II

GRAPHS FOR PHOSGENE EXPERIMENTS WITH ACTIVE CARBON

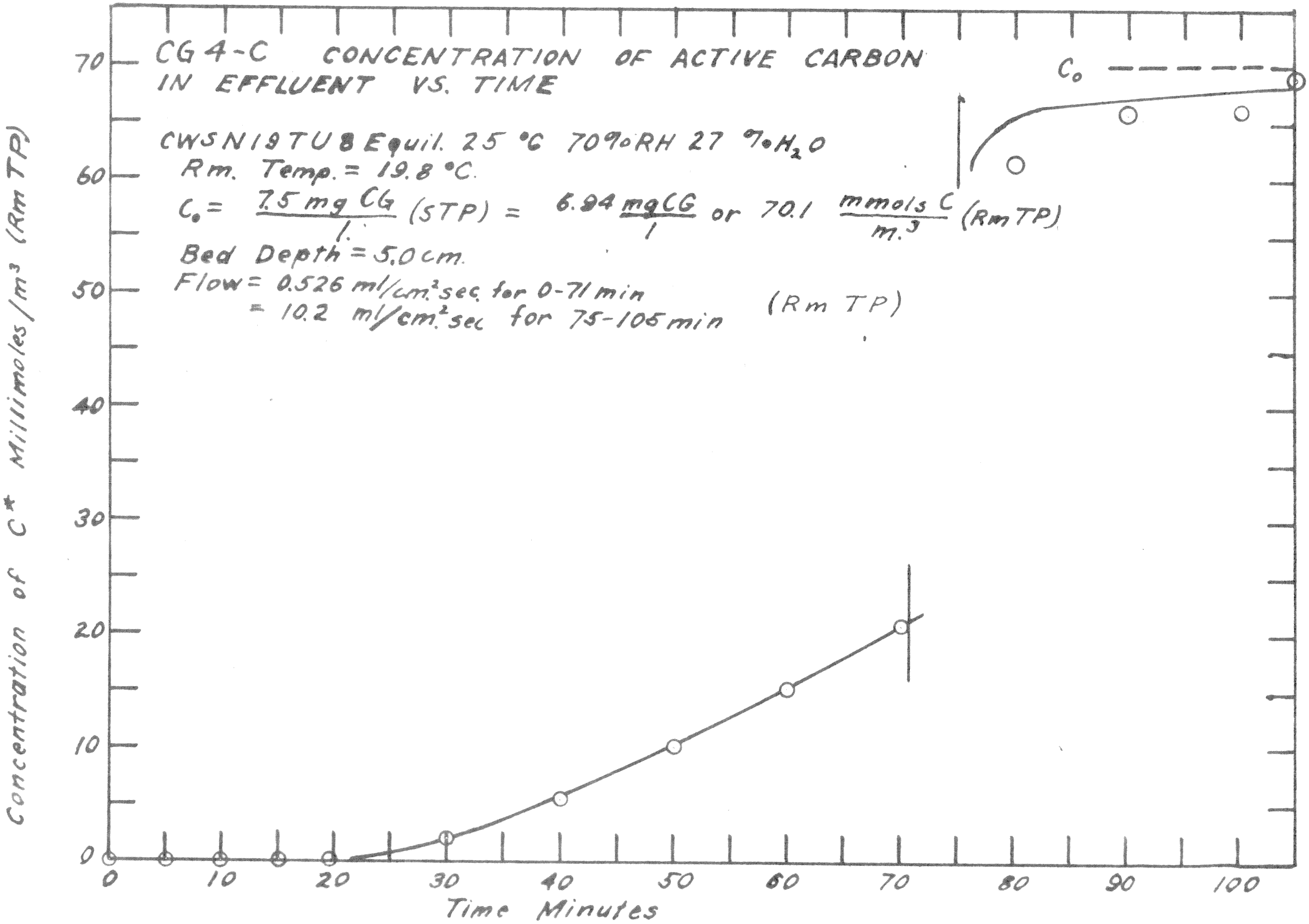
Concentration in Effluent Vs. Time

Expt. No. (Low Flow Rate)	Expt. No. (Normal Flow Rate)
CG2-C	CG7-1C
CG4-C	CG8-1C
CG5-1C	CG9-1C
CG5-2C	CG10-1C
CG6-1C	CG11-1C
CG6-2C	CG12-C
	CG14-C



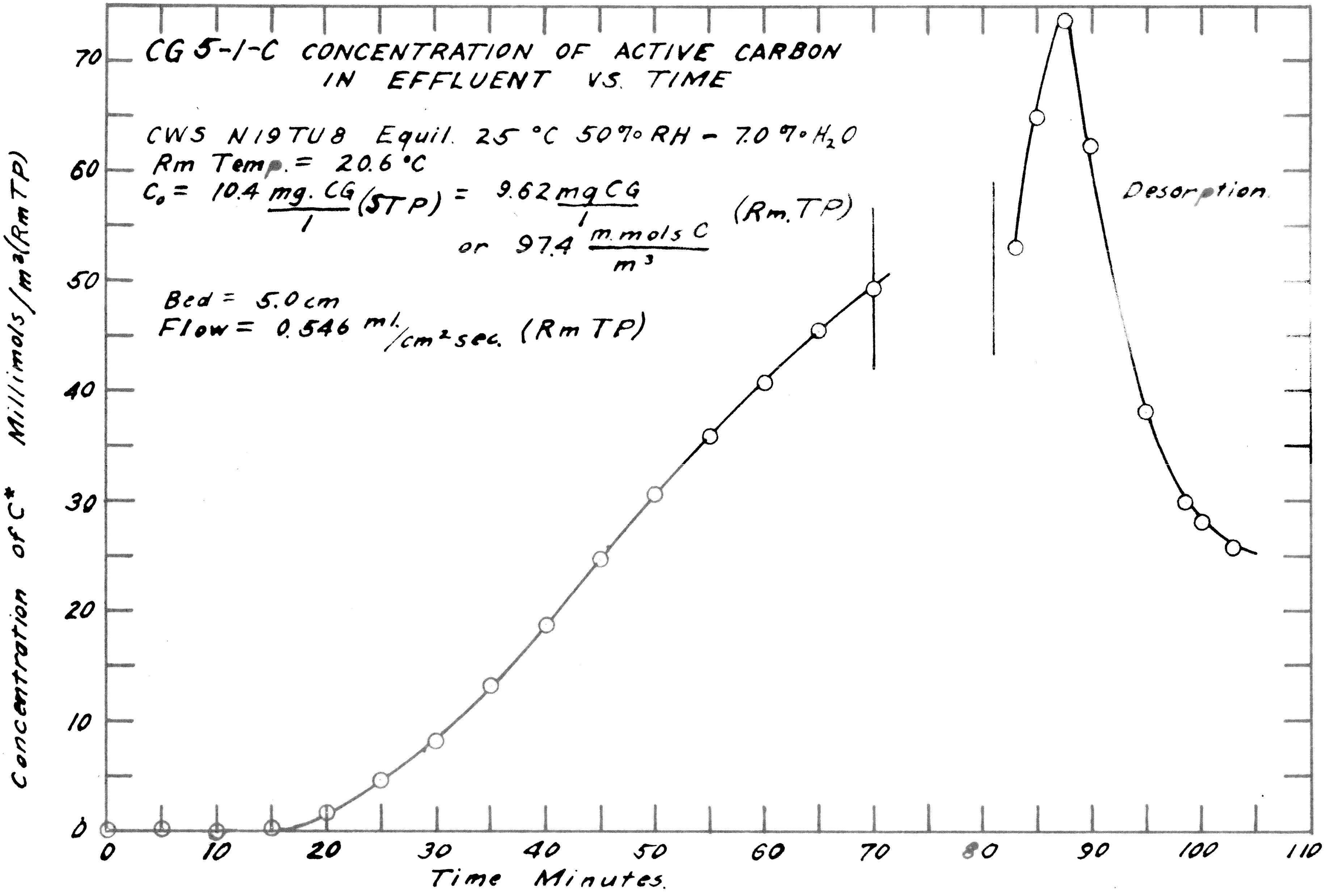
CG2-C CONCENTRATION OF ACTIVE CARBON IN EFFLUENT VS. TIME

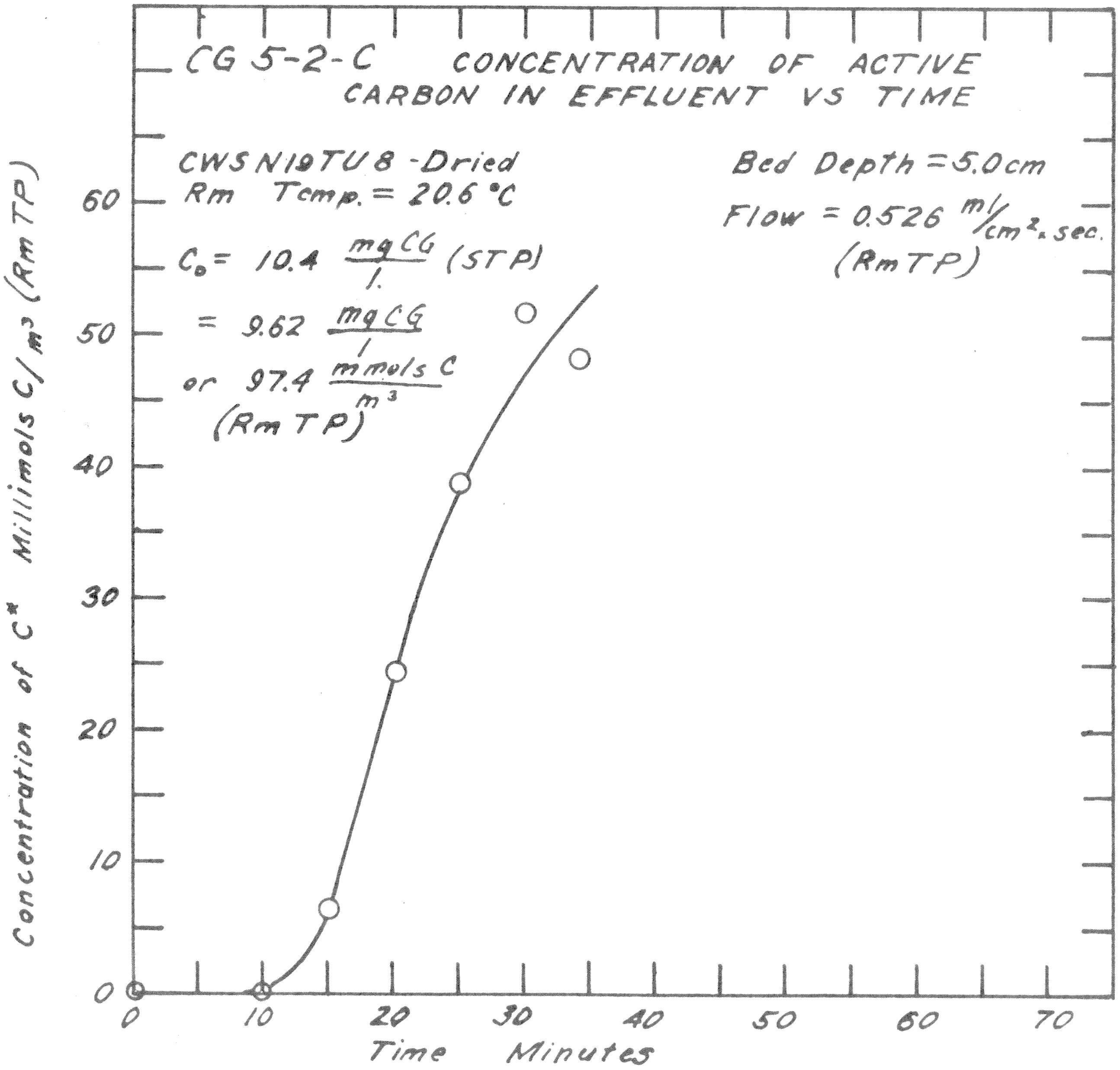
CWS N19TU8 - Dried
Rm. Temp = 20.5 °C.
$C_0 = 10.0 \frac{mg\,C6}{l.}$ (STP)
$= 9.22 \frac{mg\,C6}{l} = 93.3 \frac{mmols\,C}{m^3}$
(RmTP)
Bed Depth = 5.0 cm
Flow = 0.536 ml/cm² sec.
(RmTP)

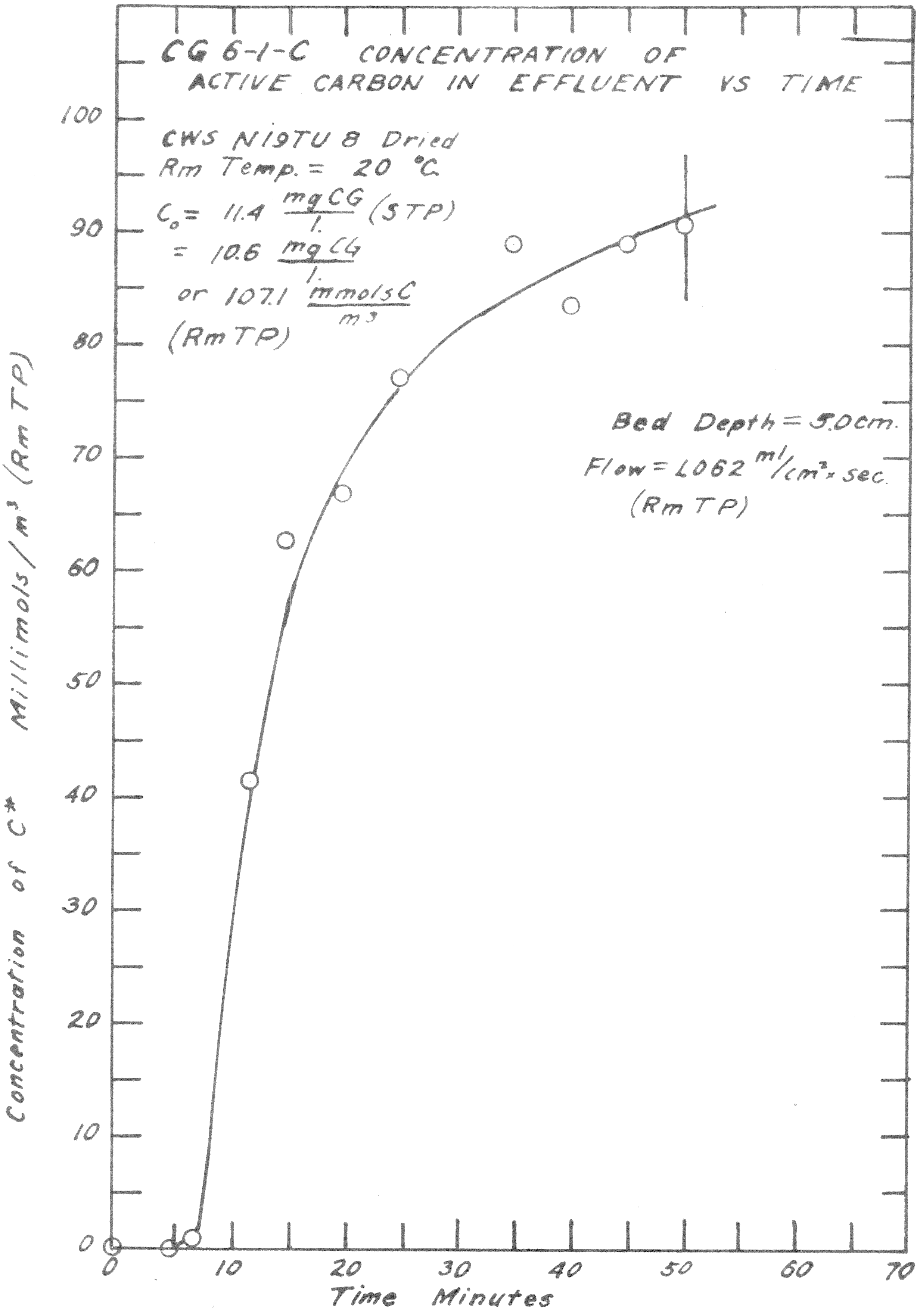


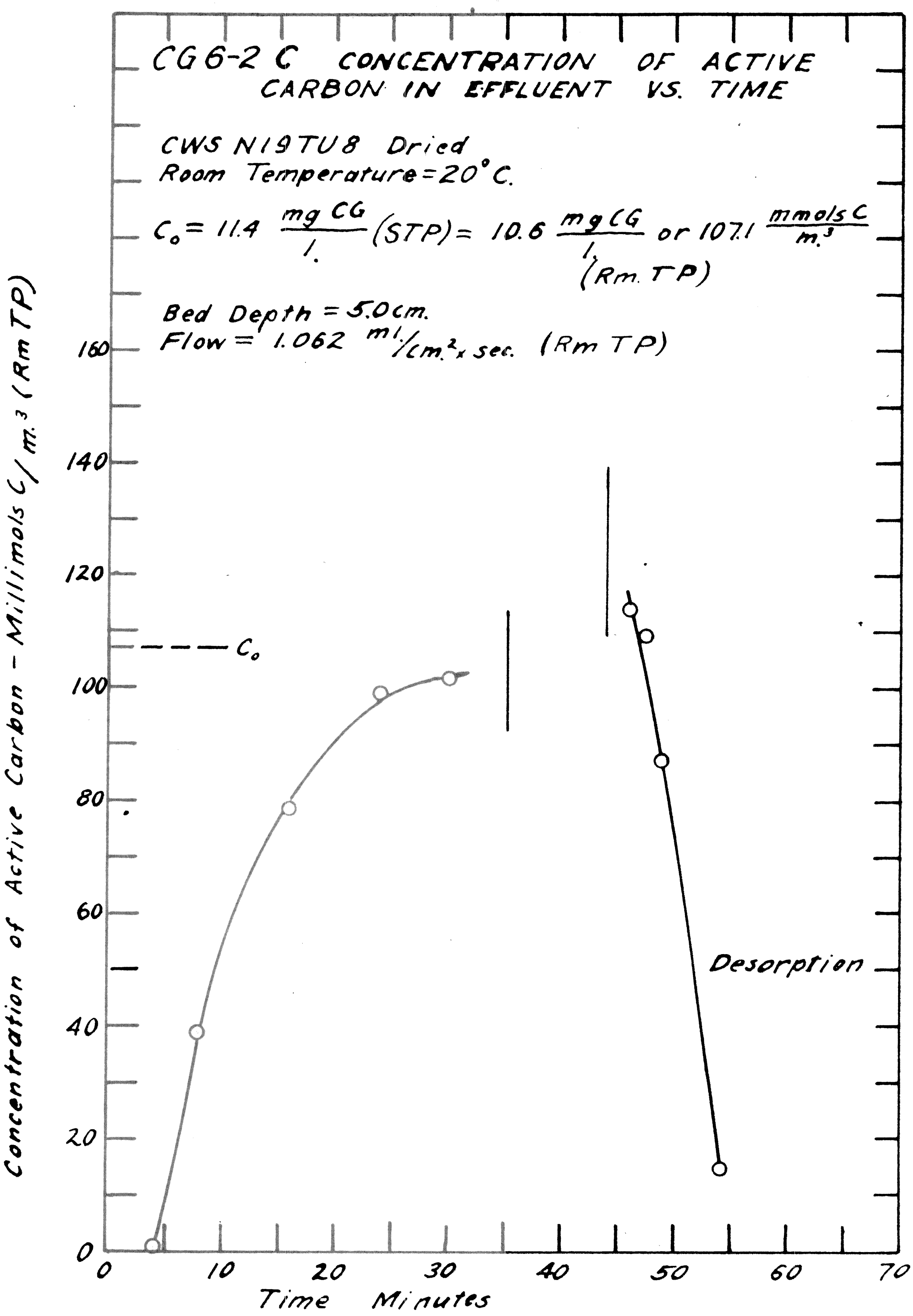
CG 4-C CONCENTRATION OF ACTIVE CARBON IN EFFLUENT VS. TIME

CWSN19TU8 Equil. 25 °C 70% RH 27 % H_2O
Rm. Temp. = 19.8 °C.
$C_0 = \frac{7.5 \text{ mg CG}}{l.}$ (STP) = $6.94 \frac{\text{mgCG}}{l}$ or $70.1 \frac{\text{mmols C}}{m.^3}$ (Rm TP)
Bed Depth = 5.0 cm.
Flow = 0.526 ml/cm.^{2}sec. for 0-71 min
= 10.2 ml/cm.^{2}sec for 75-105 min (Rm TP)


CG 5-1-C CONCENTRATION OF ACTIVE CARBON IN EFFLUENT VS. TIME
CWS N19TU8 Equil. 25 °C 50% RH - 7.0% H_2O
Rm Temp. = 20.6 °C
$C_0 = 10.4 \frac{mg.\ CG}{l} (STP) = 9.62 \frac{mg\ CG}{l}$ (Rm. TP)
or $97.4 \frac{m.mols\ C}{m^3}$
Bed = 5.0 cm
Flow = 0.546 ml./cm² sec. (Rm TP)
Desorption.
Concentration of C* Millimols/m³(Rm TP)
Time Minutes.
0
10
20
30
40
50
60
70
80
90
100
110


CG 5-2-C CONCENTRATION OF ACTIVE CARBON IN EFFLUENT VS TIME
CWS N19TU8 -Dried
Rm Temp. = 20.6 °C
$C_0 = 10.4 \frac{mg\,CG}{l.}$ (STP)
$= 9.62 \frac{mg\,CG}{l}$
or $97.4 \frac{m\,mols\,C}{m^3}$ (RmTP)
Bed Depth = 5.0 cm
Flow = 0.526 $^{ml}/_{cm^2 \times sec.}$ (RmTP)
Concentration of C* Millimols C/m³ (Rm TP)
0
10
20
30
40
50
60
0
10
20
30
40
50
60
70
Time Minutes


CG 6-1-C CONCENTRATION OF ACTIVE CARBON IN EFFLUENT VS TIME
CWS N19TU 8 Dried
Rm Temp. = 20 °C
$C_o = 11.4 \frac{mg\ CG}{l.}$ (STP)
$= 10.6 \frac{mg\ CG}{l.}$
or $107.1 \frac{mmols\ C}{m^3}$
(RmTP)
Bed Depth = 5.0 cm.
Flow = 1.062 $^{ml}/_{cm^2 \times sec.}$
(RmTP)
Concentration of C* Millimols / m³ (Rm TP)
0
10
20
30
40
50
60
70
80
90
100
Time Minutes
0
10
20
30
40
50
60
70

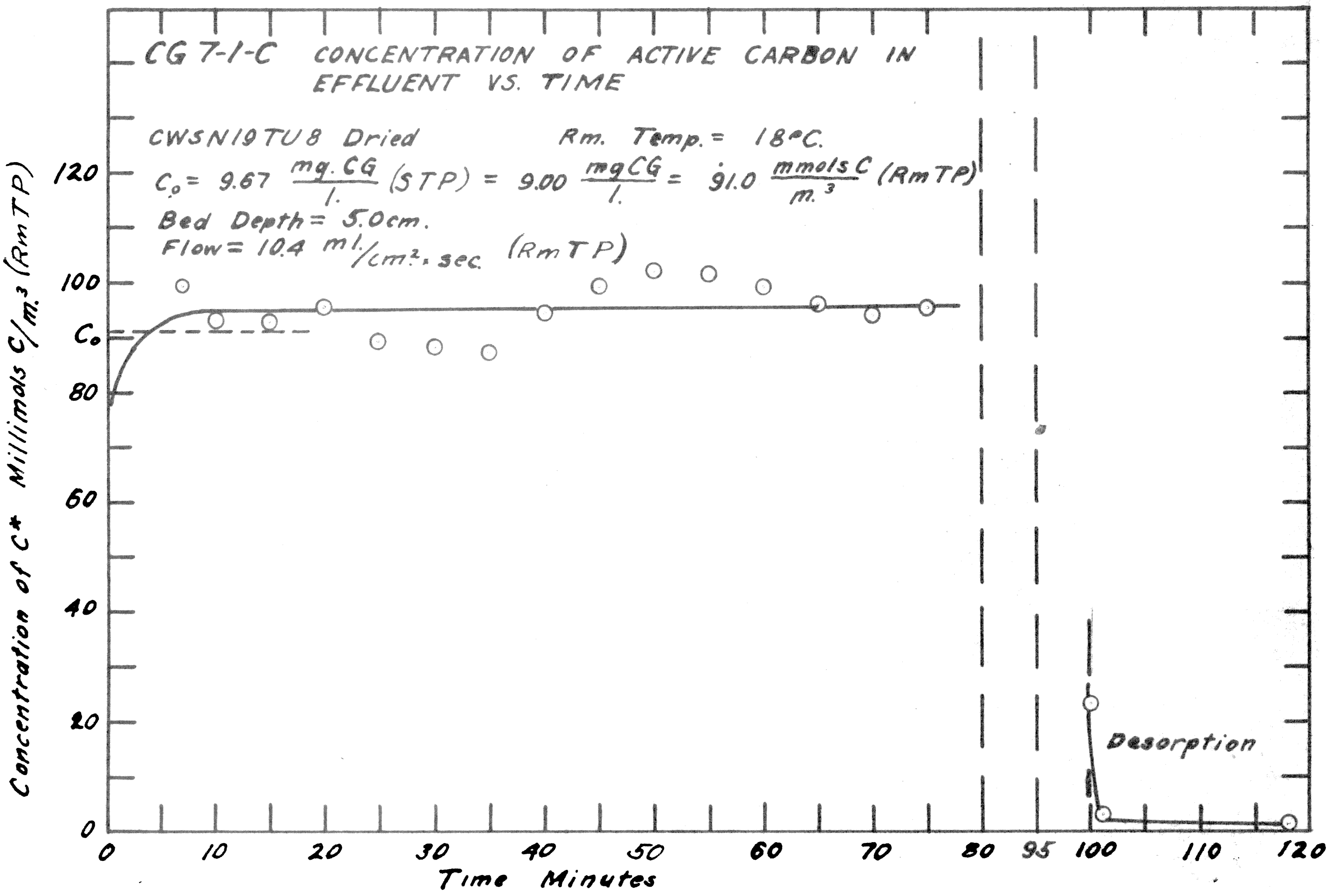


CG6-2 C CONCENTRATION OF ACTIVE CARBON IN EFFLUENT VS. TIME

CWS N19TU8 Dried
Room Temperature = 20°C.

$C_o = 11.4 \frac{mg\ CG}{l.} (STP) = 10.6 \frac{mg\ CG}{l.} (Rm.\ TP)$ or $107.1 \frac{mmols\ C}{m.^3}$

Bed Depth = 5.0 cm.
Flow = 1.062 ml./cm.² x sec. (Rm TP)



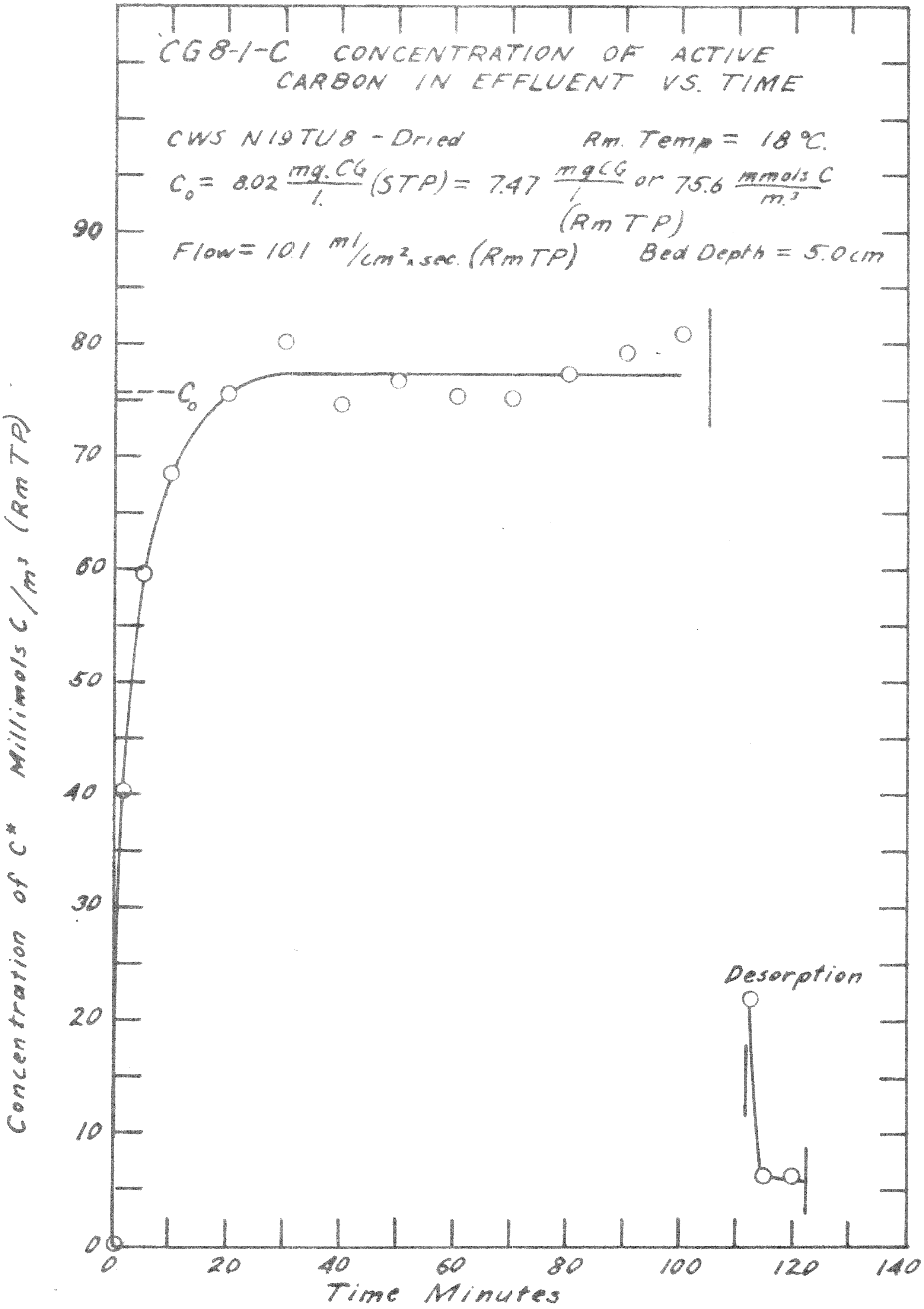
CG 7-1-C CONCENTRATION OF ACTIVE CARBON IN EFFLUENT VS. TIME

CWSN19TU8 Dried Rm. Temp. = 18°C.

$C_o = 9.67 \frac{mg.CG}{l.} (STP) = 9.00 \frac{mgCG}{l.} = \dot{9}1.0 \frac{mmols\,C}{m.^3} (RmTP)$

Bed Depth = 5.0cm.

Flow = 10.4 ml./cm.² sec (RmTP)



CG8-1-C CONCENTRATION OF ACTIVE CARBON IN EFFLUENT VS. TIME

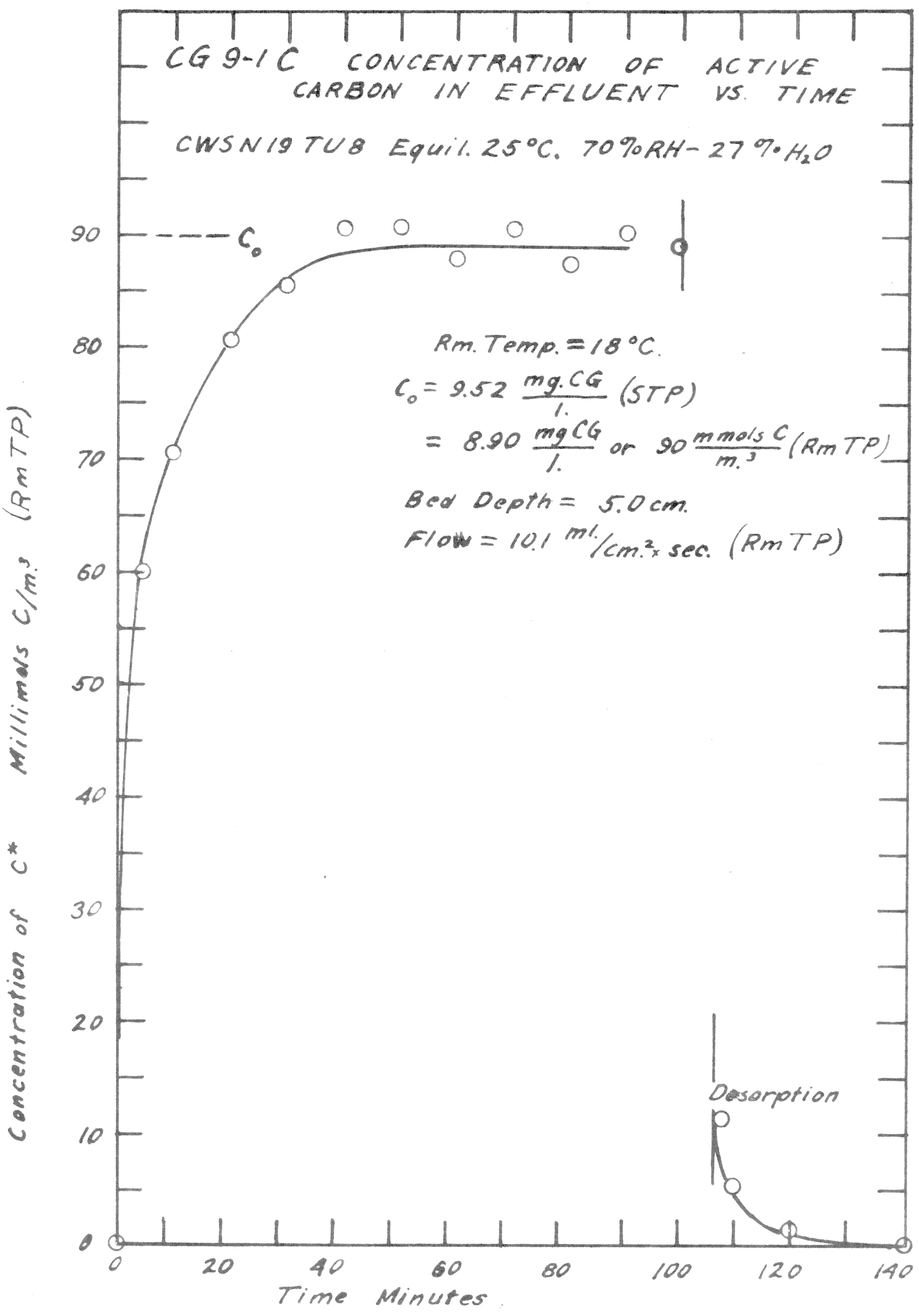
CWS N19TU8 - Dried

Rm. Temp = 18 °C.

$C_0 = 8.02 \frac{mg.CG}{l.} (STP) = 7.47 \frac{mg\,CG}{l}$ (RmTP) or $75.6 \frac{mmols\ C}{m^3}$

Flow = 10.1 ml/cm² × sec. (RmTP)

Bed Depth = 5.0 cm



CG 9-1C CONCENTRATION OF ACTIVE CARBON IN EFFLUENT VS. TIME

CWSN19TU8 Equil. 25°C. 70%RH-27% H_2O

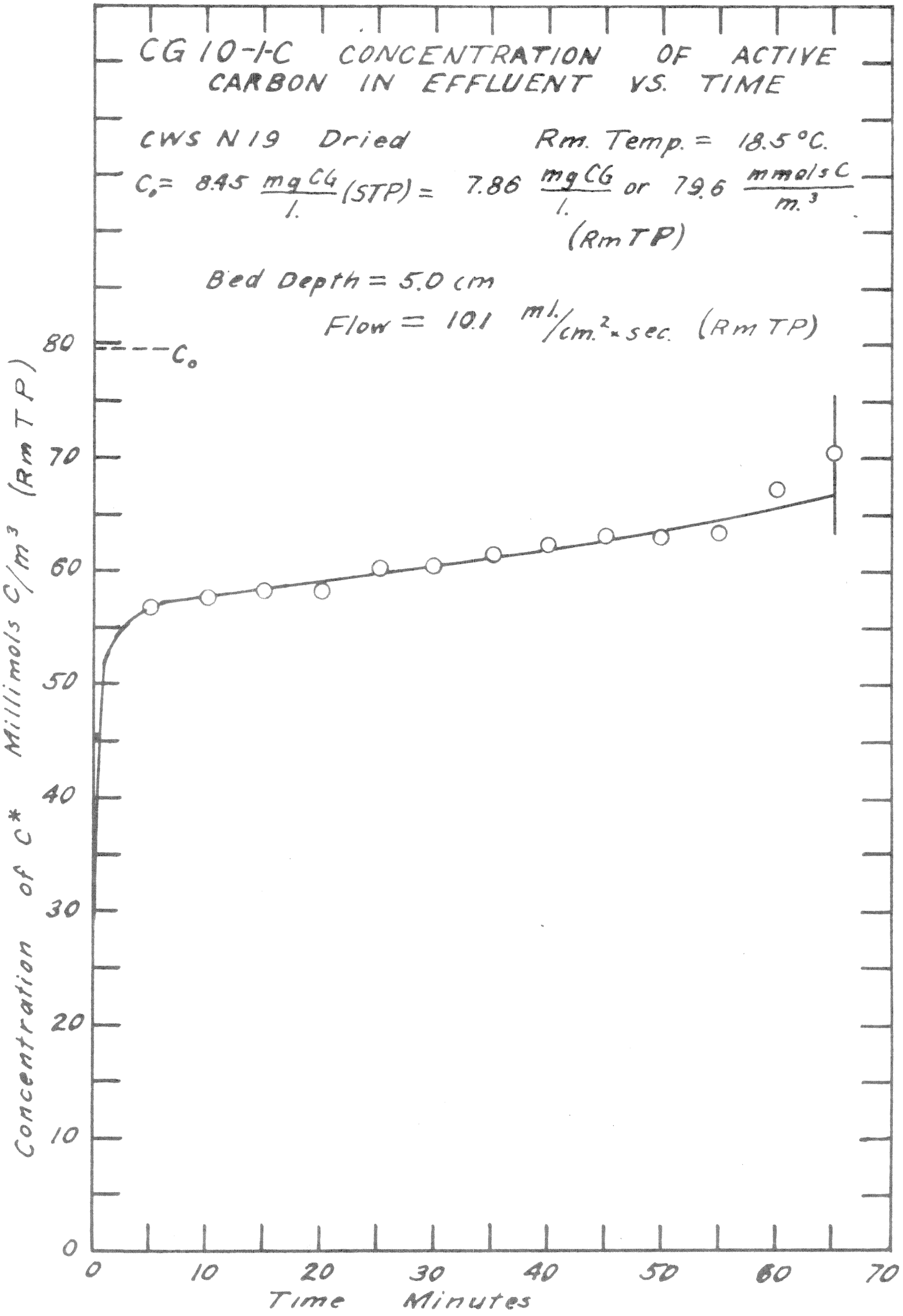
Rm. Temp. = 18°C.

$C_o = 9.52 \frac{\text{mg.CG}}{\text{l.}}$ (STP)

$= 8.90 \frac{\text{mgCG}}{\text{l.}}$ or $90 \frac{\text{m mols C}}{\text{m.}^3}$ (RmTP)

Bed Depth = 5.0 cm.

Flow = 10.1 ml./cm.^{2} x sec. (RmTP)



CG 10-1-C CONCENTRATION OF ACTIVE CARBON IN EFFLUENT VS. TIME

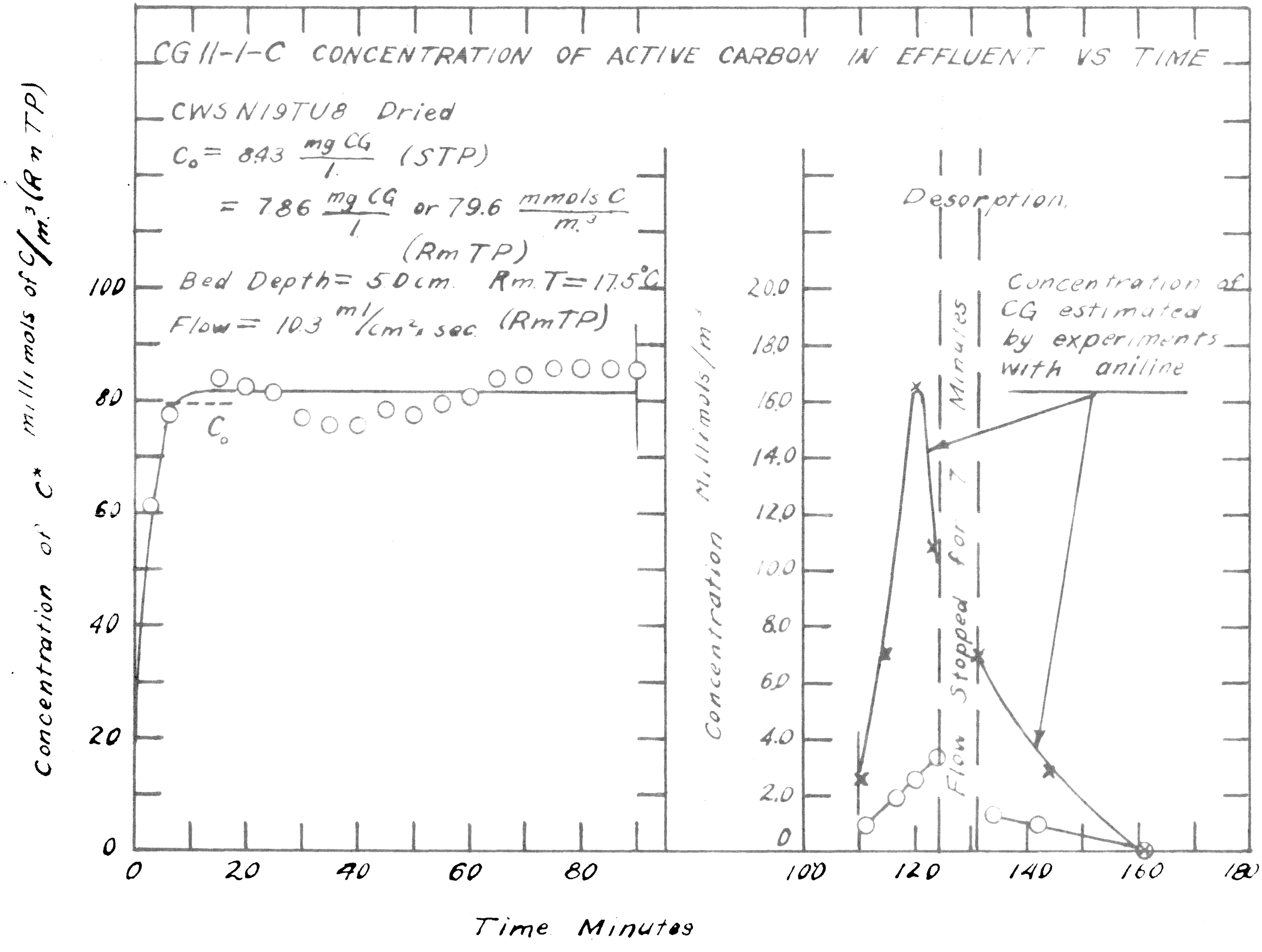
CWS N19 Dried

Rm. Temp. = 18.5 °C.

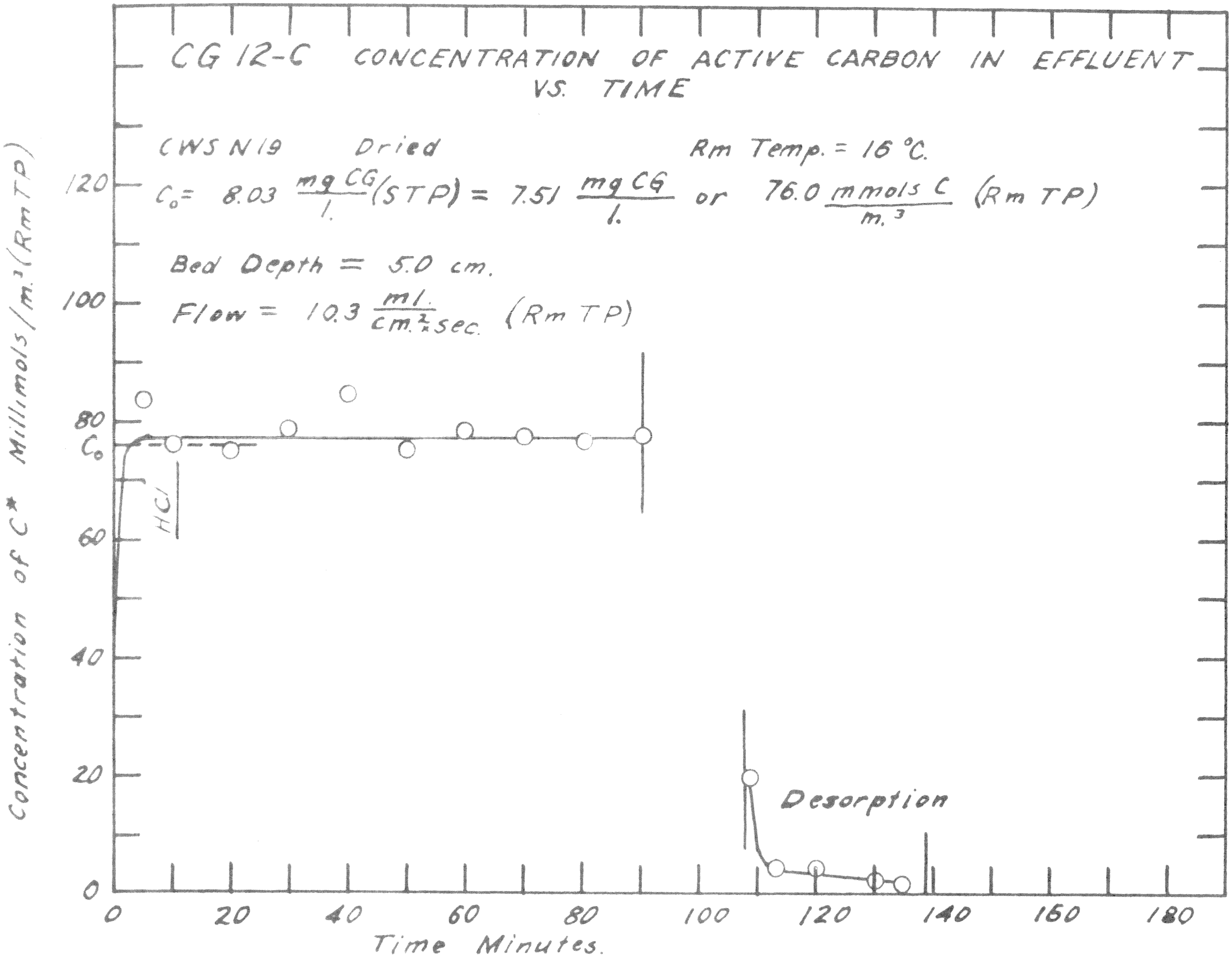
$C_o = 8.45 \frac{mg\ CG}{l.} (STP) = 7.86 \frac{mg\ CG}{l.}$ (RmTP) or $79.6 \frac{mmols\ C}{m.^3}$

Bed Depth = 5.0 cm

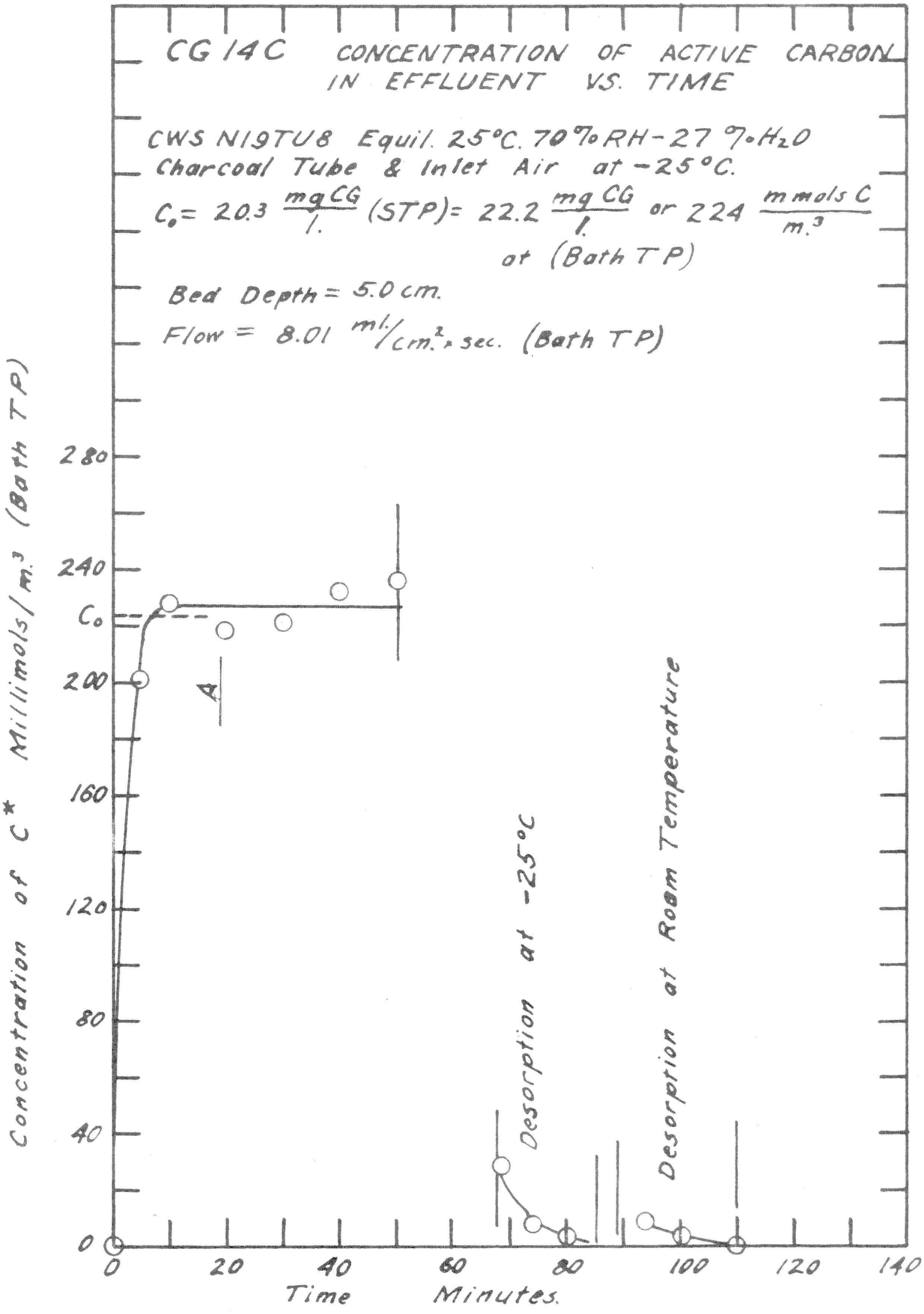
Flow = 10.1 ml./cm.² × sec. (RmTP)



CG 11-1-C CONCENTRATION OF ACTIVE CARBON IN EFFLUENT VS TIME



CG 12-C CONCENTRATION OF ACTIVE CARBON IN EFFLUENT VS. TIME



CG 14C CONCENTRATION OF ACTIVE CARBON IN EFFLUENT VS. TIME

CWS N19TU8 Equil. 25°C. 70% RH – 27 % H_2O

Charcoal Tube & Inlet Air at –25°C.

$C_0 = 20.3 \frac{mg\ CG}{l.}$ (STP) $= 22.2 \frac{mg\ CG}{l.}$ or $224 \frac{m\ mols\ C}{m.^3}$ at (Bath TP)

Bed Depth = 5.0 cm.

Flow = 8.01 ml/cm.²·sec. (Bath TP)

APPENDIX III

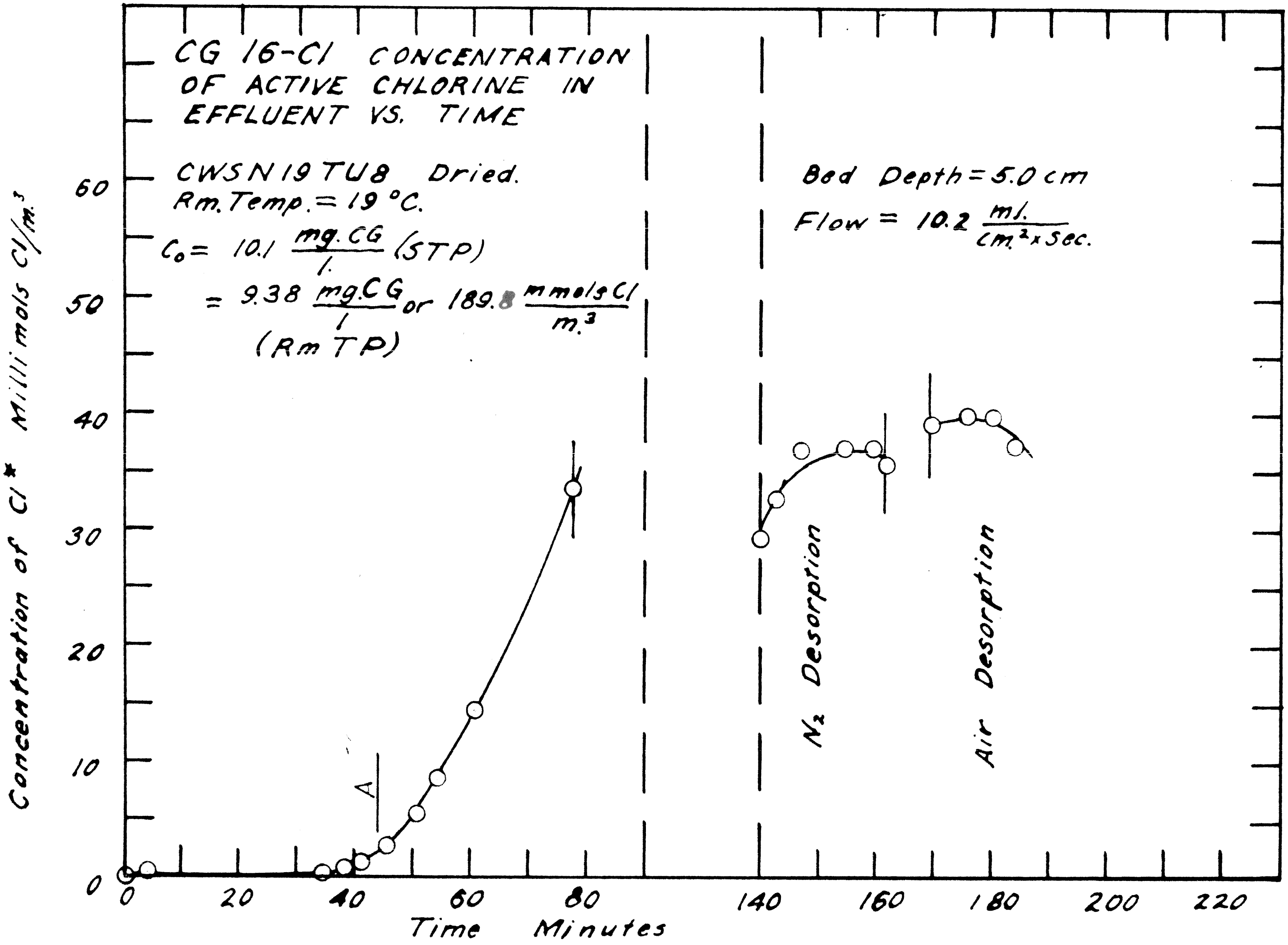
GRAPHS FOR PHOSGENE EXPERIMENTS WITH ACTIVE CHLORINE

Expt. No.	Function Plotted	Expt. No.	Function Plotted
CG16-Cl	C	CG21-1Cl	C
	L	CG21-2Cl	C
CG17-Cl	C	CG21-3Cl	C
	L	CG21-1,2,3Cl	L
CG18-2Cl	C	CG22-Cl	C
	L		L
	A		A
CG20-1,2,3Cl	C		
	L		

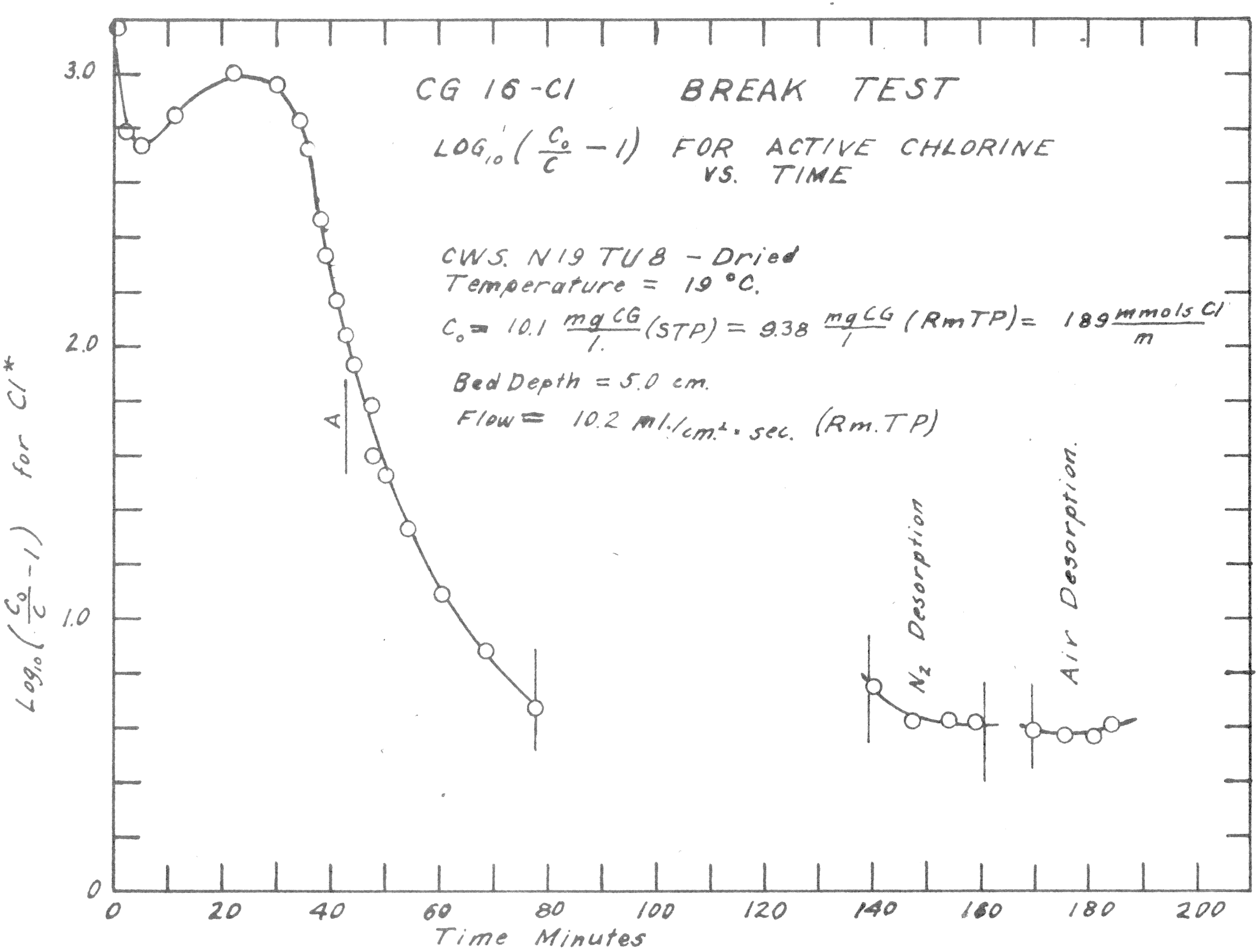
Note: A = Accumulation of activity in entrant layer vs. time

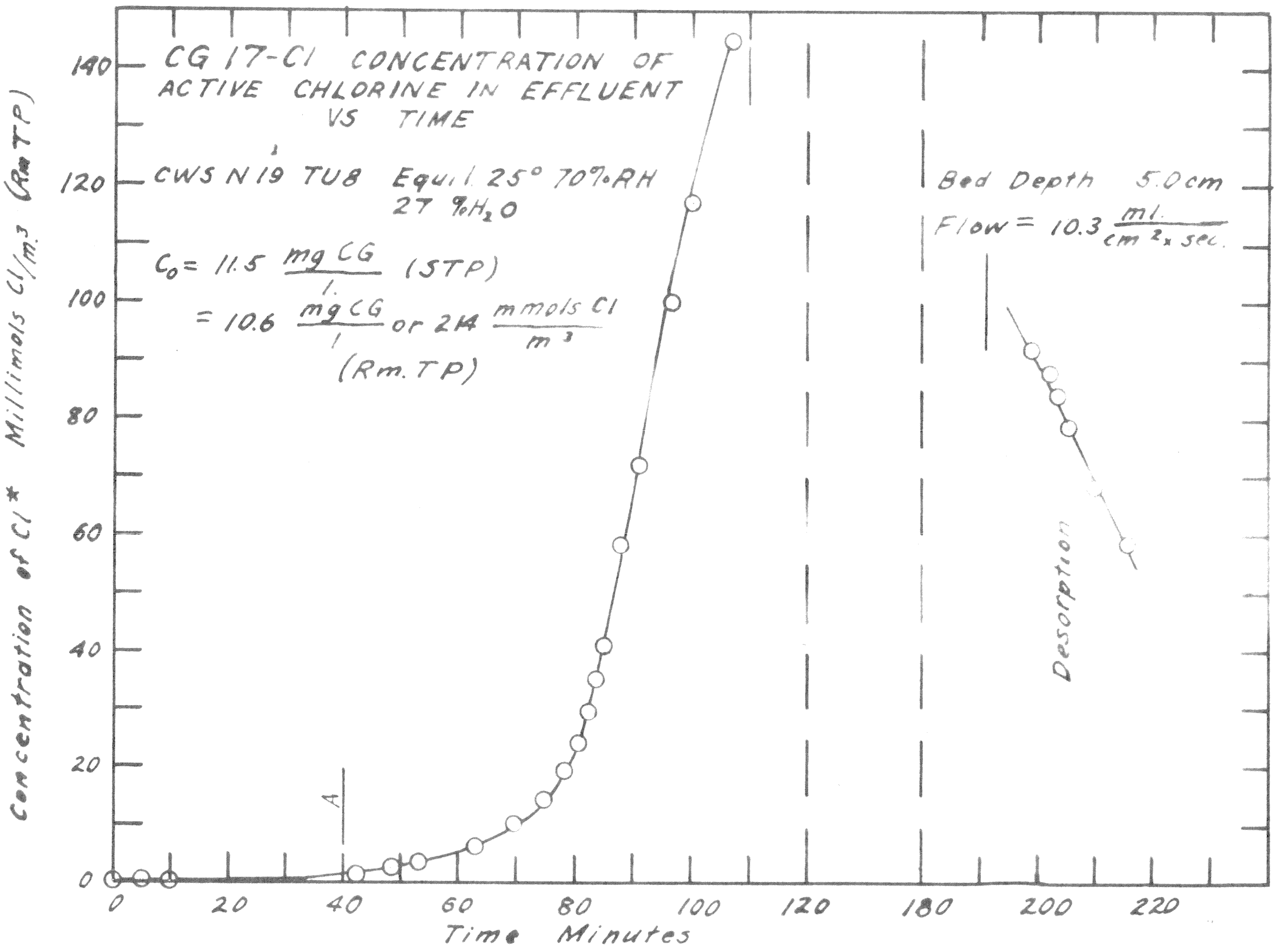
C = Concentration in effluent vs. time

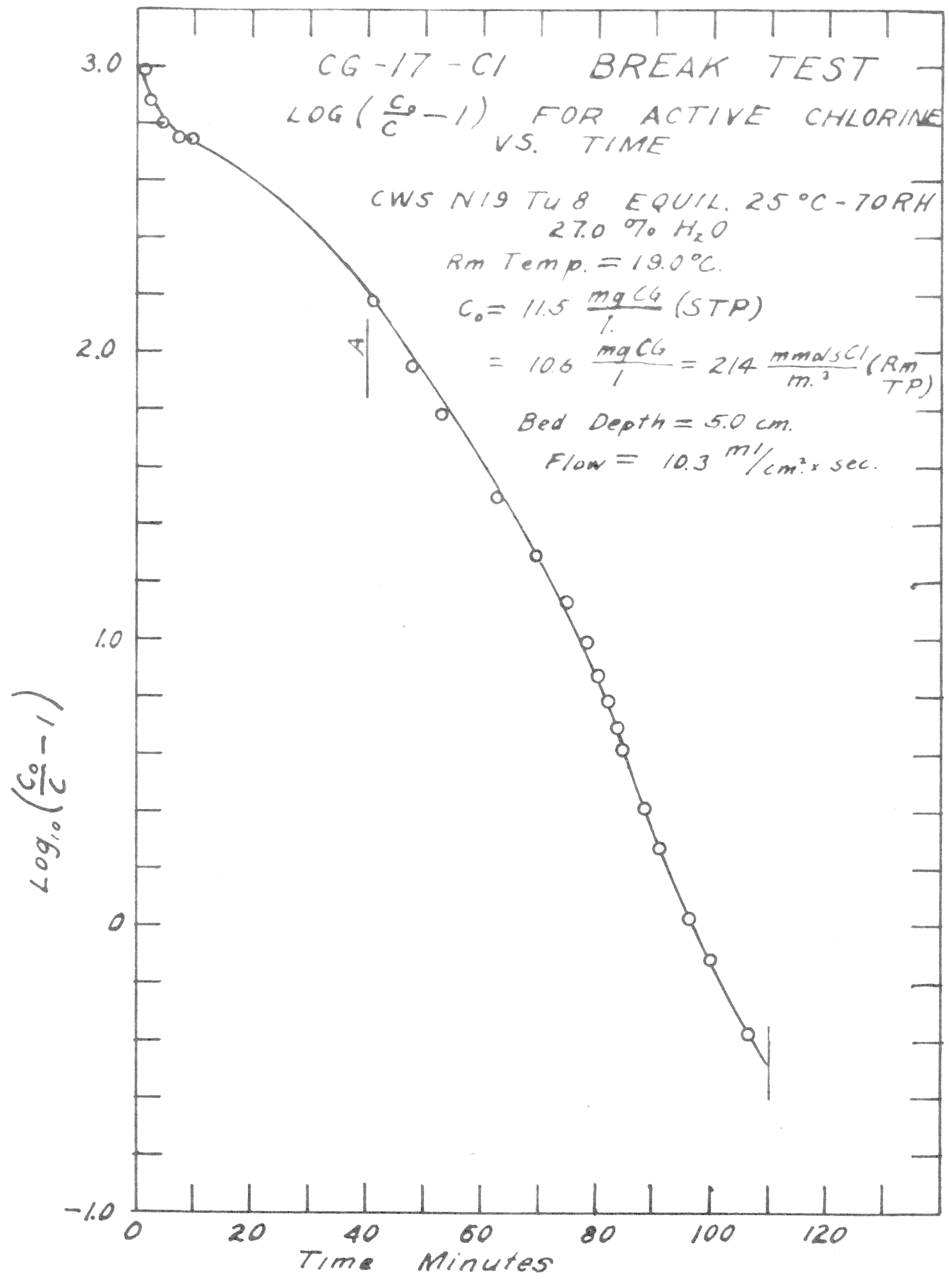
L = log $\left(\frac{c_o}{c} - 1 \right)$ vs. time



CONFIDENTIAL
CLASSIFICATION REMOVED


CG 16-Cl BREAK TEST
$LOG'_{10}\left(\frac{C_0}{C}-1\right)$ FOR ACTIVE CHLORINE VS. TIME
CWS. N19 TU8 - Dried
Temperature = 19 °C.
$C_0 = 10.1 \frac{mg\,CG}{l.}(STP) = 9.38 \frac{mg\,CG}{l}(RmTP) = 189 \frac{mmols\,Cl}{m}$
Bed Depth = 5.0 cm.
Flow = 10.2 ml./cm.² • sec. (Rm.TP)
A
N_2 Desorption
Air Desorption.
$Log_{10}\left(\frac{C_0}{C}-1\right)$ for Cl*
3.0
2.0
1.0
0
0
20
40
60
80
100
120
140
160
180
200
Time Minutes

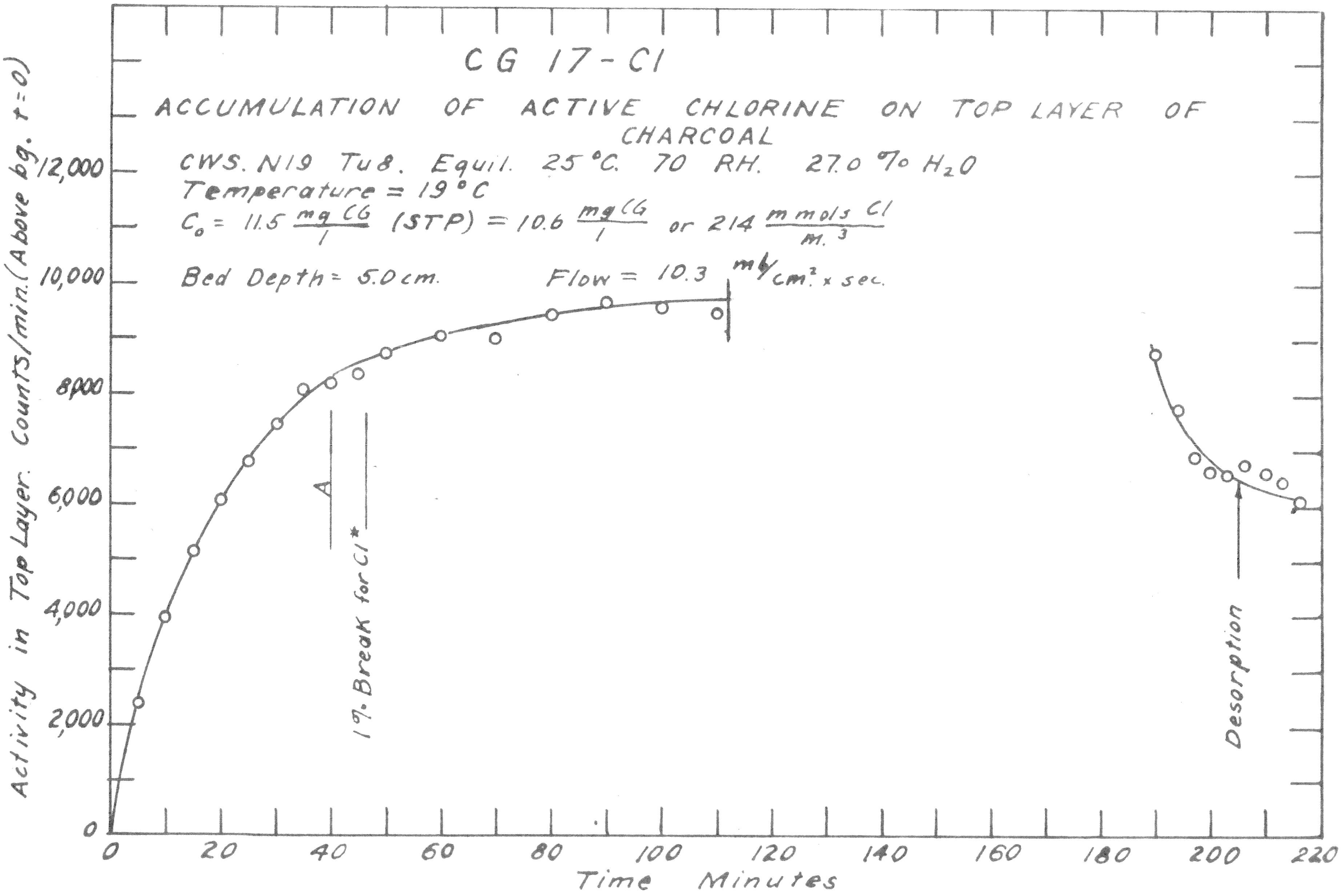

CG 17-Cl CONCENTRATION OF ACTIVE CHLORINE IN EFFLUENT VS TIME
CWS N19 TU8 Equil. 25° 70% RH
27 % H₂O
C₀ = 11.5 mg CG / l. (STP)
= 10.6 mg CG / l or 214 mmols Cl / m³
(Rm. TP)
Bed Depth 5.0 cm
Flow = 10.3 ml. / cm² x sec.
Desorption
A
Concentration of Cl* Millimols Cl/m³ (Rm TP)
Time Minutes
0
20
40
60
80
100
120
140
0
20
40
60
80
100
120
180
200
220



CG-17-Cl BREAK TEST

LOG $\left(\frac{C_0}{C}-1\right)$ FOR ACTIVE CHLORINE VS. TIME

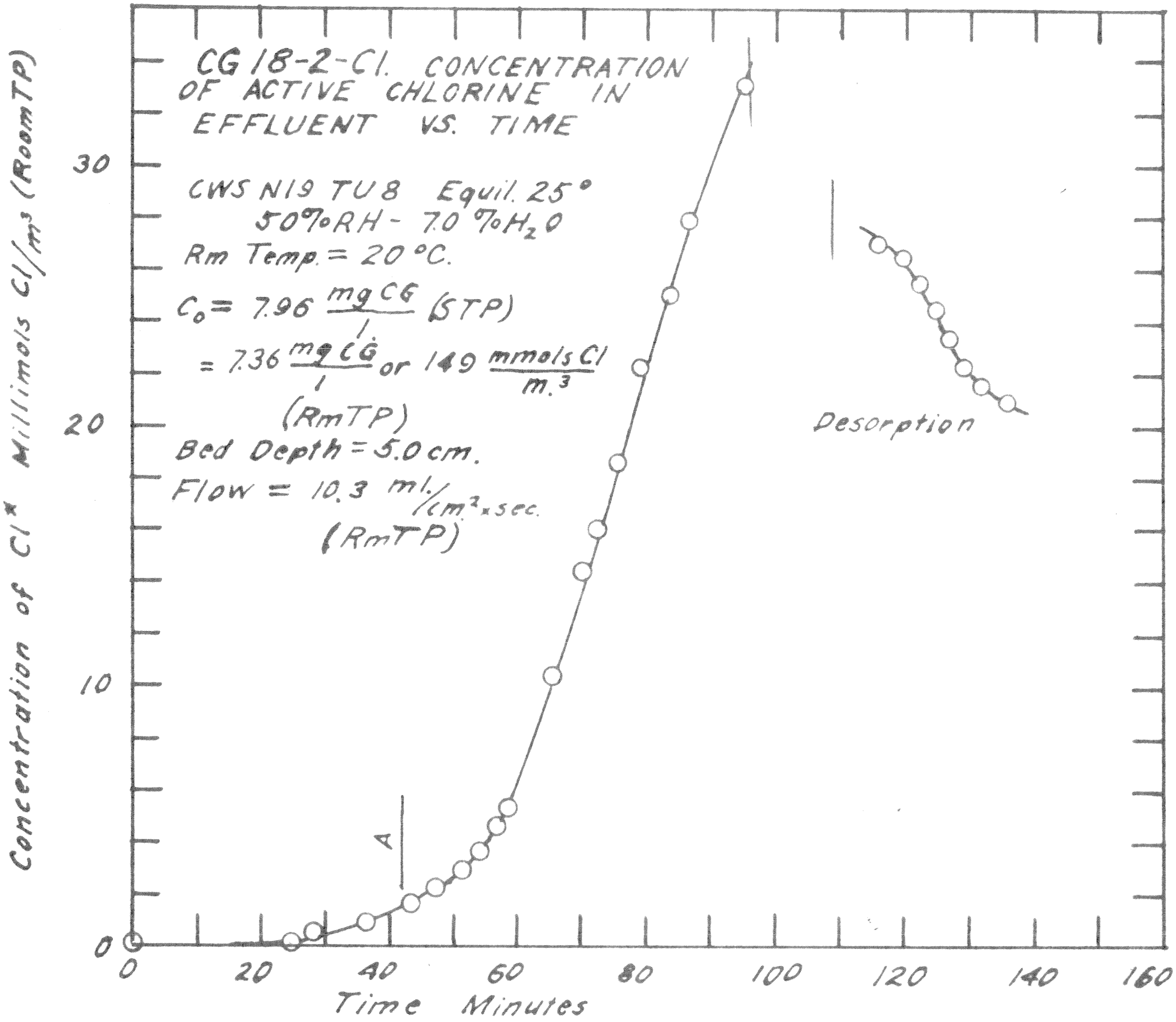
CWS N19 Tu 8 EQUIL. 25 °C - 70RH
27.0 % H_2O
Rm Temp. = 19.0°C.
$C_0 = 11.5 \frac{mg\,CG}{l.}$ (STP)
$= 10.6 \frac{mg\,CG}{l} = 214 \frac{mmols\,Cl}{m.^3}$ (Rm TP)
Bed Depth = 5.0 cm.
Flow = 10.3 ml/cm.² x sec.



CG 17-Cl

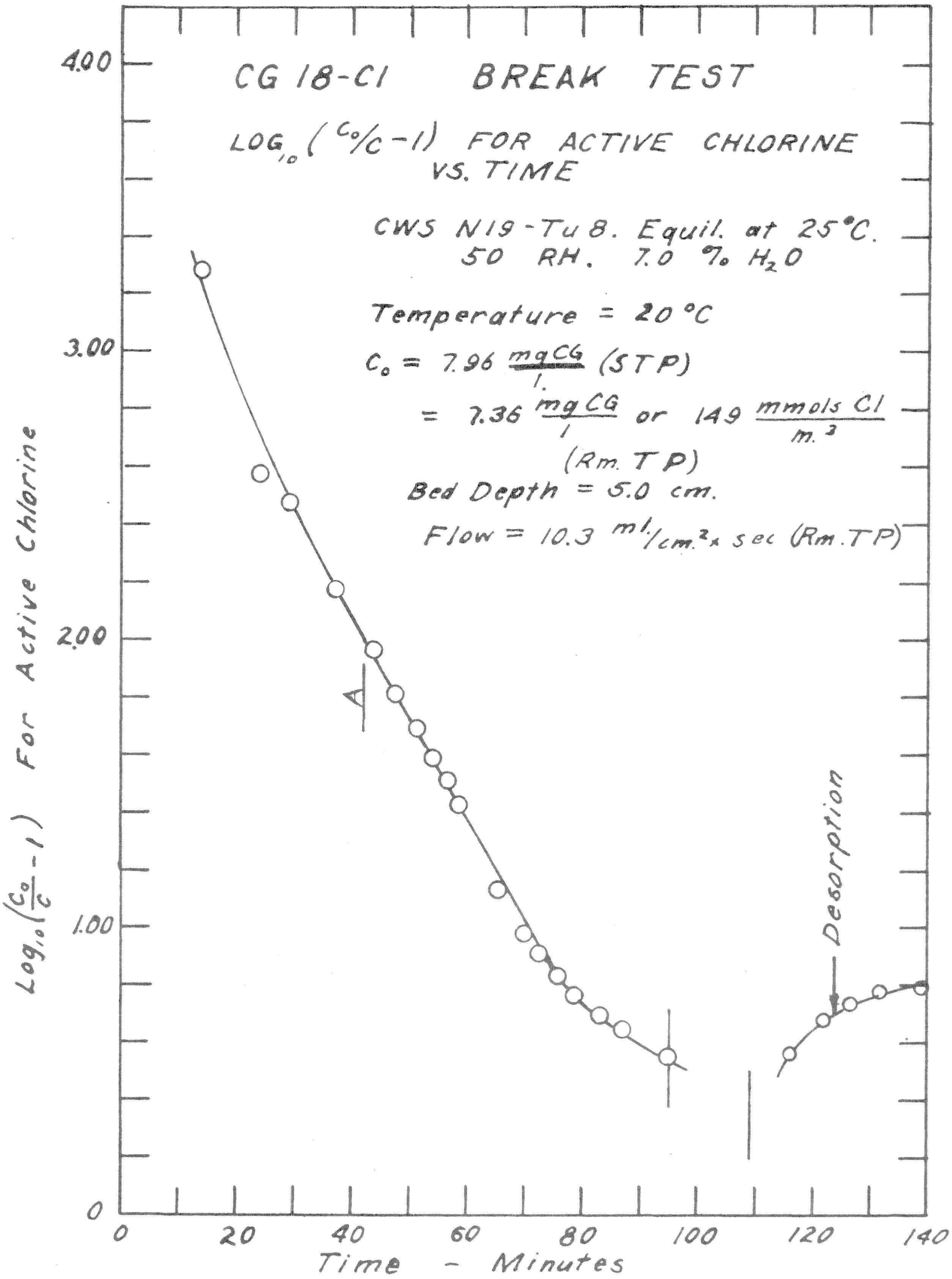
ACCUMULATION OF ACTIVE CHLORINE ON TOP LAYER OF CHARCOAL

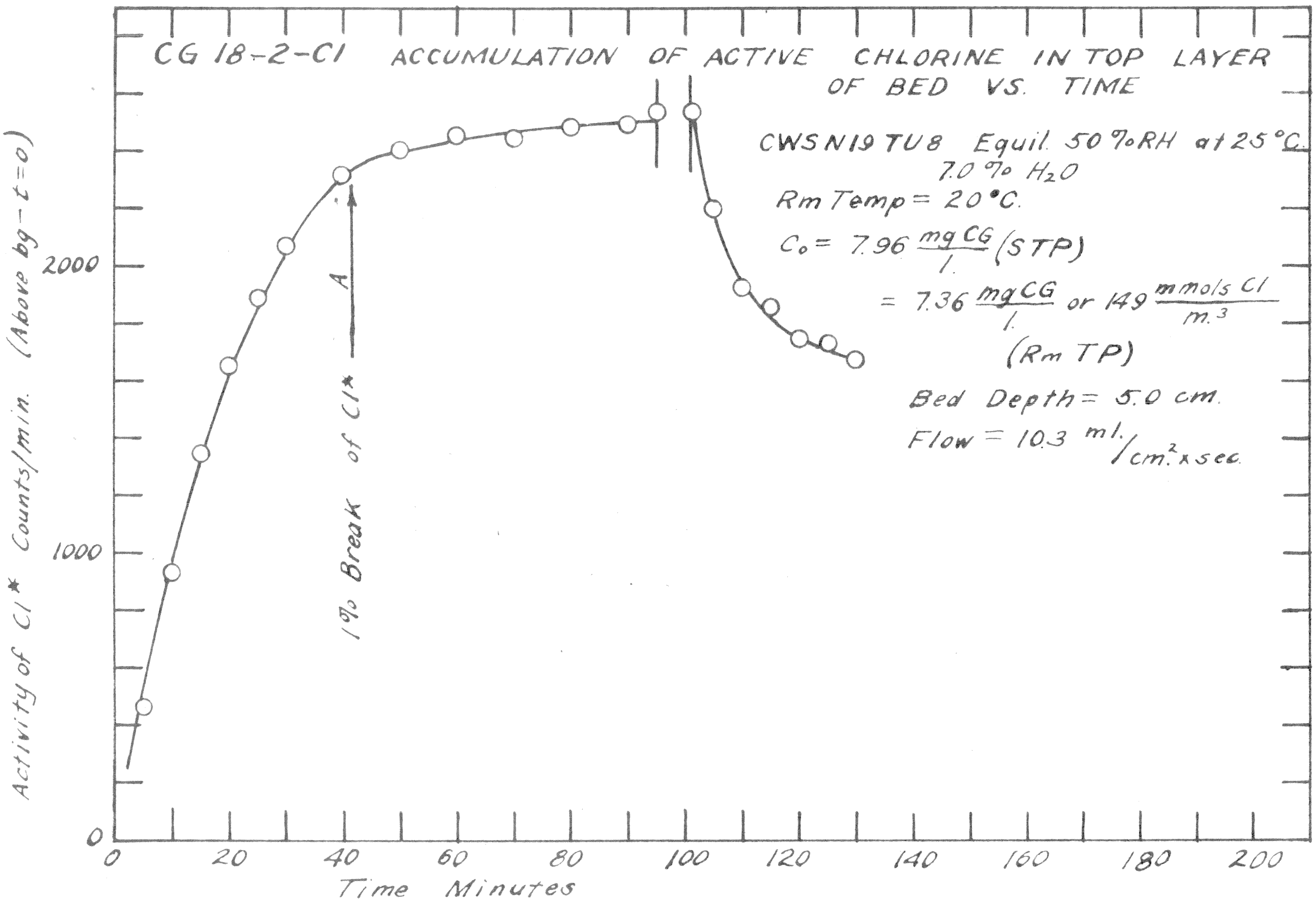
CWS. N19 Tu8. Equil. 25 °C. 70 RH. 27.0 % H_2O
Temperature = 19 °C
$C_o = 11.5 \frac{mg\ CG}{l}$ (STP) $= 10.6 \frac{mg\ CG}{l}$ or $214 \frac{m\ mols\ Cl}{M.^3}$
Bed Depth = 5.0 cm. Flow = 10.3 $ml/cm.^2 \times sec.$

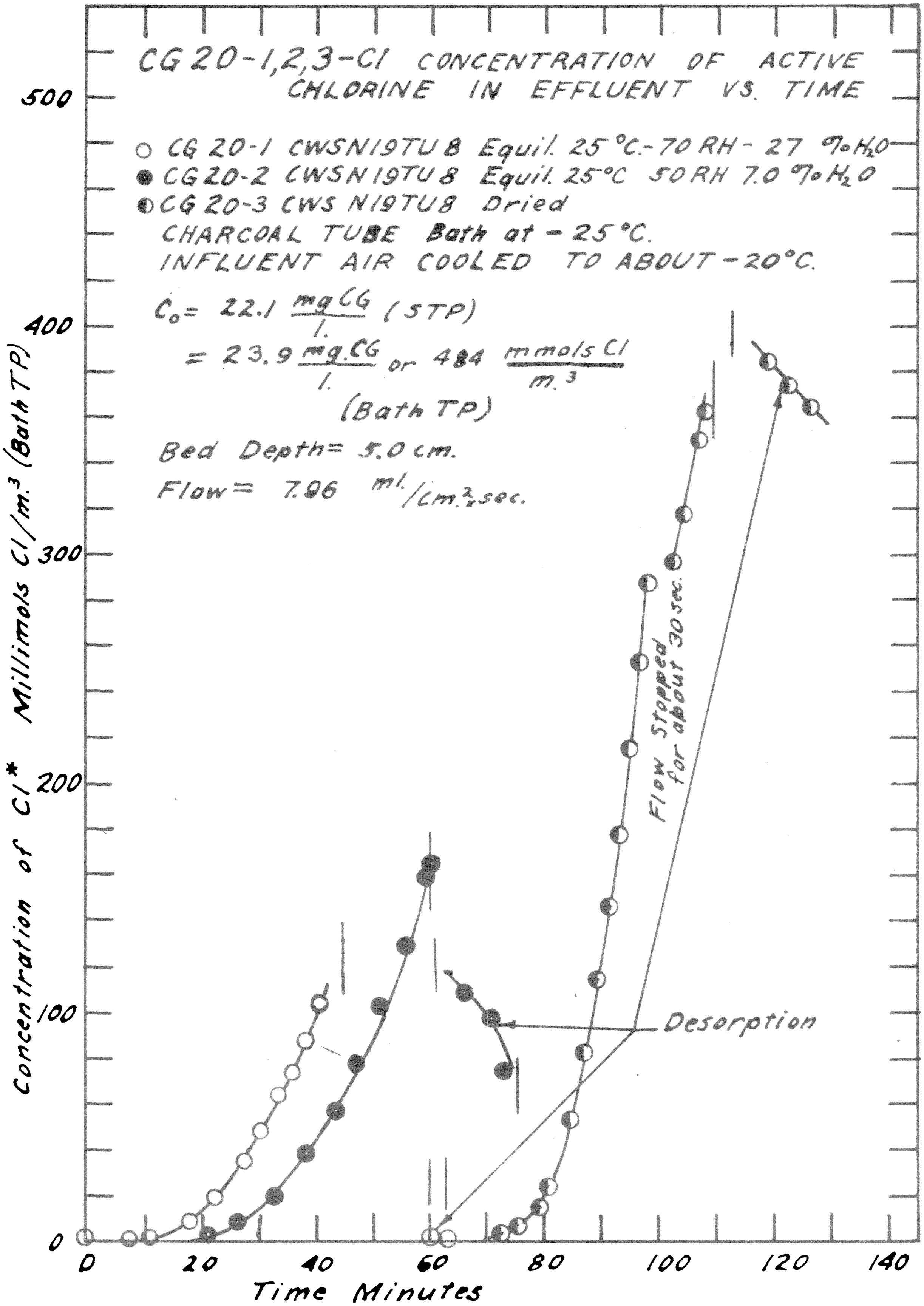


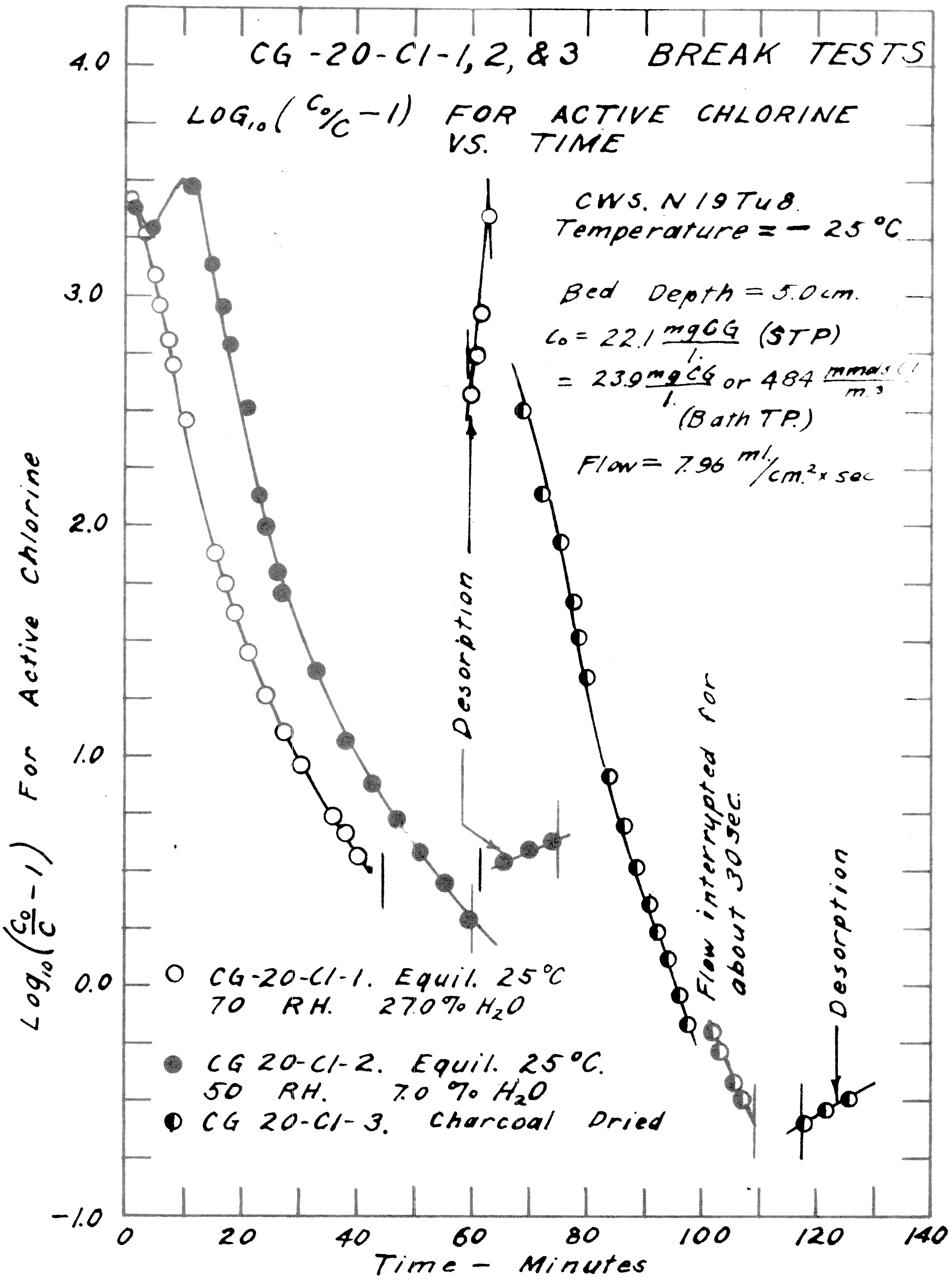
CG 18-2-Cl. CONCENTRATION OF ACTIVE CHLORINE IN EFFLUENT VS. TIME

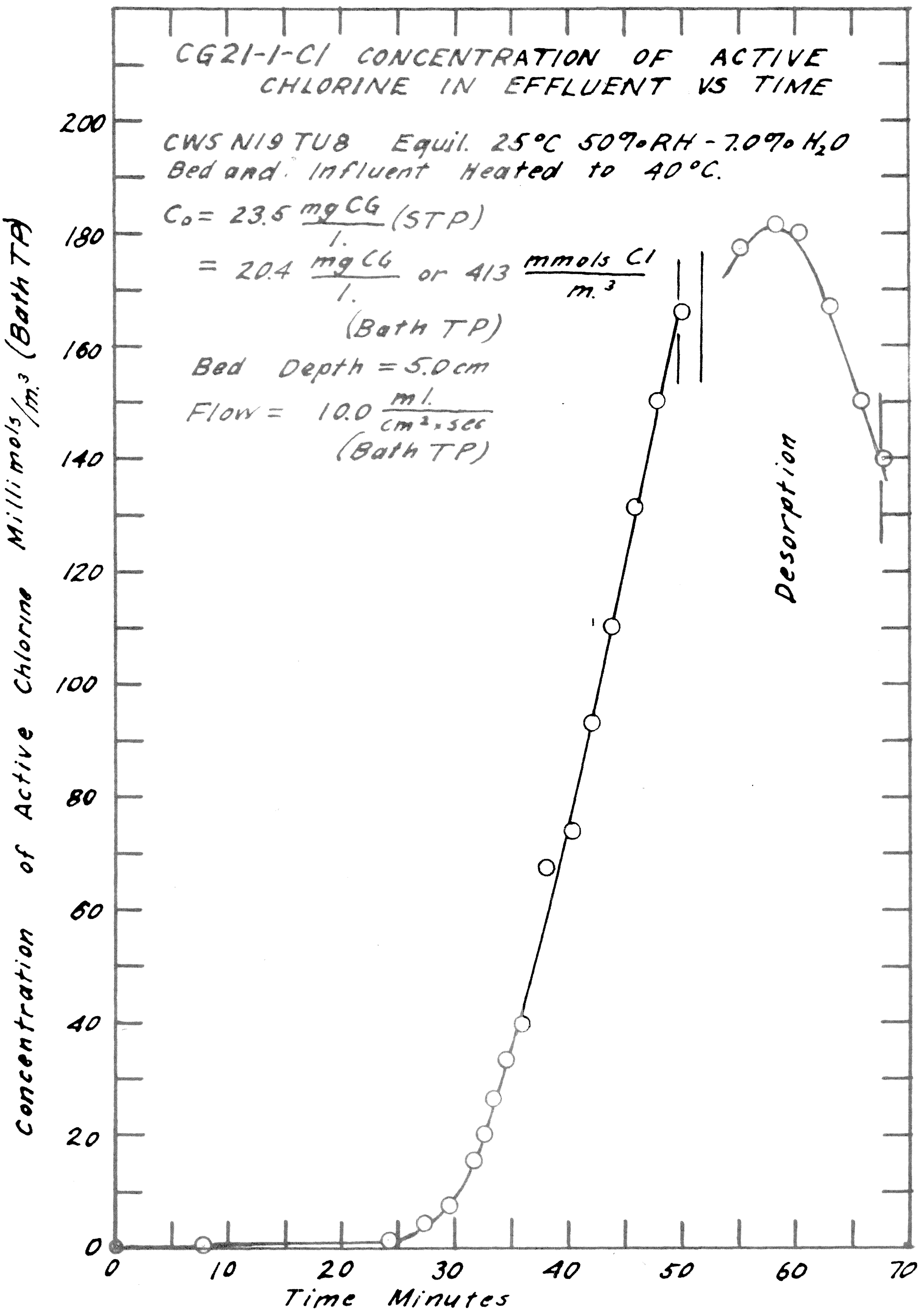
CWS N19 TU8 Equil. 25°
50% RH - 7.0 % H_2O
Rm Temp. = 20 °C.
$C_0 = 7.96 \frac{mg\ CG}{l}$ (STP)
$= 7.36 \frac{mg\ CG}{l}$ or $149 \frac{mmols\ Cl}{m.^3}$
(RmTP)
Bed Depth = 5.0 cm.
Flow = 10.3 ml./cm.^{2} x sec.
(RmTP)

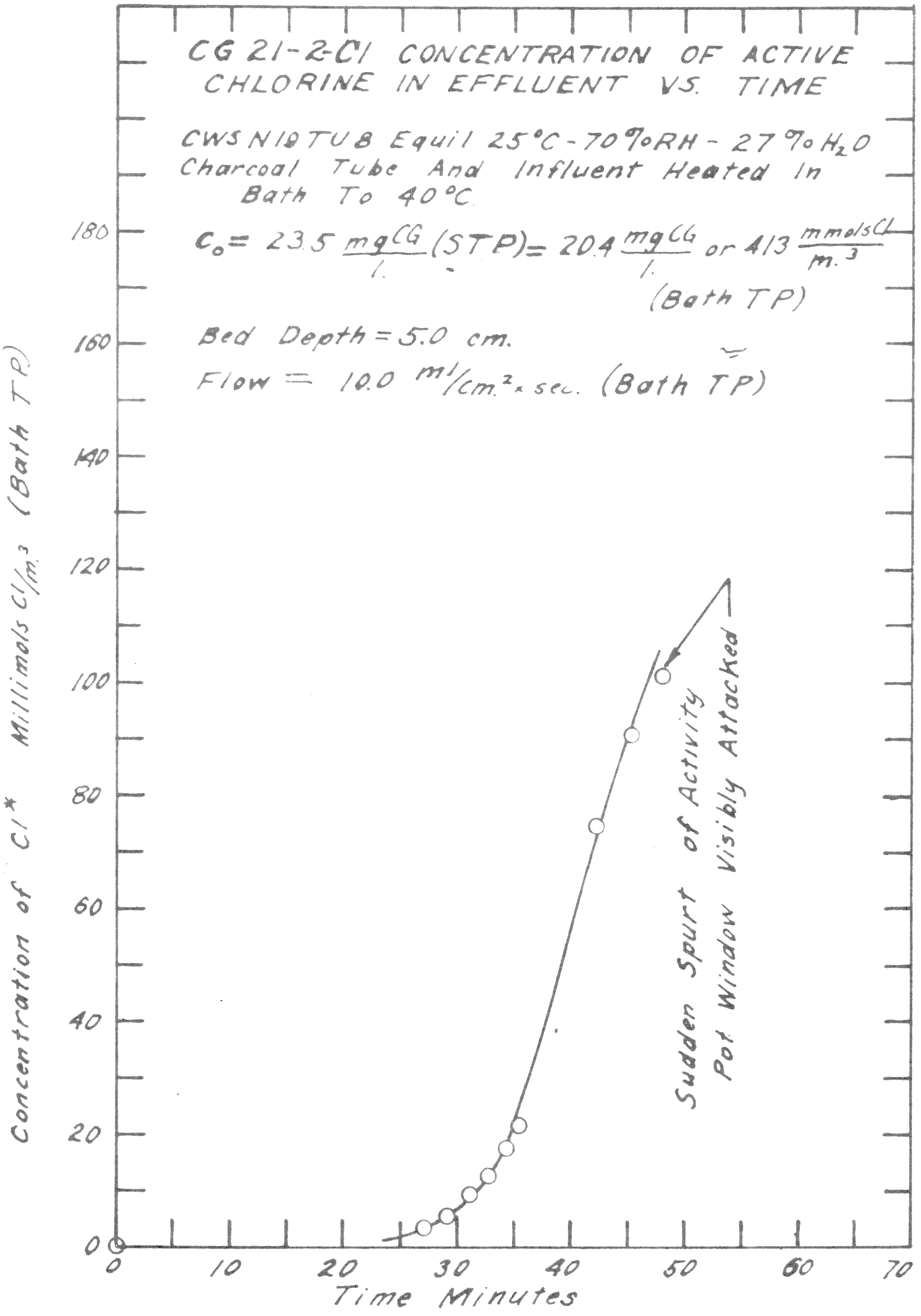

CG 18-Cl BREAK TEST
LOG$_{10}$ ($^{C_0}/_C$ -1) FOR ACTIVE CHLORINE VS. TIME
CWS N19-Tu 8. Equil. at 25°C. 50 RH. 7.0 % H_2O
Temperature = 20 °C
C_0 = 7.96 $\frac{mg CG}{l.}$ (STP)
= 7.36 $\frac{mg CG}{l}$ or 149 $\frac{mmols Cl}{m.^3}$ (Rm. TP)
Bed Depth = 5.0 cm.
Flow = 10.3 ml/cm.² × sec (Rm. TP)
A
Desorption
Log$_{10}$($\frac{C_0}{C}$ - 1) For Active Chlorine
Time - Minutes
4.00
3.00
2.00
1.00
0
0
20
40
60
80
100
120
140


CG 18-2-Cl ACCUMULATION OF ACTIVE CHLORINE IN TOP LAYER OF BED VS. TIME
CWSN19TU8 Equil. 50 %RH at 25°C.
7.0 % H_2O
Rm Temp = 20°C.
$C_o = 7.96 \frac{mg\,CG}{l.}$ (STP)
$= 7.36 \frac{mg\,CG}{l.}$ or $149 \frac{mmols\ Cl}{m.^3}$
(Rm TP)
Bed Depth = 5.0 cm.
Flow = 10.3 ml./cm.^{2} x sec.
1% Break of Cl*
A
Activity of Cl* Counts/min. (Above bg - t=0)
0
1000
2000
Time Minutes
0
20
40
60
80
100
120
140
160
180
200


CG 20-1,2,3-Cl CONCENTRATION OF ACTIVE CHLORINE IN EFFLUENT VS. TIME
○ CG 20-1 CWSN19TU8 Equil. 25 °C.-70 RH - 27 %H_2O
● CG 20-2 CWSN19TU8 Equil. 25°C 50 RH 7.0 %H_2O
◐ CG 20-3 CWS N19TU8 Dried
CHARCOAL TUBE Bath at - 25 °C.
INFLUENT AIR COOLED TO ABOUT - 20°C.
$C_0 = 22.1 \frac{mg\,CG}{l.}$ (STP)
$= 23.9 \frac{mg.CG}{l.}$ or $484 \frac{mmols\,Cl}{m.^3}$
(Bath TP)
Bed Depth = 5.0 cm.
Flow = 7.96 ml./cm.² x sec.
Flow Stopped for about 30 sec.
Desorption
Concentration of Cl* Millimols Cl/m.³ (Bath TP)
0
100
200
300
400
500
Time Minutes
0
20
40
60
80
100
120
140


CG -20-Cl-1, 2, & 3 BREAK TESTS
LOG₁₀ (Co/C − 1) FOR ACTIVE CHLORINE VS. TIME
CWS. N 19 Tu 8.
Temperature = − 25 °C
Bed Depth = 5.0 cm.
Co = 22.1 mg CG / l. (STP)
= 23.9 mg CG / l. or 484 mmols Cl / m.³ (Bath T.P.)
Flow = 7.96 ml./cm.² × sec
Desorption
Flow interrupted for about 30 sec.
Desorption
○ CG-20-Cl-1. Equil. 25°C 70 RH. 27.0% H₂O
● CG 20-Cl-2. Equil. 25°C. 50 RH. 7.0% H₂O
◐ CG 20-Cl-3. Charcoal Dried
Log₁₀ (Co/C − 1) For Active Chlorine
4.0
3.0
2.0
1.0
0.0
−1.0
0
20
40
60
80
100
120
140
Time − Minutes


CG21-1-Cl CONCENTRATION OF ACTIVE CHLORINE IN EFFLUENT VS TIME
CWS N19 TU8 Equil. 25°C 50% RH - 7.0% H_2O
Bed and Influent Heated to 40°C.
$C_0 = 23.5 \frac{mg\ CG}{l.}$ (STP)
$= 20.4 \frac{mg\ CG}{l.}$ or 413 $\frac{mmols\ Cl}{m.^3}$
(Bath TP)
Bed Depth = 5.0 cm
Flow = 10.0 $\frac{ml.}{cm^2 \times sec}$
(Bath TP)
Desorption
Concentration of Active Chlorine Millimols/$m.^3$ (Bath TP)
0
20
40
60
80
100
120
140
160
180
200
0
10
20
30
40
50
60
70
Time Minutes

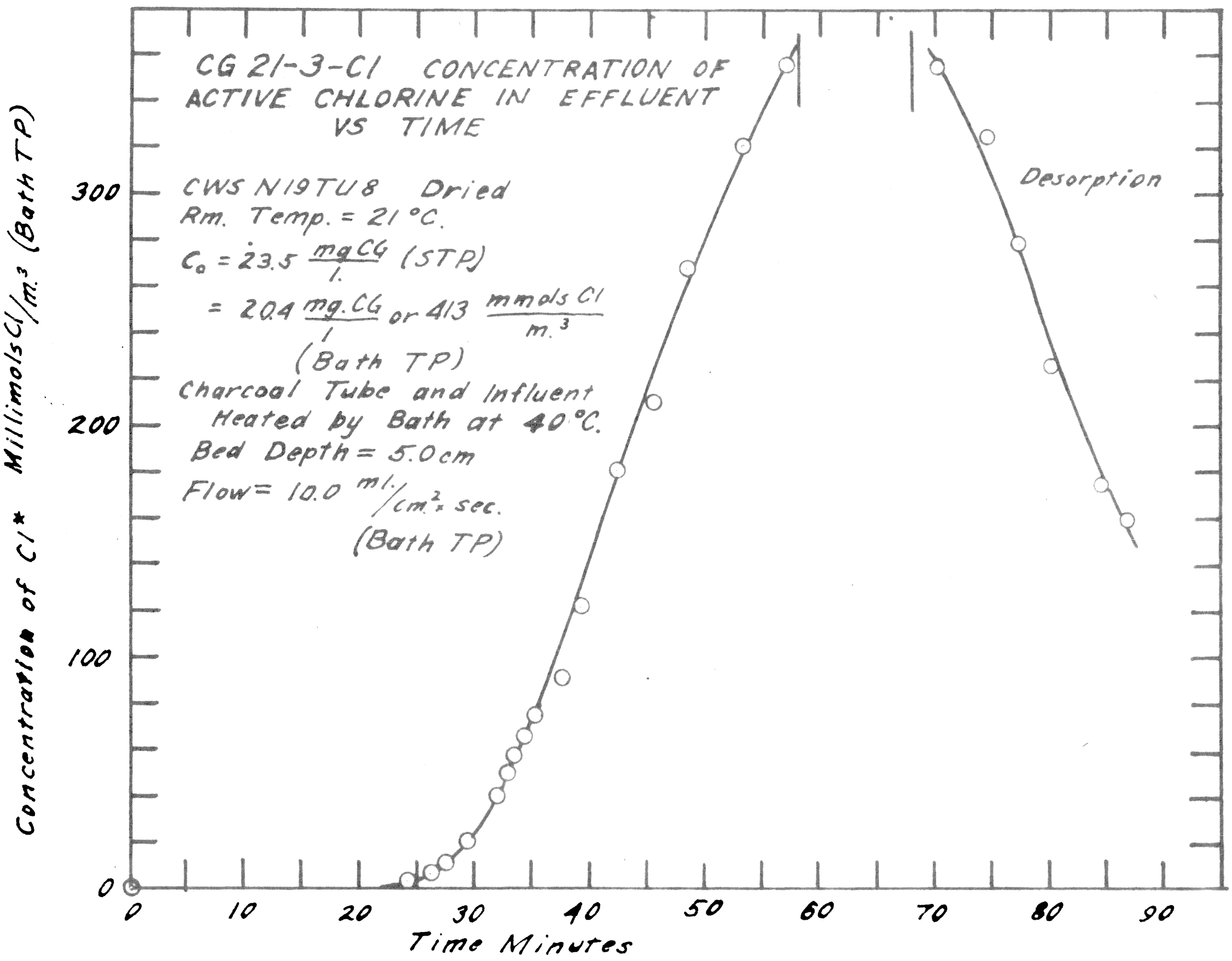


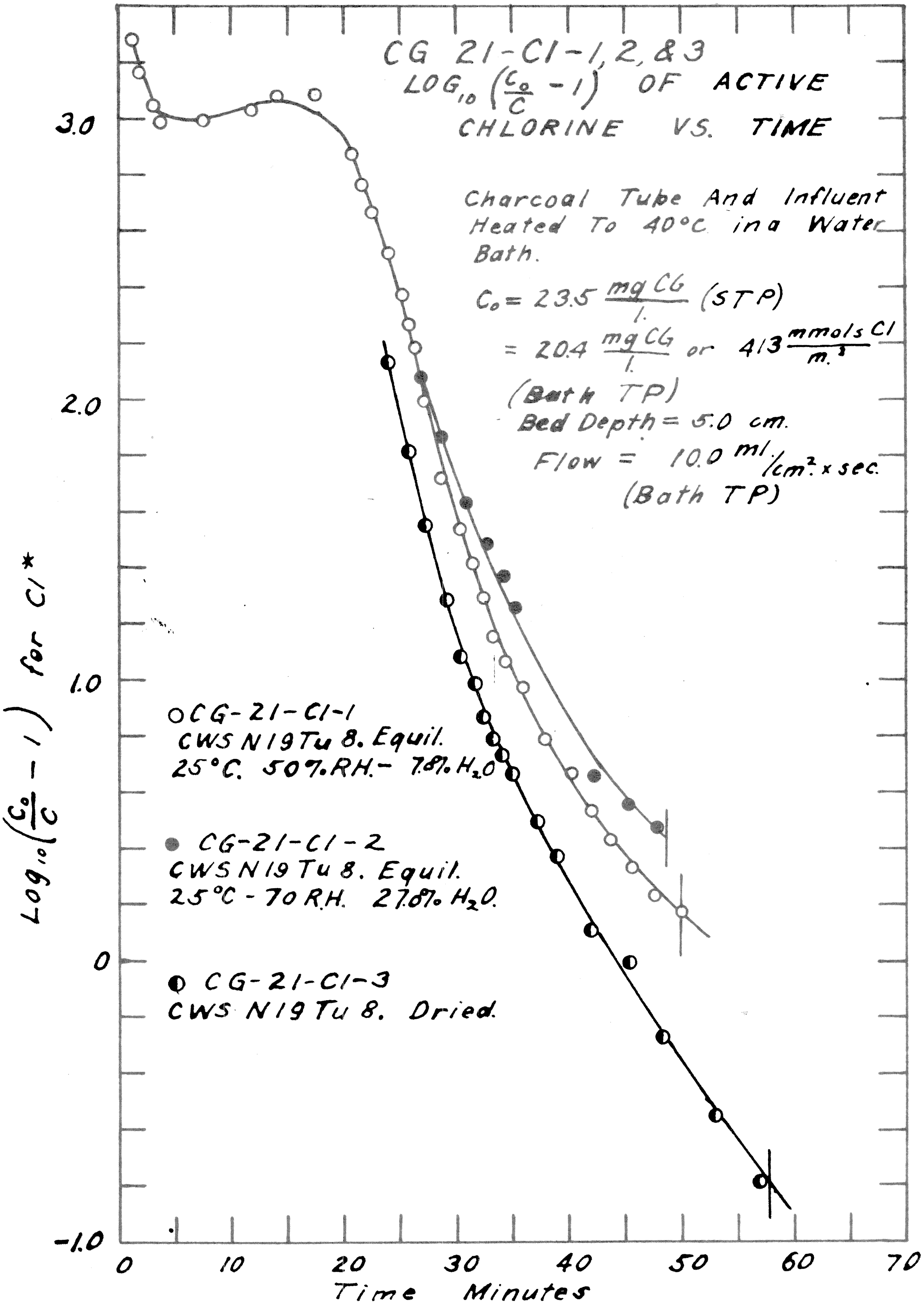
CG 21-2-Cl CONCENTRATION OF ACTIVE CHLORINE IN EFFLUENT VS. TIME

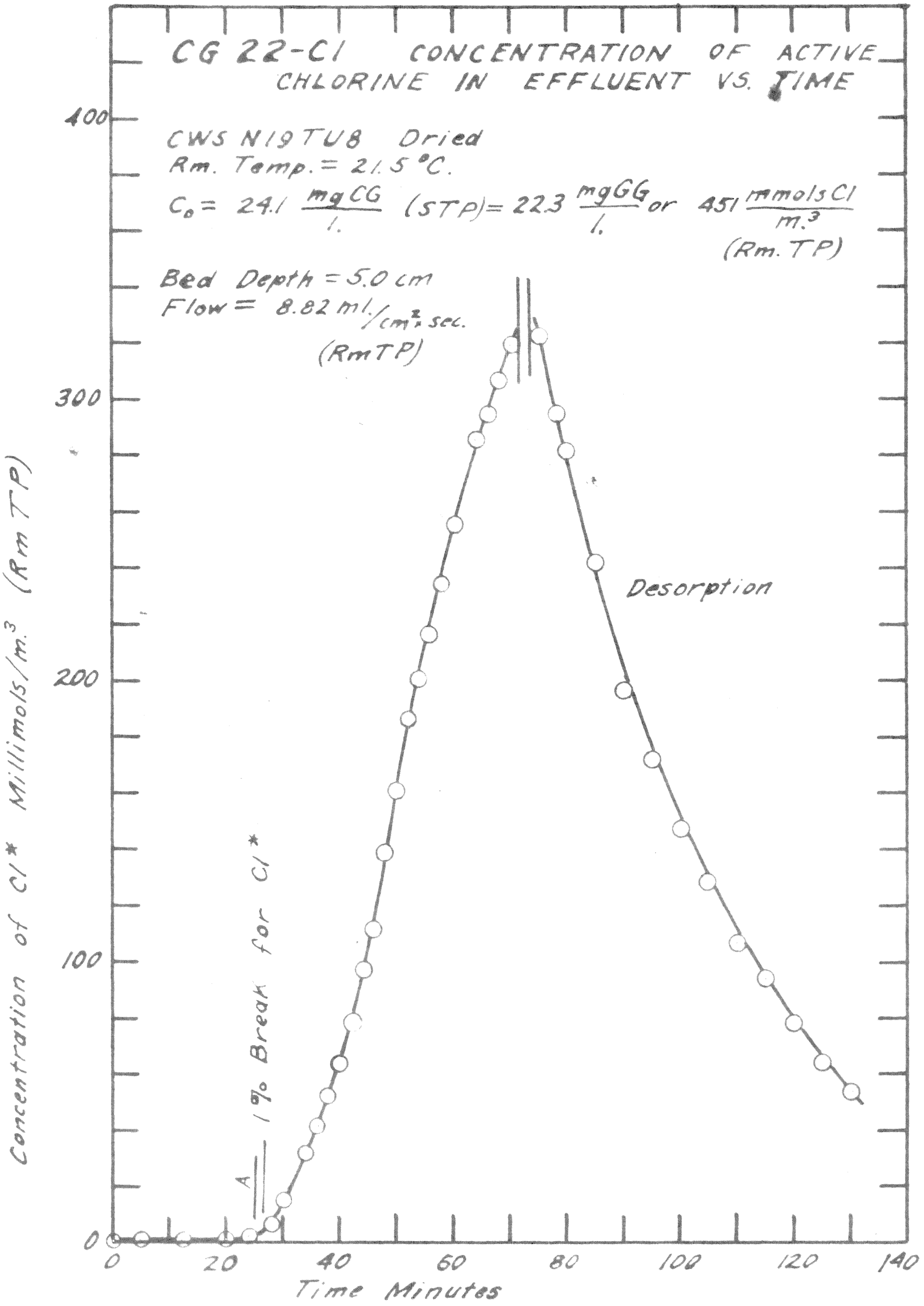
CWS N19TU8 Equil 25°C - 70% RH - 27% H_2O
Charcoal Tube And Influent Heated In
Bath To 40°C

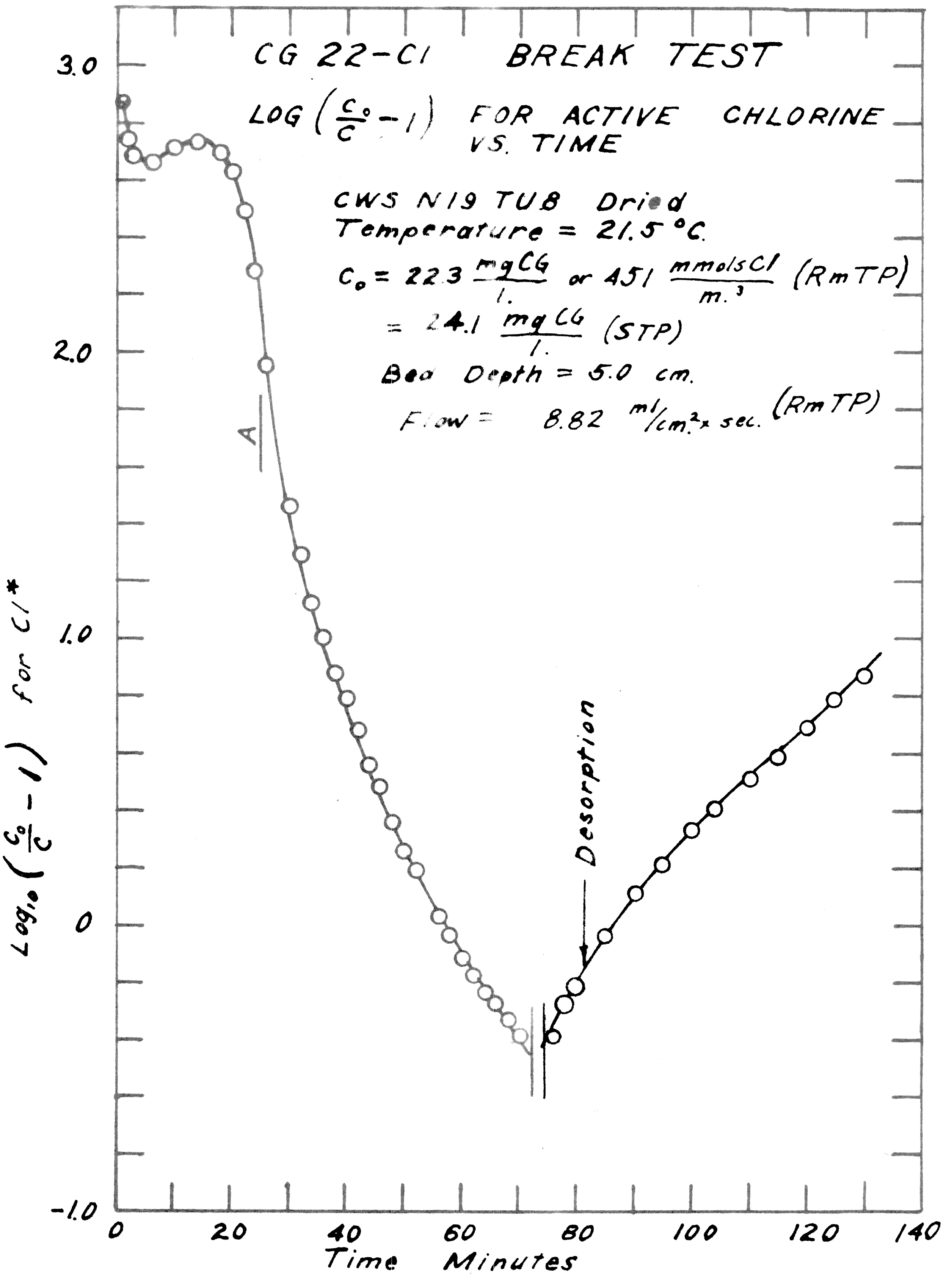
$C_0 = 23.5 \frac{mg\,CG}{l.}$ (STP) $= 20.4 \frac{mg\,CG}{l.}$ or $413 \frac{mmols\,Cl}{m.^3}$
(Bath TP)

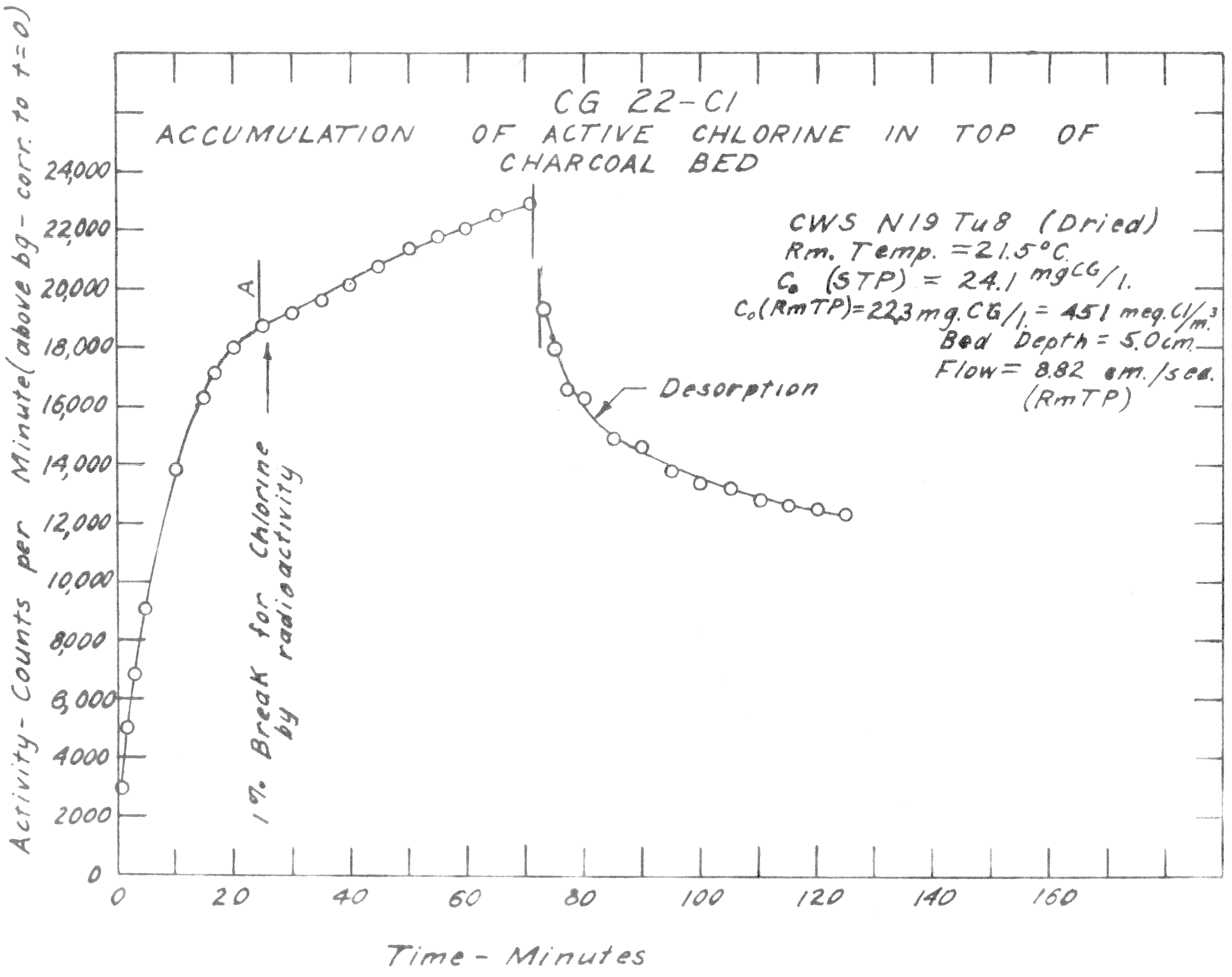
Bed Depth = 5.0 cm.
Flow = 10.0 $ml/cm.^2 \times sec.$ (Bath TP)


CG 21-3-Cl CONCENTRATION OF ACTIVE CHLORINE IN EFFLUENT VS TIME
CWS N19TU8 Dried
Rm. Temp. = 21 °C.
$C_o = 23.5 \frac{mg CG}{l.}$ (STP)
$= 20.4 \frac{mg. CG}{l}$ or $413 \frac{mmols Cl}{m.^3}$
(Bath TP)
Charcoal Tube and Influent Heated by Bath at 40 °C.
Bed Depth = 5.0 cm
Flow = $10.0 \frac{ml.}{cm^2 \times sec.}$
(Bath TP)
Desorption
Concentration of Cl* Millimols Cl/m.³ (Bath TP)
0
100
200
300
Time Minutes
0
10
20
30
40
50
60
70
80
90


CG 21-Cl-1, 2, & 3
$LOG_{10}\left(\frac{C_o}{C}-1\right)$ OF ACTIVE CHLORINE VS. TIME
Charcoal Tube And Influent Heated To 40°C in a Water Bath.
$C_o = 23.5 \frac{mg\ CG}{l.}$ (STP)
$= 20.4 \frac{mg\ CG}{l.}$ or $413 \frac{mmols\ Cl}{m.^3}$
(Bath TP)
Bed Depth = 5.0 cm.
Flow = $10.0\ ml./cm.^2 \times sec.$ (Bath TP)
○ CG-21-Cl-1
CWS N19 Tu 8. Equil. 25°C. 50% RH. - 7.8% H_2O
● CG-21-Cl-2
CWS N19 Tu 8. Equil. 25°C - 70 R.H. 27.8% H_2O.
◐ CG-21-Cl-3
CWS N19 Tu 8. Dried.
$Log_{10}\left(\frac{C_o}{C}-1\right)$ for Cl*
3.0
2.0
1.0
0
-1.0
0
10
20
30
40
50
60
70
Time Minutes


CG 22-Cl CONCENTRATION OF ACTIVE CHLORINE IN EFFLUENT VS. TIME
CWS N19TU8 Dried
Rm. Temp. = 21.5°C.
$C_o = 24.1 \frac{mg\,CG}{l.}\ (STP) = 22.3 \frac{mg\,GG}{l.}$ or $451 \frac{mmols\,Cl}{m.^3}$ (Rm. TP)
Bed Depth = 5.0 cm
Flow = 8.82 ml./cm². sec. (RmTP)
Desorption
A
1% Break for Cl*
Concentration of Cl* Millimols/m.³ (Rm TP)
0
100
200
300
400
0
20
40
60
80
100
120
140
Time Minutes


CG 22-Cl BREAK TEST
LOG $(\frac{C_o}{C} - 1)$ FOR ACTIVE CHLORINE VS. TIME
CWS N19 TUB Dried
Temperature = 21.5 °C
C_o = 22.3 mgCG/l. or 451 mmolsCl/m.³ (RmTP)
= 24.1 mgCG/l. (STP)
Bed Depth = 5.0 cm.
Flow = 8.82 ml/cm.² x sec. (RmTP)
A
Desorption
$Log_{10}(\frac{C_o}{C} - 1)$ for Cl*
3.0
2.0
1.0
0
-1.0
0
20
40
60
80
100
120
140
Time Minutes



CG 22-Cl
ACCUMULATION OF ACTIVE CHLORINE IN TOP OF CHARCOAL BED

APPENDIX IV

TEMPERATURE MEASUREMENTS FOR PHOSGENE TESTS.

Expt. No.

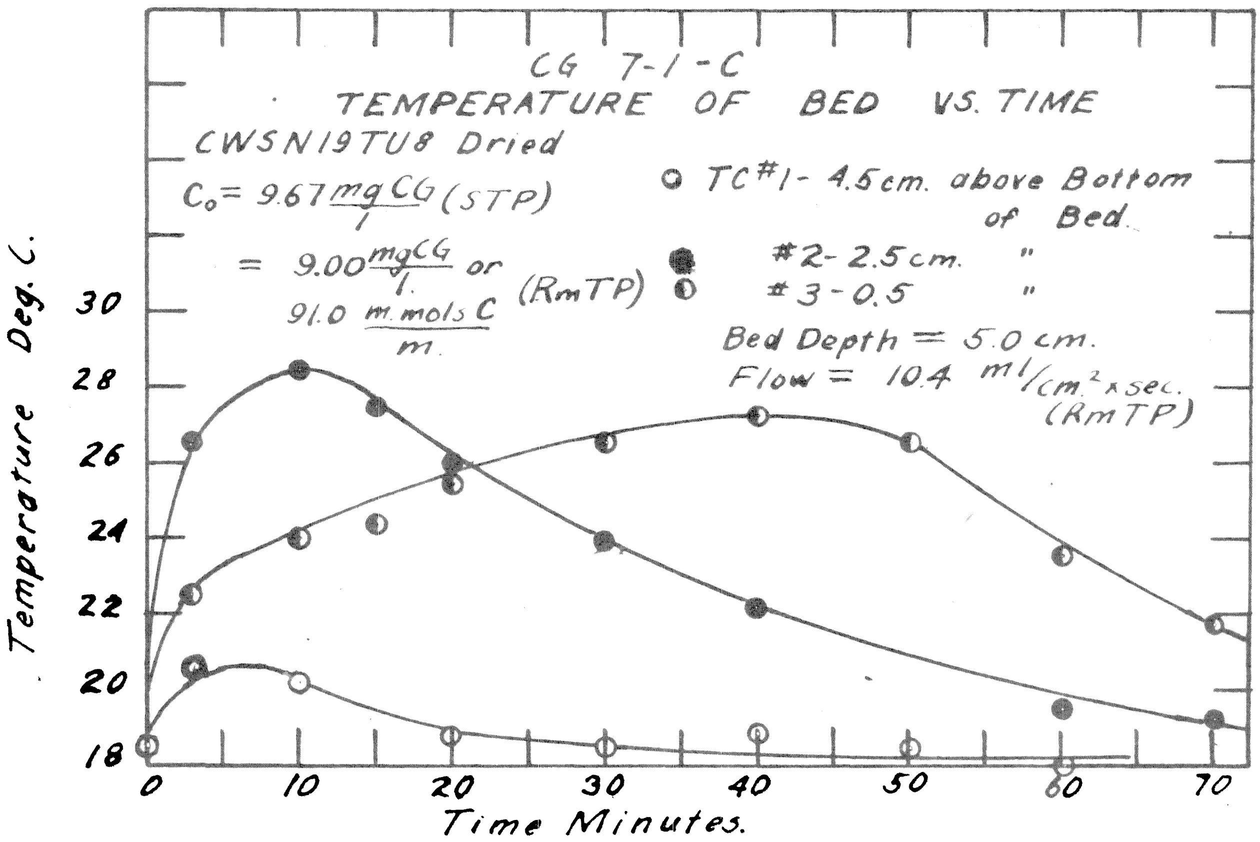
CG7-1, 8-1C

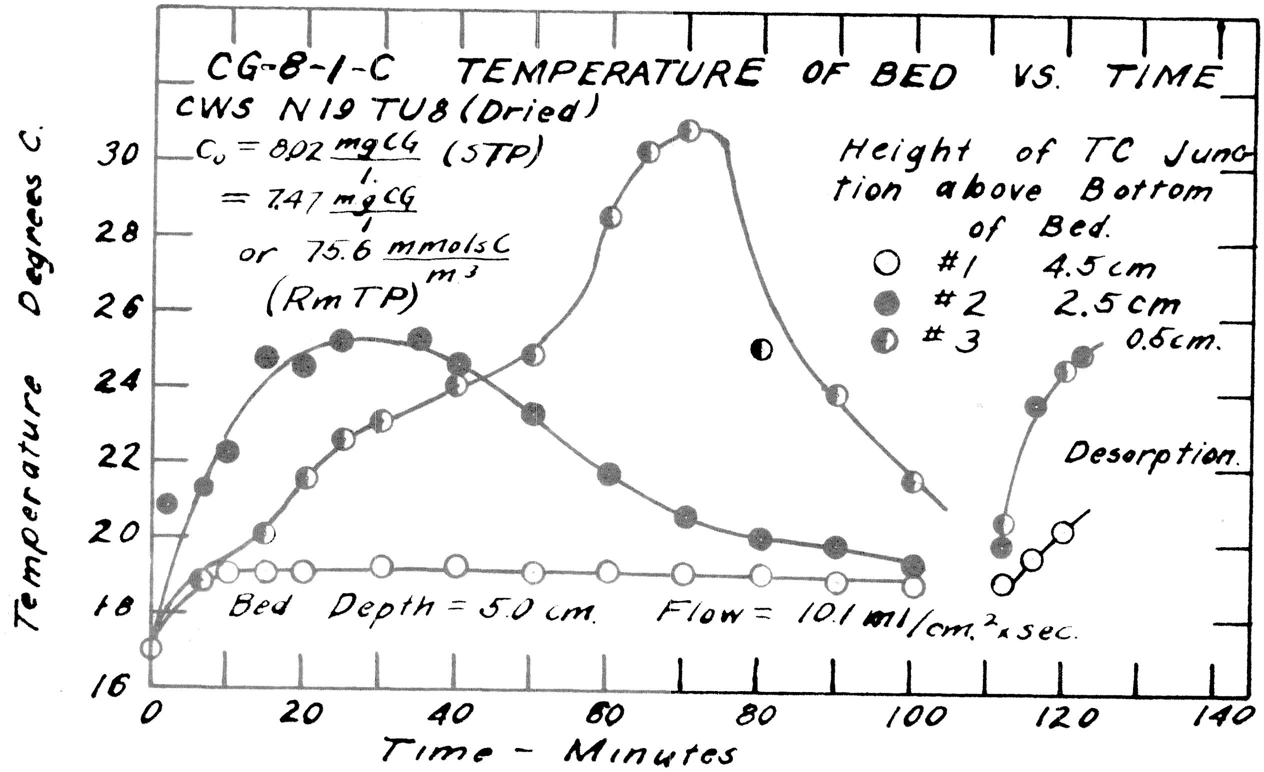
CG9, 10C

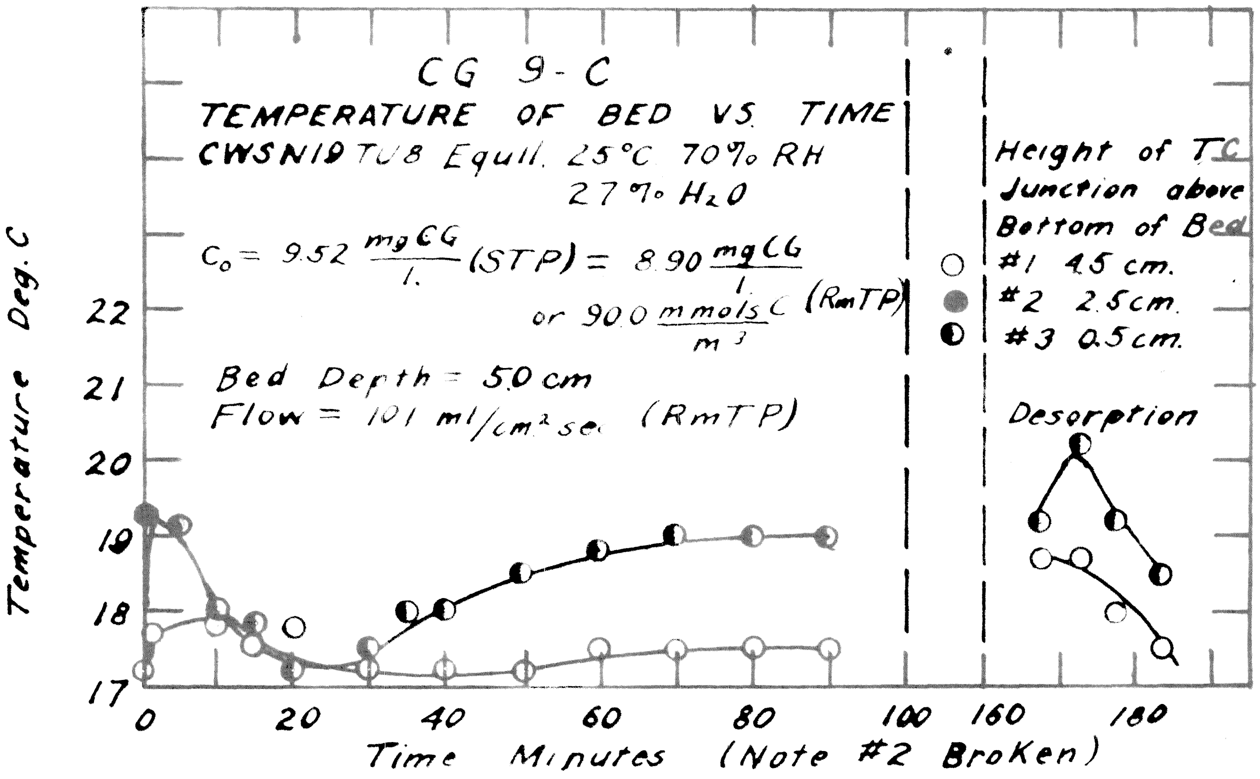
CG11, 12C

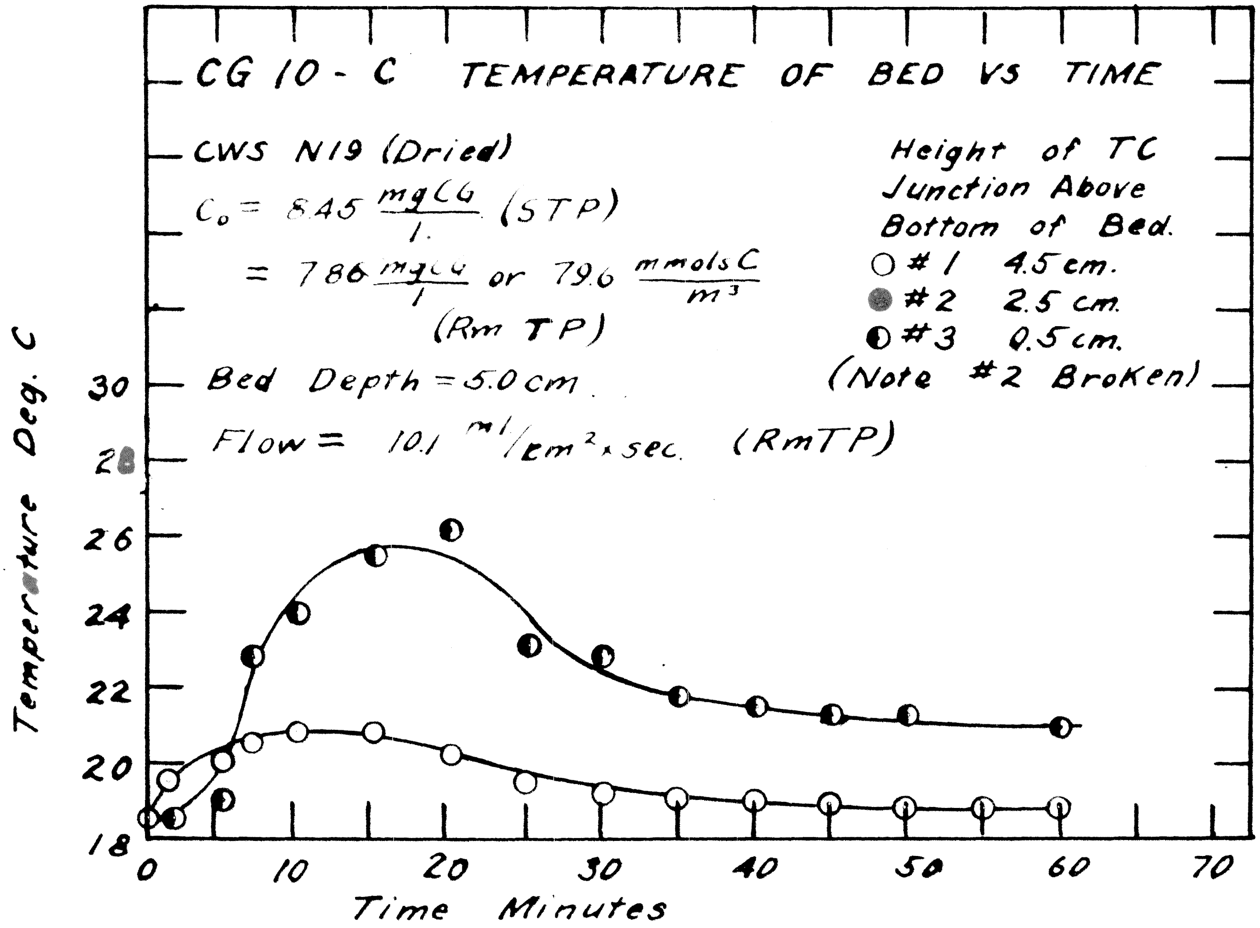
CG15, 16C1

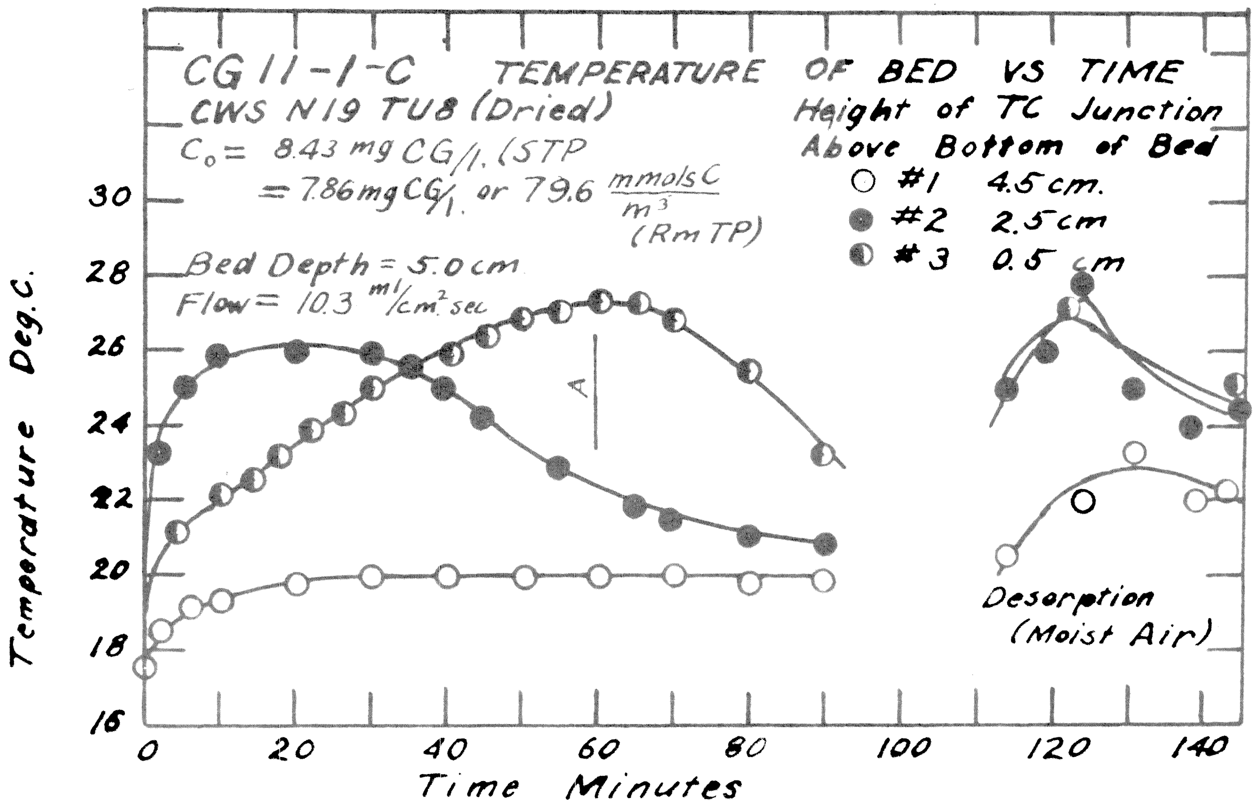
CG17, 18C1

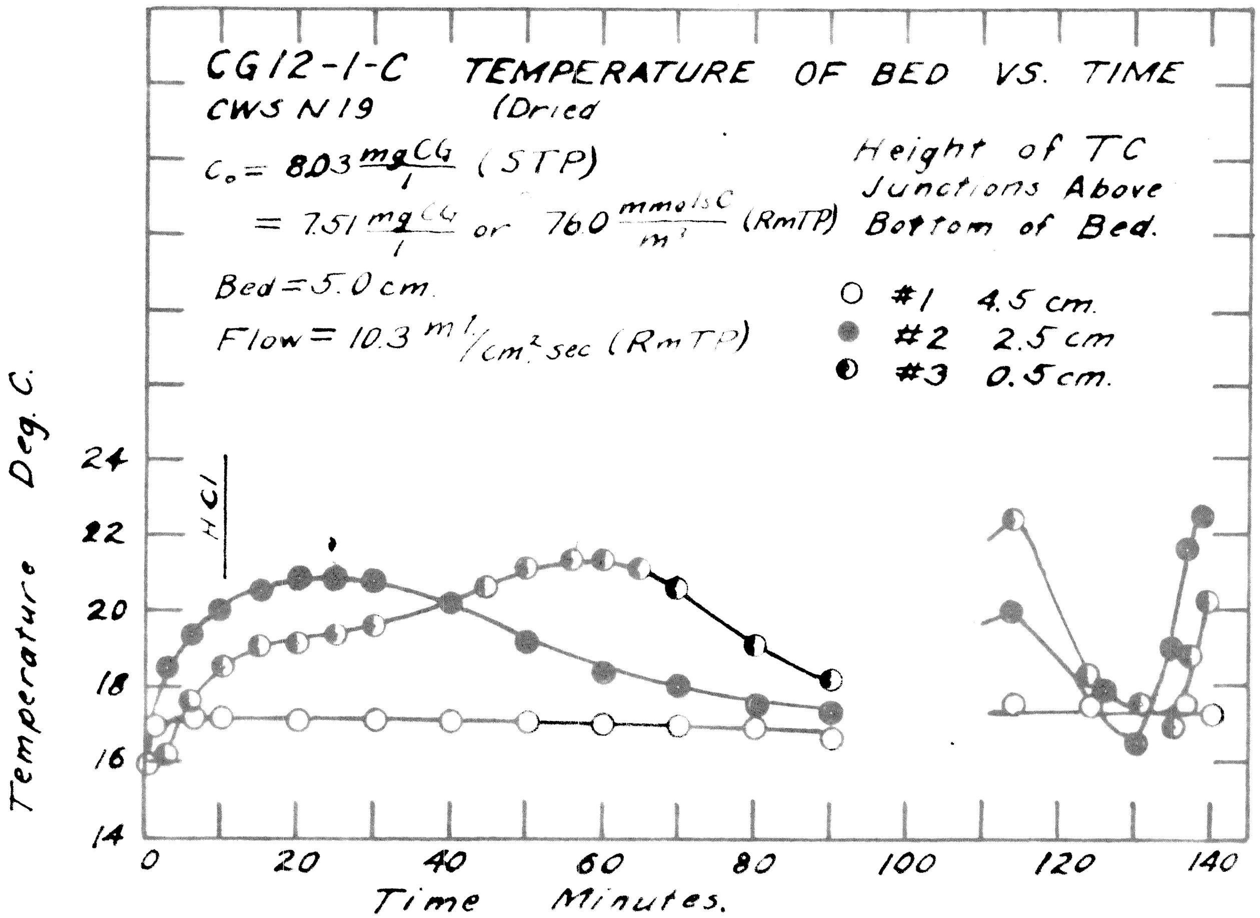

CG 7-1-C
TEMPERATURE OF BED VS. TIME
CWSN19TU8 Dried
C₀ = 9.67 mg CG / l (STP)
= 9.00 mg CG / l or 91.0 m.mols C / m. (RmTP)
○ TC#1 - 4.5 cm. above Bottom of Bed.
● #2 - 2.5 cm. "
◐ #3 - 0.5 "
Bed Depth = 5.0 cm.
Flow = 10.4 ml/cm.² x sec. (RmTP)
Temperature Deg. C.
18
20
22
24
26
28
30
0
10
20
30
40
50
60
70
Time Minutes.

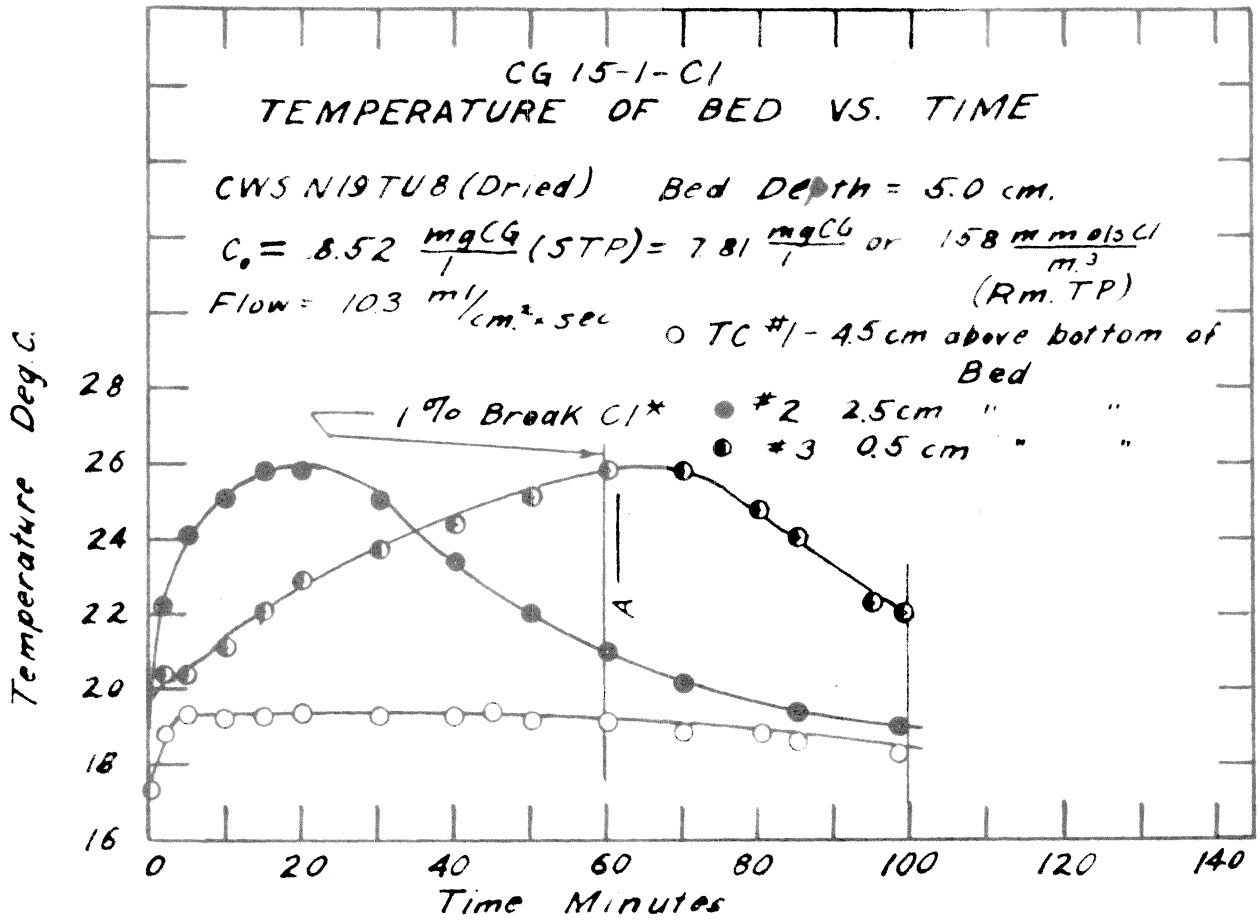

CG-8-1-C TEMPERATURE OF BED VS. TIME
CWS N19 TU8 (Dried)
C₀ = 8.02 mg CG / l. (STP)
= 7.47 mg CG / l
or 75.6 mmols C / m³ (RmTP)
Height of TC Junction above Bottom of Bed.
○ #1 4.5 cm
● #2 2.5 cm
◐ #3 0.5 cm.
Desorption.
Bed Depth = 5.0 cm.
Flow = 10.1 ml/cm.² x sec.
Temperature Degrees C.
16
18
20
22
24
26
28
30
0
20
40
60
80
100
120
140
Time - Minutes


CG 9-C
TEMPERATURE OF BED VS TIME
CWSN19TU8 Equil. 25°C 70% RH
27% H2O
Co = 9.52 mgCG/l. (STP) = 8.90 mgCG/l or 90.0 mmolsC/m³ (RmTP)
Bed Depth = 5.0 cm
Flow = 101 ml/cm² sec (RmTP)
Height of TC Junction above Bottom of Bed
○ #1 4.5 cm.
● #2 2.5 cm.
◐ #3 0.5 cm.
Desorption
Temperature Deg. C
17
18
19
20
21
22
0
20
40
60
80
100
160
180
Time Minutes (Note #2 Broken)

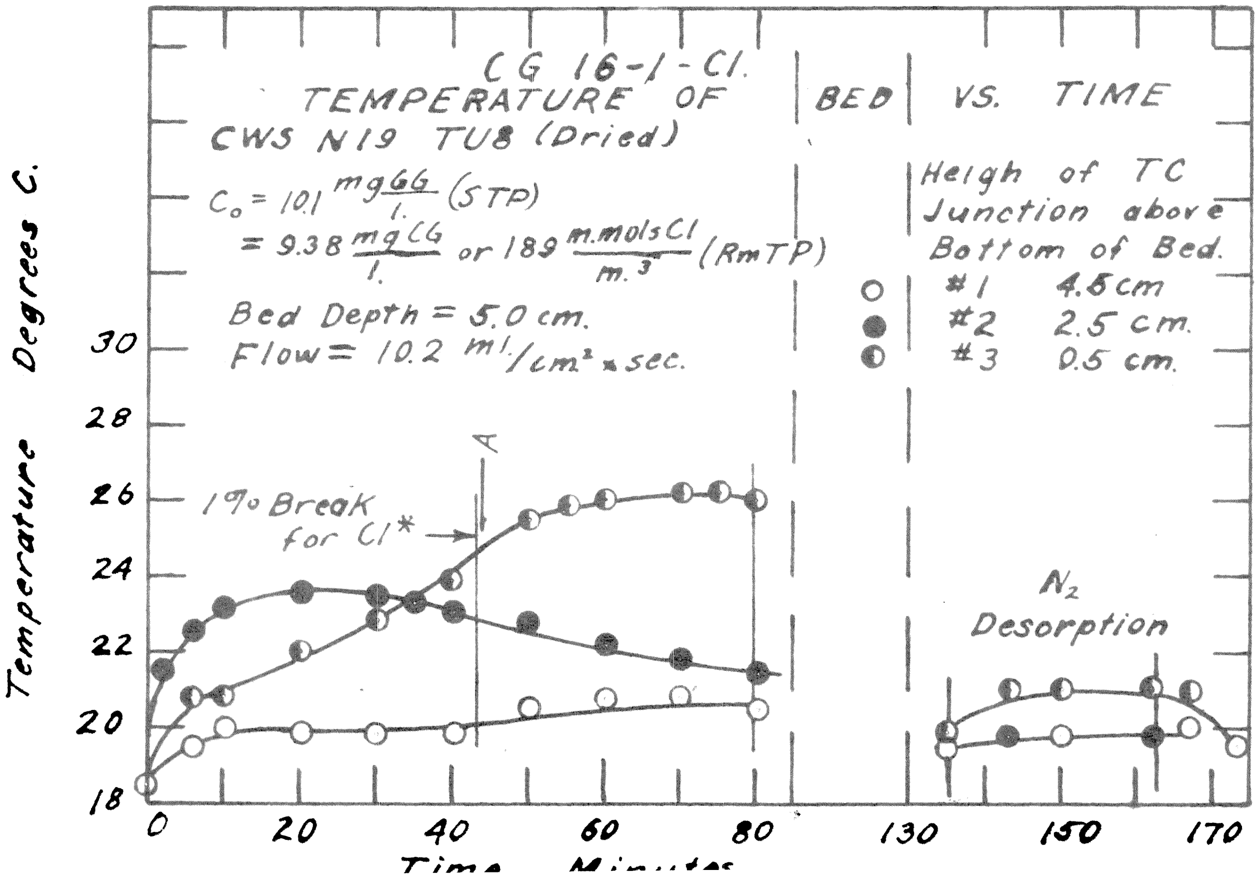

CG 10-C TEMPERATURE OF BED VS TIME
CWS N19 (Dried)
Co = 8.45 mgCG/l. (STP)
= 7.86 mgCG/l or 79.6 mmolsC/m³
(Rm TP)
Bed Depth = 5.0 cm
Flow = 10.1 ml/cm² x sec. (RmTP)
Height of TC Junction Above Bottom of Bed.
○ #1 4.5 cm.
● #2 2.5 cm.
◐ #3 0.5 cm.
(Note #2 Broken)
Temperature Deg. C
18
20
22
24
26
28
30
0
10
20
30
40
50
60
70
Time Minutes


CG 11-1-C TEMPERATURE OF BED VS TIME
CWS N19 TU8 (Dried)
C_o = 8.43 mg CG/l. (STP
= 7.86 mg CG/l. or 79.6 mmols C/m³ (RmTP)
Bed Depth = 5.0 cm
Flow = 10.3 ml/cm² sec
Height of TC Junction Above Bottom of Bed
○ #1 4.5 cm.
● #2 2.5 cm
◐ #3 0.5 cm
A
Desorption (Moist Air)
Temperature Deg. C.
16
18
20
22
24
26
28
30
0
20
40
60
80
100
120
140
Time Minutes

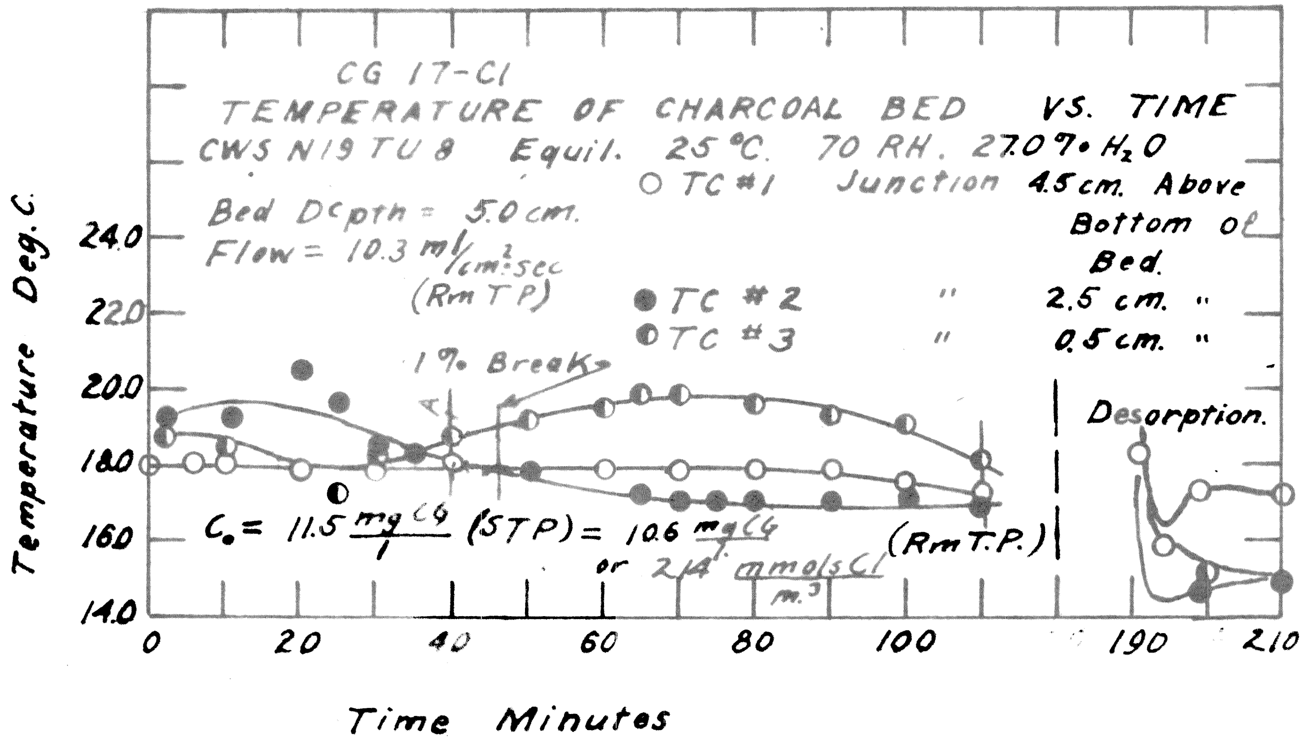

CG 12-1-C TEMPERATURE OF BED VS. TIME
CWS N19 (Dried
C_o = 8.03 mg CG/l (STP)
= 7.51 mg CG/l or 76.0 mmols C/m³ (RmTP)
Bed = 5.0 cm.
Flow = 10.3 ml/cm² sec (RmTP)
Height of TC Junctions Above Bottom of Bed.
○ #1 4.5 cm.
● #2 2.5 cm
◐ #3 0.5 cm.
HCl
Temperature Deg. C.
14
16
18
20
22
24
0
20
40
60
80
100
120
140
Time Minutes.

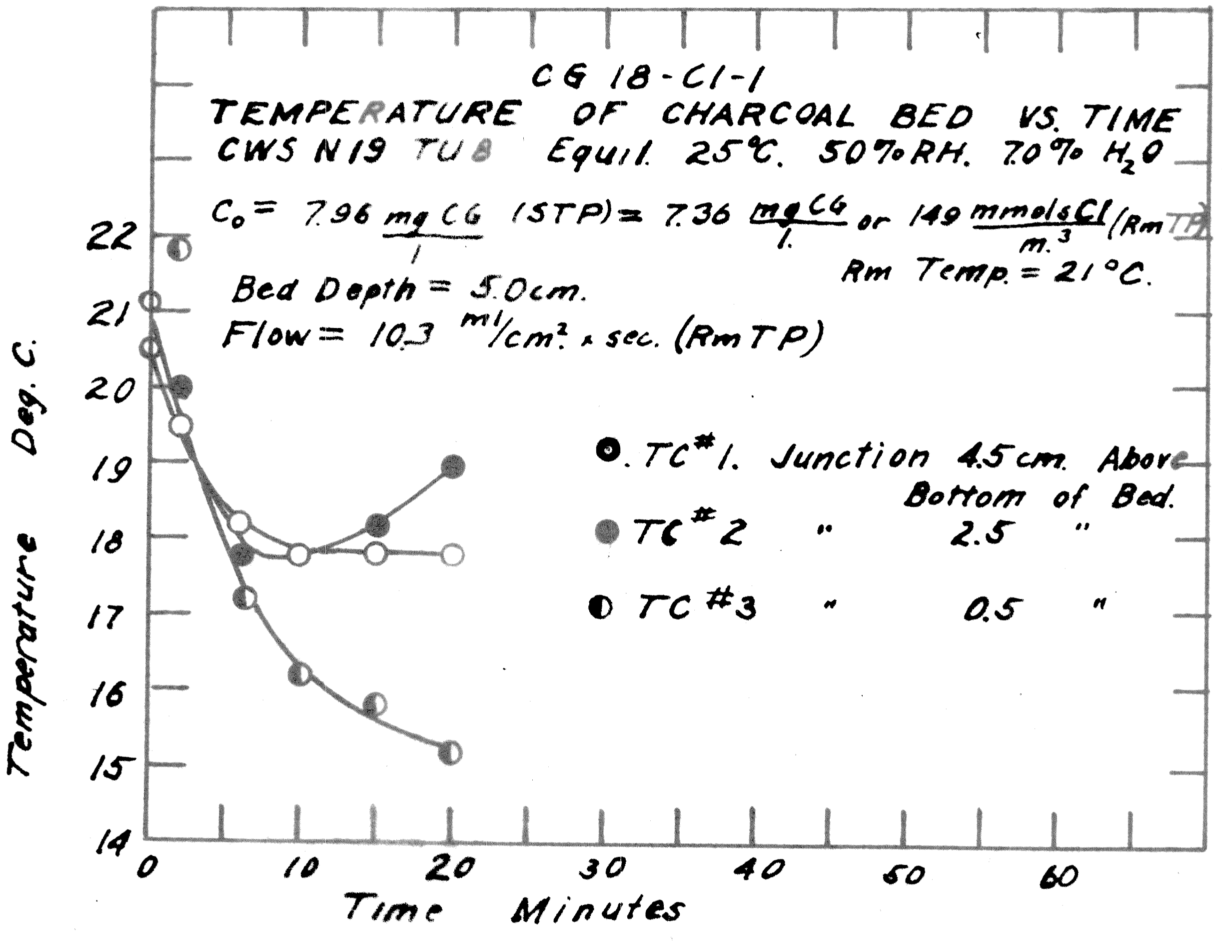


CG 15-1-Cl
TEMPERATURE OF BED VS. TIME
CWS N19TU8 (Dried)
Bed Depth = 5.0 cm.
$C_0 = 8.52 \frac{mg\,CG}{l}$ (STP) $= 7.81 \frac{mg\,CG}{l}$ or $158 \frac{m\,mols\,Cl}{m^3}$ (Rm. TP)
Flow = 10.3 $ml/cm^2 \times sec$
○ TC #1 - 4.5 cm above bottom of Bed
● #2 2.5 cm " "
◐ #3 0.5 cm " "
1% Break Cl*
A
Temperature Deg. C.
16
18
20
22
24
26
28
0
20
40
60
80
100
120
140
Time Minutes



CG 16-1-Cl.
TEMPERATURE OF BED VS. TIME
CWS N19 TU8 (Dried)
$C_0 = 10.1 \frac{mg\,CG}{l.}$ (STP)
$= 9.38 \frac{mg\,CG}{l.}$ or $189 \frac{m.mols\,Cl}{m.^3}$ (RmTP)
Bed Depth = 5.0 cm.
Flow = 10.2 $ml./cm^2 \times sec.$
Heigh of TC Junction above Bottom of Bed.
○ #1 4.5 cm
● #2 2.5 cm.
◐ #3 0.5 cm.
1% Break for Cl*
A
N_2 Desorption
Temperature Degrees C.
18
20
22
24
26
28
30
0
20
40
60
80
130
150
170
Time Minutes


CG 17-C1
TEMPERATURE OF CHARCOAL BED VS. TIME
CWS N19 TU 8 Equil. 25°C. 70 RH. 27.0% H2O
○ TC #1 Junction 4.5 cm. Above Bottom of Bed.
● TC #2 " 2.5 cm. "
◐ TC #3 " 0.5 cm. "
Bed Depth = 5.0 cm.
Flow = 10.3 ml/cm² sec (Rm T P)
1% Break
Desorption.
C0 = 11.5 mg CG/l (STP) = 10.6 mg CG/l (RmT.P.) or 214 mmols Cl/m³
24.0
22.0
20.0
18.0
16.0
14.0
0
20
40
60
80
100
190
210
Temperature Deg. C.
Time Minutes


CG 18-C1-1
TEMPERATURE OF CHARCOAL BED VS. TIME
CWS N19 TU8 Equil. 25°C. 50% RH. 7.0% H2O
C0 = 7.96 mg CG/l (STP) = 7.36 mg CG/l. or 149 mmols Cl/m³ (RmTP)
Rm Temp. = 21°C.
Bed Depth = 5.0cm.
Flow = 10.3 ml/cm² x sec. (RmTP)
○ TC #1. Junction 4.5 cm. Above Bottom of Bed.
● TC #2 " 2.5 "
◐ TC #3 " 0.5 "
22
21
20
19
18
17
16
15
14
0
10
20
30
40
50
60
Temperature Deg. C.
Time Minutes

Propositions

1. The Navy should modify its present high altitude oxygen rebreather to incorporate an automatic nitrogen purging pump and pressure relief assembly in the breathing bag.

2. The kinetics for the elimination of elementary nitrogen in the human body may be defined by the differential equations

$$\frac{dx}{dt} = k_1(a_1p - x)$$

$$\frac{dy}{dt} = k_2(a_2p - y)$$

where

$x + y$ = Amount of nitrogen dissolved in the body fluids and tissues.

t = Time.

p = Partial pressure of nitrogen in inspired air.

Tentative values of the constants may be evaluated from Behnke's[x] experimental work. The solution of these equations, when combined with the proper condition equations, permits the calculation of nitrogen partial pressures in rebreather apparatus under a variety of conditions.

[x] Behnke, U.S. Nav. M. Bull. 35, 219 (1937)

3. A more useful expression for the response of a counting rate-meter than that given by Shiff and Evans[x] is

$$f(t) = K\left(I_R + RC\,\frac{dI_R}{dt}\right)$$

where

$f(t)$ = The counting rate

I_R = The current through the tank curcuit resistor

t = Time

RC = The time constant for the tank circuit

[x] Shiff and Evans, Rev. of Sci, Inst., 7, 456 (1936)

4. The "temperature correction" factors, provided with the Army Air Forces oxygen test kit of the Scholander Type[x], are for sea level pressures only. A simple addition to the correction formula would permit the apparatus to be used at low pressures and would avoid confusion.

[x] NRC Report, CAM #57, P. F. Scholander

5. The analysis of arsine-air mixtures with the "conventional" iodometric methods is unreliable because of the slow absorption of arsine by KI_3 solutions. However the portable apparatus of Tutwiler[x], developed for the rapid determination of H_2S in coal gas can be modified for analyses of mixtures of interest to charcoal tube testing, 5-10 mg/L, to give an accuracy of 1-2%.

[x] Tutwiler, J.A.C.S., <u>23</u>, 173, (1901)

6. For the assumed kinetics equation for charcoal tube testing[x], the equation is proposed

$$\frac{\partial N}{\partial t} = a(c-bN)$$

where

N = The concentration of material on the absorbent
c = The concentration of the toxic gas in the air.
t = Time
a,b Constants

A simple solution of this equation from which the parameters could be easily obtained might prove of value for correlating charaocoal performance.

[x] Thesis

7. The use of an "ideal" closed circuit breathing system for studying cases of radium poisoning would permit the measurement of higher

radon concentrations, the order of 20 times greater, in the expired air.

8. The techniques reported for the measurement of vapor pressure[x] of D_2O have not possessed an accuracy consistent with the purity with which the material may be prepared. If accurate values are needed, further determinations must be made, possibly using a direct measurement rather than a differential tensimeter.

[x] Lewis and McDonald, J.A.C.S., 55, 3057 (1933)
Miles and Menzies, J.A.C.S., 58, 1067 (1936)
Riesenfild and Chang, Z. Phys. Chem. B33 120, (1936)

9. The static method of Iwase and Sano[x] for measuring the equilibria of H_2O and H_2 over a metal-metal oxide system does not eliminate thermal diffusion, contrary to claims.

[x] Iwase and Sano, Sci. Rpts. Tohoku Imp. Univ. 1936 465

10. Teaching assignments for graduate student assistants in the Division of Chemistry should be arranged to give, so far as is possible, each man a year with an organic chemistry course, a year with a physical or analytical chemistry course and a year with at least one recitation group.