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PERSPIRATION POISONING OF PROTECTIVE CLOTHING
MATERIALS - PART I -
EXPERIMENTAL RESULTS AND EVALUATION

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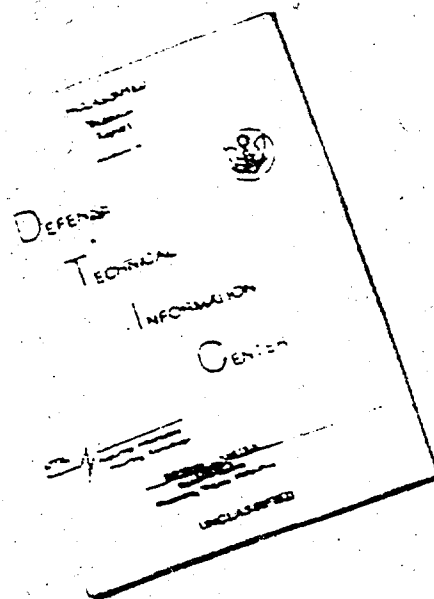
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A protective overgarment material of carbon-impregnated polyurethane foam has been developed by the US Army Natick R&D Command, Natick, Massachusetts. The objectives of the work reported here were to study the dynamics of carbon tetrachloride vapor adsorption, the effect of perspiration poisoning, and methods to alleviate perspiration poisoning for this material.		

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#20 Abstract (continued)

As a reference for further work, a central composite statistical design of experiments was conducted on the carbon-impregnated foam in a vapor test apparatus to study adsorption dynamics. The vapor penetration through the bed was monitored by a gas chromatograph.

The work resulted in the development of a mathematical model for the breakthrough time (the time at which the exiting vapor concentration is 5% of the inlet concentration). This model suggests that the breakthrough time varies directly as the number of carbon impregnated foam layers, or bed depth, and inversely as the gas flow rate and inlet gas concentration.

One of the problems hindering the efficient use of this foam material as a protective overgarment was its poisoning by human sweat during use. The loss of adsorptive capacity of the material was studied by adding sweat and measuring the residual capacity by the amount of carbon tetrachloride adsorbed under equilibrium and dynamic conditions. The organic constituents of sweat were shown to be mainly responsible for the poisoning action. The poisoning effects of individual constituents of sweat were also determined. These indicated that lactic acid was primarily responsible.

The possibility of increasing the capacity of the existing foam material by radiation treatment was studied. The irradiation of the material was performed in a Cobalt-60 source at a dose rate of 0.43 megarads per hour for various lengths of time. The results, however, were inconclusive.

To reduce the deleterious effects of sweat on the adsorptive properties of carbon impregnated foam, the possibility of selective removal of the primary poisoning agent in sweat (lactic acid) was studied. This was accomplished by chemically modifying an undershirt material, through which the sweat must pass before coming in contact with the foam, to give it ion exchange properties. This was achieved by the introduction of amino substituent groups with basic properties onto the cellulosic molecules of the cotton undergarment under such conditions that the fabric structure was retained. The cellulose, thus chemically modified, was in reality an insoluble base which functioned as an anion exchanger to remove lactic acid. The adsorptive capacity and breakthrough time of the carbon impregnated foam material were improved when sweat treatment occurred through a modified undergarment as compared to unmodified undergarment.

The breakthrough characteristics and adsorptive capacity of a number of other protective overgarment materials were evaluated and compared with the polyurethane foam.

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PERSPIRATION POISONING OF PROTECTIVE CLOTHING MATERIALS

PART I

EXPERIMENTAL RESULTS AND EVALUATION

INTRODUCTION

A program to develop clothing materials to protect against chemical agents has been active at the U. S. Army Natick R&D Command for some time, and has resulted in a protective overgarment material which incorporates activated charcoal to adsorb chemical agents. One material, for example, consists of a layer of polyurethane foam bonded to a nylon tricot and impregnated with activated carbon held on the material with a polymer latex binder. The material is found very effective for short periods of time, but due to its thermal insulating properties the adsorptive capacity for toxic gases is reduced because of adsorbent contamination by human perspiration. This problem is referred to as "poisoning".

The objectives of this project were to study the dynamics of carbon tetrachloride adsorption by various clothing materials, the effects of perspiration on the adsorption characteristics, and methods of abatement of perspiration poisoning under conditions which could be correlated with field use. This report is the final report on work carried out at N. C. State University during a two-year project beginning July 1, 1972.

Unsteady adsorption characteristics of a fixed-bed flow-through system are characterized by the variation of the effluent concentration with time (break-through curve). If a mathematical model can be developed describing the dynamic behavior of a given system, the investigator will have a better understanding of the ways in which the physical properties of the adsorption system affect the adsorption process. The accuracy of such models for well-defined systems has been demonstrated by the excellent agreement of experimental and theoretical transmission curves of $C(z,t)/C_0$ versus time obtained by Schneider and Smith^{1,2}.

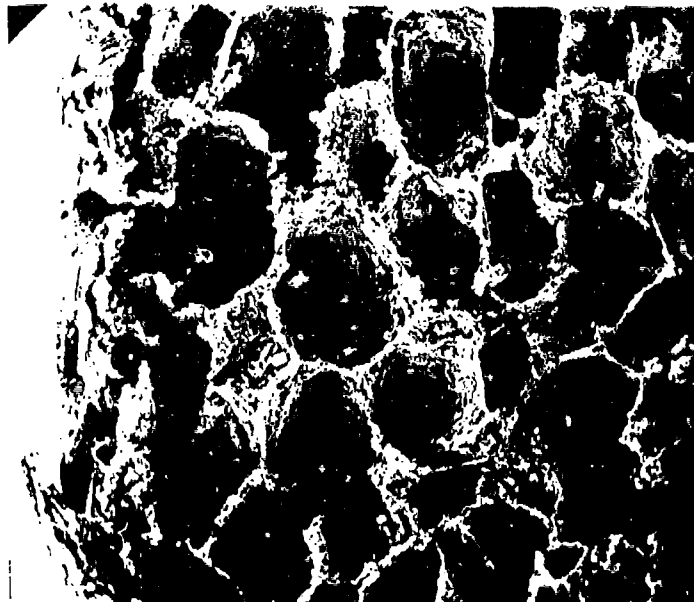
¹Schneider, P. and J. M. Smith. Adsorption rate constants from chromatography. A.I.Ch.E. J., Vol. 14, 762 (1968).

²Schneider, P. and J. M. Smith. Chromatographic study of surface diffusion. A.I.Ch.E. J., Vol. 14, 886 (1968).

The work performed during this study was on a system in which the adsorbent was activated carbon impregnated in foam material with a nylon backing. Inherent uncertainties for this system included the amount of carbon in a foam sample, carbon particle size, non-homogeneity of foam material samples, and the characterization of flow through a foam matrix embedded with activated carbon. Samples of the carbon impregnated foam material were received as bolts of cloth which were found to vary in adsorptive capacity, thickness and porosity. Pictures of this material were examined under a scanning electron microscope. Figure 1a is an edge view and shows that approximately six cells of the polyurethane foam must be traversed to penetrate the foam. It also indicates that the gas passage is very tortuous with many changes in the direction of flow. Figure 1b shows the foam side of the material at a magnification of 100. It reveals the variation in carbon particle distribution throughout the foam. Figure 2a is of the same site as Figure 1b but at a magnification of 1000 while Figure 2b shows the nylon side. Both Figures 2a and 2b show the carbon particles clustered in the foam structure and on the nylon, respectively, and indicate that a wide range of particle sizes is present. These microphotographs indicate the irregularity of the adsorbent beds and the difficulty of using directly the models proposed in much of the literature.

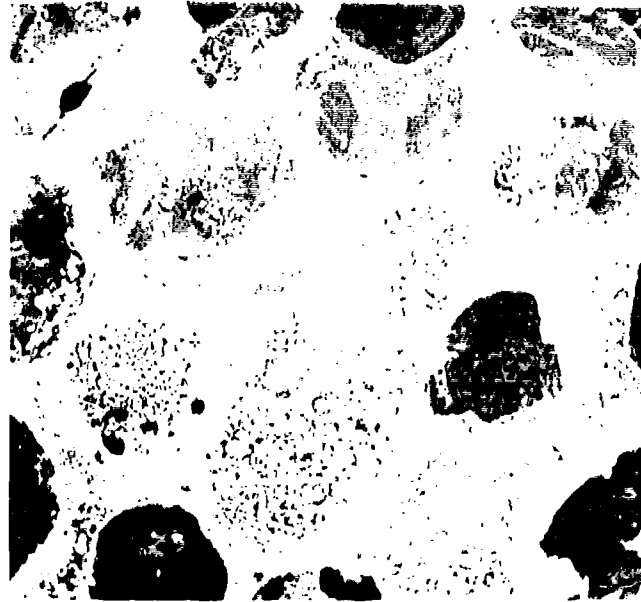
Samples of carbonless foam and of the activated carbon itself were also viewed under the microscope. Pictures resulting from this examination are shown in Figure 3 and Figure 4. Comparison of the micrograph of the carbon with those of the carbon impregnated foam indicate that the particles shown on the foam are most likely carbon particles and not parts of the foam structure or particles of latex.

The initial part of this study was directed towards developing a model for the adsorption of carbon tetrachloride vapor by carbon impregnated foam which would describe the complete breakthrough curve. In addition, the influence of temperature, flow, and concentration were investigated to form a basis for the sweat poisoning studies. Carbon tetrachloride was suggested as an adsorbate by the Natick R&D Command since a correlation exists between carbon tetrachloride and the toxic gases in which the army is interested. The work resulted in the development of a mathematical model based on an overall mass transfer rate coefficient. The model is discussed in detail by



(a)

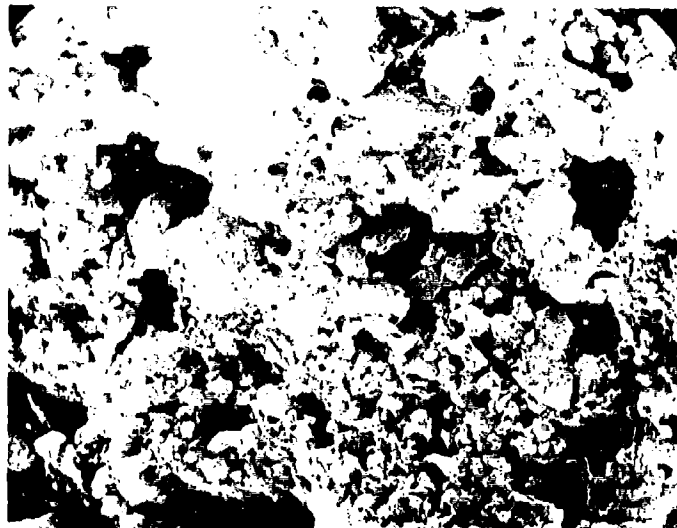
Edge view x 26 - Nylon side at top



(b)

Foam side x 100

Figure 1. Photomicrographs of Carbon Impregnated Foam Material



(a)

Foam side x 1000



(b)

Nylon side x 300

Figure 2. Photomicrographs of Carbon Impregnated Foam Material

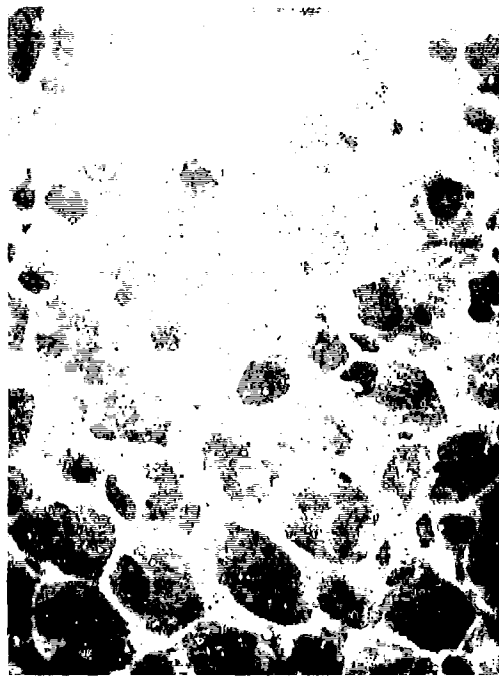


Figure 3. Carbonless Foam x 25

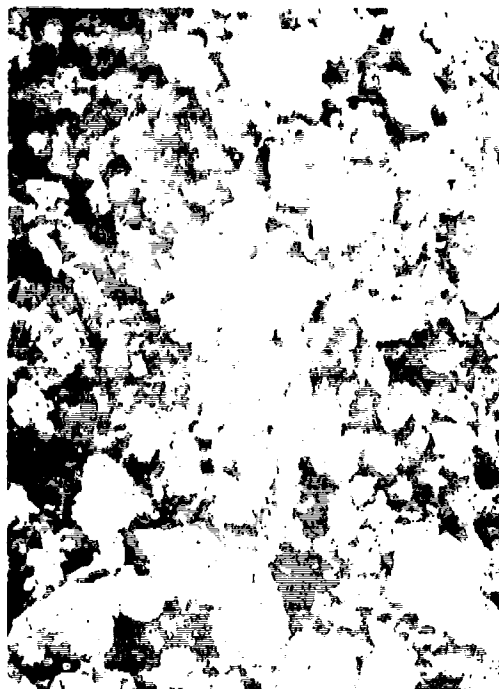


Figure 4. Activated Carbon x 1000

Branscome³. To evaluate the breakthrough time, i.e., the run time at which the exit vapor concentration is 5% of the inlet concentration, from the Branscome model requires considerable numerical computer computation. Accordingly, a simplified model for the breakthrough time was developed as a function of system parameters, and is discussed later in this report.

One of the problems hindering the efficient use of carbon impregnated foam material as a protective overgarment is its "poisoning" by human perspiration. The loss of adsorptive capacity of the material was studied by adding sweat and measuring the residual activity by the amount of carbon tetrachloride adsorbed under equilibrium and dynamic conditions. The poisoning effects of the individual constituents of sweat were also studied to determine the primary poisoning agent in sweat.

To reduce the sweat poisoning of the protective clothing, a study of the selective removal of the primary poisoning agent in sweat was conducted. The possibility of increasing the capacity of the existing foam material by radiation treatment was also studied.

A number of different materials were tested and compared for breakthrough and adsorptive capacity. This work is discussed in the appendix and the materials are listed in Table A-19.

Results of all dynamic adsorptive runs made during this project are given in Tables A-1 through A-18. The tables are arranged in the order shown in Table A-19, and will be referenced in appropriate sections of this report.

³Branscome, M. R. Mathematical model for a complex adsorption bed. M.S. thesis, North Carolina State University, Raleigh, N. C. (1974). See also Part II of this report as follows; Ferrell, J. K., R. W. Rousseau and M. R. Branscome, Perspiration poisoning of protective clothing materials - Part II - Mathematical model for a complex adsorption bed, TR-75-55-CE&MEL, Contract DAAG17-72-G0004, US Army Natick Research and Development Command, Natick, Mass. (1974).

STATEMENT OF THE PROBLEM

The purpose of this investigation was to conduct adsorption rate studies on carbon impregnated foam material developed by the U. S. Army Natick R&D Command for use as a protective overgarment to adsorb toxic gases. The objectives of this program were as follows:

1. A complete analysis of diffusion and flow through carbon impregnated foam material at the breakthrough time, which involves
 - (i) the development of a mathematical model for the complex adsorption bed
 - (ii) investigation of the effects of bed depth, flow rate, inlet concentration, residence time, and temperature on the breakthrough time
 - (iii) experimental verification of the model
2. An investigation of the effects of sweat poisoning of the carbon impregnated foam material. This involves isolating the constituents of sweat which poison the cloth by obtaining
 - (i) equilibrium adsorptive capacity
 - (ii) dynamic adsorptive capacity
3. Control of sweat poisoning. This involves
 - (i) increasing the existing capacity of the carbon impregnated foam material
 - (ii) selective removal of the primary poisoning agent in sweat.

LITERATURE REVIEW

This literature review will deal primarily with adsorption theory. Literature on the effects of sweat poisoning and methods of control will be discussed in the chapters dealing with the subject.

The study of adsorption may be divided into two parts: thermodynamics and kinetics. The former deals with equilibria, and the latter with rate processes. Although many studies have been made on the thermodynamic properties involved in the physical adsorption of gaseous adsorbates by adsorbents⁴, relatively few studies have concentrated on the adsorption kinetics up to the breakthrough time of the transmission or breakthrough curve.

Various Types of Breakthrough Curves

The design of fixed-bed adsorbers involves the prediction of the concentration-time relationship, or breakthrough curve, of the effluent stream. The shape of the breakthrough curve is determined by the

- (a) residence time of the solute in the column
- (b) rate of solute removal
- (c) adsorption equilibrium expressed by an adsorption isotherm

Figure 5 shows the shape of various breakthrough curves⁵.

⁴Brunauer, S. The adsorption of gases and vapors, Vol. I, Physical Adsorption. Princeton University Press, Princeton, N. J. (1945).

⁵Bohart, G. S. and E. Q. Adams. Some aspects of the behavior of charcoal with respect to chlorine. J. of American Chemical Society, 42, 523 (1920).

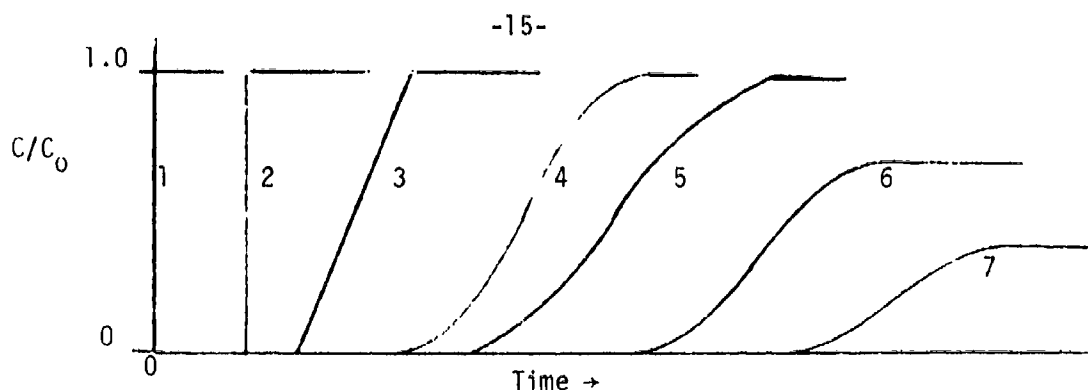


Figure 5. Breakthrough Curves for a Step Change in Inlet Concentration

Curve 1 represents the limit approached by the breakthrough curve for a non-adsorbing material. The gas appears beyond the adsorbent bed in full concentration at time zero.

An ideal adsorbent, infinitely fine-grained and reacting instantaneously with the adsorbate would give a curve of type 2. The length of the lower horizontal portion represents the adsorptive capacity of the adsorbent and the instantaneous breakthrough occurs at some time greater than zero.

An adsorbent in a container with a uniformly varying thickness from one side to the other would give a breakthrough curve of type 3.

The cases just considered have assumed that the adsorption is instantaneous. If this assumption is not made, it becomes necessary to make some assumption for the rate of adsorption. The simplest probable one is that the rate is proportional to the fraction of its adsorptive capacity which the adsorbent still retains and to the concentration of adsorbate in the gas. This amounts to assuming a monolayer adsorption of the adsorbate (which is probably true) and that the adsorbent is perfectly uniform in respect to its rate of adsorbing the adsorbate (which is certainly not exactly so). Other factors which tend to "round off" the curve are, notably, reversibility of the adsorption reaction and nonhomogeneity of composition or packing of the adsorbent. Curve 4 is a symmetrical curve with its point of inflection at 50% breakthrough.

If, however, the rate of adsorption falls off more rapidly than the residual capacity of the adsorbent, as will be the case if the adsorbent consists of two or more constituents of unequal reactivity, an unsymmetrical curve will be obtained. This is illustrated by curve 5.

The adsorbent may act as a catalyst for reaction between the adsorbates. The breakthrough curve will then reach a value lower than 100% when the uptake capacity of the adsorbent has been exhausted; if the rate of catalysis is great enough in proportion to the rate at which adsorbate is being supplied, no adsorbate will be transmitted, however long the experiment be continued. This is illustrated by curves of type 6 and 7.

Effect of Various Factors on the Breakthrough Curve

There are numerous factors which determine the change in concentration of a gas effluent from an adsorbent bed. They are as follows:

1. The nature of the adsorbent

A striking variation in adsorption is exhibited by different adsorbates. The general similarity in form of the breakthrough curves obtained suggests that the process involved is qualitatively the same for all, and the service time of various adsorbents may depend more upon the variations in the proportions of active or relatively inactive constituents in each, than upon the differences between the materials as a whole. There is however, no correspondence between the apparent densities of the adsorbent and the service life obtained.

2. The nature of the adsorbate

The breakthrough curve is affected by the physical and chemical properties of the adsorbate such as density, latent heat, polarity, light adsorption, etc.

3. Temperature

As is generally recognized, the equilibrium and dynamic capacity of adsorbents for adsorbates decreases as the temperature is elevated because ordinary adsorption is reversible.

4. The bed depth

Curves relating the depth of bed versus the breakthrough time (life-thickness curves) have become one of the most common methods of representing the performance of an adsorbent bed. A survey of performance data shows that two types of "life-thickness" curves are encountered. The simplest case is the linear relation such as that shown in curve A of Figure 6. A curvature of the

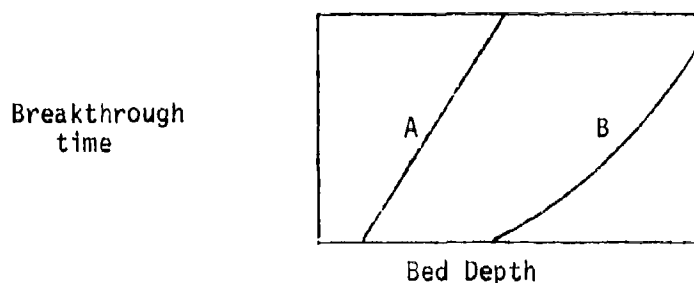


Figure 6. Life-thickness curves for an adsorbent

life-thickness curve as the depth of layer becomes greater (curve B) is a consequence of the peculiar effect of relatively inactive constituents⁶. Whether or not curvature occurs, the life-thickness curves intersect the bed depth axis at a finite value. It follows then, that there exists a critical bed depth, below which the life is zero.

5. Nature of gas flow in the adsorbent bed

The flow of fluids, through beds of granular solids is very complicated^{7,8} for, as is quite obvious, the flow channels are very tortuous

⁶Klotz, I. M. The adsorption wave. Chemical Reviews, Vol. 39, 241 (1946).

⁷Bird, R. B., W. E. Stewart and E. N. Lightfoot. Transport phenomena. John Wiley and Sons, Inc., New York (1960).

⁸Knudsen, J. G. and D. L. Katz. Fluid dynamics and heat transfer. McGraw-Hill Book Co., Inc., New York, N. Y. (1958).

and nonuniform. Flow in porous material is complicated by the fact that the process in very small pores (Knudsen flow) is different from that in larger pores (bulk diffusion). The Knudsen diffusivity is a function of pore size while the bulk value is a function of pressure⁹.

6. Capacity of adsorbent

A clear statement of what is meant by capacity of an adsorbent is not as readily available in a flow type experiment as it is in the static case. In the latter situation, capacity refers to the amount of gas picked up by a unit weight of adsorbent after sufficient time has elapsed for equilibrium to have been attained. The inapplicability of such a definition is particularly evident for a gas where the effluent end of the bed has still not reached a steady state after a considerable length of time.

The primary value of a measure of capacity is in the prediction of the dependence of breaktime on bed depth. Consequently, it is customary to define saturation capacity of a unit gross volume of adsorbent for an adsorbate in terms of the slope of a life-thickness curve. In this manner, two samples which show linear life-thickness curves can be compared reliably in their performance under a set of conditions requiring a slight extrapolation from the measured ones. It is realized, of course, that such a capacity may be far different from the final equilibrium value. Nevertheless, it is more useful than a definition based on a static experiment. At small bed depths, the breaktime will be determined primarily by the critical bed depth of the adsorbent, since the critical bed depth will be a large fraction of the total bed. On the other hand, in deep beds, the critical bed depth becomes less important, and the capacity becomes more important. In large depths capacity is the determining factor.

⁹Robertson, J. L. and J. M. Smith. Flow and diffusion characteristics of alumina catalyst pellets. A.I.Ch.E. J., Vol. 9, No. 3, 342 (1963).

7. Effect of adsorbent particle size

If more than one step contributes to the rate of removal of a gas from the carrier stream, the critical bed depth is a function of two terms (to be discussed later) - one representing that portion of the critical bed due to slowness of diffusion of gas from the carrier stream to the surface of the adsorbent and the other representing the fraction due to processes occurring within the adsorbent. The former is a function of Reynolds number (a function of adsorbent particle size), Schmidt number and the concentration of the adsorbate while the latter is a function of concentration only.

8. Other factors are

- (a) geometrical state of the adsorbent
- (b) relative amount of other gases already present in the adsorbent
- (c) nature of the shape of the isotherm - unfavorable, linear, favorable and irreversible¹⁰.

Mechanism of Adsorption in a Flow System

It is very important to elucidate the mechanism of the adsorption process in a flow system for various gases on different types of adsorbents¹¹. Such an understanding should suggest additional treatments for the improvement of the adsorbent and should also indicate when the natural limit to such improvement has been attained.

The problem of predicting the adsorption wave (i.e., adsorption in a flow system) has not been solved in a completely general form, primarily because of the prodigious mathematical difficulties entailed. Nevertheless, a number of exact solutions exist for several real adsorptive cases. Simplified special cases have been considered and with these results as guides, it has been possible to develop several semi-empirical approaches to the problems of performance and mechanism of adsorption.

¹⁰Weber, T. W. and R. K. Chakravorty. Pore and solid diffusion models for fixed bed adsorbers. A.I.Ch.E. J., Vol. 20, 228 (1974).

¹¹Bischoff, K. B. and D. M. Himmelblau. Survey of mass transfer. Ind. and Eng. Chem., Vol. 56, 12, 61 (1964).

It is generally recognized that the removal of a gas by a porous adsorbent involves one or more of the following steps:

(a) External transfer or film diffusion

This involves transfer of the component from the main body of the gas phase to the external surface of the adsorbent particle.

(b) Internal diffusion or pore diffusion

(i) Diffusion of the molecules of gas into or along the surface of the macropores of the adsorbent particle

(ii) Diffusion within the micropores of the particle

(c) Adsorption - desorption at the surface of the adsorbent

The relative importance of each of these steps may vary widely with the particular conditions under which the removal is taking place. A clear understanding of the fluid flow in porous medium is necessary for detailed work with mathematical modeling of a dynamic adsorption system^{12,13,14,15,16,17}.

The so-called external, or film diffusion, may be modeled by the transfer of an adsorbate molecule through a quiescent layer (the boundary layer) of carrier fluid surrounding a particle of adsorbent¹⁸. This step is strongly influenced by the flow rate of the gas stream, by the diffusion coefficient of the gas and by the particle size of the adsorbent, but is relatively unaffected by temperature.

¹²Collins, H. W. and K. C. Chao. A dynamic model for multicomponent fixed bed adsorption. A.I.Ch.E. Sym. Series, Vol. 69, 134 (1973).

¹³Dean, H. A. and Leon Lapidus. A computational model for predicting and correlating the behavior of fixed bed reactors: (1) Deviation of model for nonreactive systems (2) Extension to chemically reactive systems. A.I.Ch.E. J., Vol. 6, 656 and 663 (1960).

¹⁴Foster, R. N. and J. B. Butt. A computational model for the structure of porous materials employed in catalysis. A.I.Ch.E. J., Vol. 12, 180 (1966).

¹⁵Furusawa, T. and J. M. Smith. Diffusivities from dynamic adsorption data. A.I.Ch.E. J. Vol. 19, 401 (1973).

¹⁶Wakao, N. and J. M. Smith. Diffusion and reaction in porous catalyst. Ind. Eng. Chem. Fundam., Vol. 3, 123 (1964).

¹⁷Wheeler, A. Advances in Catalysis. Volume III. Reinhold Publishing Co., New York, N. Y. (1951).

¹⁸Suzuki, M. and J. M. Smith. Dynamics of diffusion and adsorption in a single catalyst pellet. A.I.Ch.E. J., Vol. 18, 326 (1972).

The importance of the process of flow of adsorbate in pores and on the surface (pore diffusion) is determined by such factors as the particle size and the structural characteristics of the pores. A general survey is presented in the Chemistry and Physics of Interfaces, ACS Symposium Monograph, 1965. Additional references are^{19,20,21,22}. The works of Amundson, Rosen and Smith are classics, modifications and extensions of which comprise much of the modern work.

The process of adsorption - desorption equilibrium is treated by essentially four separate techniques: semi-empirical two-dimensional analogues for equations of state; kinetic models such as Langmuir's²³; potential models such as the Dubinin-Polanyi theory²⁴; and statistical mechanics²⁵. Each of these has an extensive literature in its own right. This process is highly sensitive to temperature.

The combination of the processes detailed above have been summarized

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- ¹⁹Edeskuty, F. J. and N. R. Amundson. Mathematics of adsorption IV. Effect of intraparticle diffusion in agitated static systems. J. Phy. Colloid Chem., 56, 148 (1952).
- ²⁰Edeskuty, F. J. and N. R. Amundson. Effect of intraparticle diffusion. Ind. Eng. Chem., 44, 1698 (1952).
- ²¹Hashimoto, N. and J. M. Smith. Macropore diffusion in molecular sieve pellets by chromatography. Ind. Eng. Chem. Fundam., Vol. 12, 353 (1973).
- ²²Rosen, J. B. General numerical solution for solid diffusion in fixed beds. Ind. Eng. Chem., Vol. 46, 1590 (1954).
- ²³Pierce, C. and R. N. Smith. Heats of adsorption IV. J. Phy. & Colloid Chem., Vol. 54, 795 (1950).
- ²⁴Dubinin, M. M., B. P. Bering and V. V. Serpinsky. Theory of volume filling for vapor adsorption. J. Coll. Inst. Sci, 21, 378 (1966).
- ²⁵Pisamen, L. M. Diffusion in porous media of a random structure. Chem. Eng. Sci., Vol. 24, 1227-1238 (1974).

and compared^{25a,26,27,28,29,30}. In general, non-linear partial differential equations are the result for consideration of combinations of processes (a), (b) and (c). These can be handled by essentially one of the three techniques:

- (a) complete analytical solutions for the adsorbate concentration in the carrier fluid and on the surface of the adsorbent³⁰
- (b) numerical solutions of the coupled differential equation³¹
- (c) conversion by Laplace transform of the differential equations to algebraic relations^{1,3}

Tables of some general mathematical solutions to fairly complete models are given in Part II of this report.

Complete Breakthrough Curve

With the advent of ion exchange columns and the new prominence of gas chromatography and catalysis, a series of papers was published on the dynamics of fluid flow entering and exiting fixed-bed columns.

Klotz⁶ presented an account of the movement of the distribution

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- Amundson, N. R., A note on the mathematics of adsorption in beds. J. Phy. and Colloid Chem., 52, 1153-1157 (1950).
- ²⁶Amundson, N. R. Mathematics of adsorption in beds II. J. Phy. and Colloid Chem., 54, 812-820 (1953).
- ²⁷Amundson, N. R. Mathematics of adsorption in beds III. Radial flow. J. Phy. and Colloid Chem., 54, 821-829 (1953).
- ²⁸Glueckauf, E. Theory of chromatography. Part 9. The theoretical plate concept in column separations. Trans Faraday Soc., 51, 34-44 (1955).
- ²⁹Kyte, W. S. Non-linear adsorption in fixed beds: the Freundlich isotherm. Chem. Eng. Sci., Vol. 28, 1853 (1973).
- ³⁰Masamune, S. and J. M. Smith. Adsorption rate studies - interaction of diffusion and surface processes. A.I.Ch.E. J., Vol. 11, 34 (1965).
- ³¹Garg, D. R. and D. M. Ruthven. The performance of molecular sieve adsorption columns: systems with micropore diffusion control. Chem. Eng. Sci., Vol. 29, 571-581 (1974).
- ¹Schneider, P. and J. M. Smith. Adsorption rate constants from chromatography. A.I.Ch.E. J., Vol. 14, 762 (1968).
- ³Branscome, M. R. Mathematical model for a complex adsorption bed. M.S. thesis, North Carolina State University, Raleigh, N. C. (1974).
- ⁶Klotz, I. M. The adsorption wave. Chemical Reviews, Vol. 39, 241 (1946).

curve during the continuous passage of gas through a bed of adsorbent. Thomas³², in a note on the interpretation of the kinetic behavior in deep bed chromatography for vapor, with a linear adsorption isotherm affected by the finite rate of diffusion in the solid adsorbent or exchanger, showed the relation of exit to inlet concentration to be described by an infinite summation series of Bessel's functions. Rosen³³ solved the general problem of the transient behavior of a linear fixed bed system, where the adsorption rate was determined by the combined effect of liquid film and solid diffusion into spherical particles. Both exact and approximate forms of solution were presented. In a later publication Rosen²² showed that the exit concentration was dependent upon three dimensionless parameters, which were proportional to the surface film resistance, the effective bed length, and the residence time.

Tien and Thodos³⁴ developed mathematical relationships applicable to ion exchange systems exhibiting the nonlinear equilibrium relationship shown by the Freundlich adsorption isotherm. The set of integral-differential equations developed were dependent on parameters involving time, position, and the relative resistances of the liquid and solid phases. These were solved by numerical methods. Useful insight was also obtained from asymptotic solutions by Garg and Ruthven^{35,36}. These gave the limiting

³²Thomas, H. C. Solid diffusion in chromatography. *Journal of Chemical Physics*, Vol. 19, 1213 (1951).

³³Rosen, J. B. Kinetics of a fixed bed system for solid diffusion into spherical particles. *J. Chem. Phys.*, Vol. 20, 387 (1952).

²²Rosen, J. B. General numerical solution for solid diffusion in fixed beds. *Ind. Eng. Chem.*, Vol. 46, 1590 (1954).

³⁴Tien, C. and G. Thodos. Ion exchange kinetics for systems of nonlinear equilibrium relationships. *A.I.Ch.E. J.*, Vol. 5, 373 (1959).

³⁵Garg, D. R. and D. M. Ruthven. Theoretical prediction of breakthrough curves for molecular sieve adsorption columns-I; asymptotic solutions. *Chem. Eng. Sci.*, Vol. 28, 791-798 (1973).

³⁶Garg, D. R. and D. M. Ruthven. Theoretical prediction of breakthrough curves for molecular sieve adsorption columns-II; general isothermal solution for micropore diffusion control. *Chem. Eng. Sci.*, Vol. 28, 799-805 (1973).

forms of the breakthrough curves for sufficiently long columns. Such solutions are relatively easy to obtain, since in the asymptotic limit the boundary conditions imposed by the mass balance assume a simplified form.

Vermeulen and coworkers^{37,38,39,40,41} derived a model for isothermal conditions assuming the adsorption isotherm to be of the Langmuir type. They derived a generalized differential equation which in the integrated form gave the ratio of exit to inlet concentration as a function of four dimensionless parameters concerned with equilibrium, column capacity, solution capacity and throughput (defined as the ratio of the solution to the column capacities). For the specialized case of nearly irreversible adsorption, Vermeulen et al. established a set of correlation curves for the number of transfer units exhibited by the absorbent bed in its gas breakthrough curve as a function of the Peclet number of the fluid flow. Robell and coworkers^{42,43} used these correlation techniques of Vermeulen in breakthrough tests on beds of coconut shell activated carbon having an average particle diameter of 0.038 cm. Comparisons between calculated and experimental data were quite good, despite the fact that Robell's adsorption data did not follow the Langmuir equation.

Underhill^{44,45} studied the adsorption of fission gases of krypton and

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- ³⁷Vermeulen, T. and N. Hiester. Ion exchange chromatography of trace components - a design theory. Ind. Eng. Chem., Vol. 44, 636 (1952).
- ³⁸Vermeulen, T. and N. Hiester. Saturation performance of ion exchange and adsorption columns. Chem. Eng. Prog., Vol. 48, 505 (1952).
- ³⁹Vermeulen, T. Theory for irreversible and constant pattern solid diffusion. Ind. Eng. Chem., Vol. 45, 1664 (1953).
- ⁴⁰Vermeulen, T. Separation by adsorption methods. Adv. Chem. Chem. Engrg., Vol. 2, 147 (1958).
- ⁴¹Vermeulen, T. Advances in chemical engineering. Vol. 2, Academic Press, New York, N. Y. (1958).
- ⁴²Robell, A. J., F. G. Borgardt and E. V. Ballou. Gaseous contaminant removal by adsorption. Chem. Eng. Prog. Sym. Ser., Vol. 62, 76 (1966).
- ⁴³Robell, A. J. and R. P. Merrill. Gaseous contaminant removal by adsorption: II. Adsorption dynamics in fixed beds. Chem. Eng. Prog. Sym. Ser., Vol. 65, No. 96, 100-108 (1969).
- ⁴⁴Underhill, D. W. A mechanistic analysis of fission-gas holdup beds. Nuclear Applications, Vol. 6, 544 (1969).
- ⁴⁵Underhill, D. W. An experimental analysis of fission-gas holdup beds. Nuclear Applications, Vol. 8, 255 (1970).

xenon by a bed of activated carbon granules. The retention time in the bed was long compared to their half lives. For very low gas concentrations, and within the constraints of a linear adsorption isotherm, the general equation derived by Madey and coworkers^{46,47} was found to apply.

Of the many adsorption models presented in the literature, that of Schneider and Smith¹ seems the most useful for this work, and a complete discussion of this model is given in Part II of this report.

Breakthrough Time

In the absence of a satisfactory, simple, mathematical theory of adsorption up to the breakthrough time, investigators have been forced to develop semiempirical methods of treating data. One of the earliest relations describing the process of gaseous adsorbate removal from a flowing air stream by an adsorbent was that of Bohart and Adams⁵.

For the literature review section of this report, symbols are defined in the text. For the remainder of the report symbols are also defined in the list of symbols.

$$t_b = \frac{N_0}{\alpha C_0 V} \left[z - \frac{\alpha V}{N_0 k_1} \ln \left(\frac{C_0}{C_b} \right) - 1 \right] \quad (1)$$

where N_0 was the saturation capacity of the adsorbent in grams of adsorbate per cm^3 of adsorbent, α the porosity, C_0 the inlet vapor concentration in grams per cm^3 of air, V the interstitial velocity of adsorbate

⁴⁶ Madey, R. A physical theory of adsorption of a radioactive gas. Trans. Amer. Nucl. Soc., Vol. 4, 354 (1961).

⁴⁷ Madey, R., R. A. Fiore, E. Pflumm and T. E. Stephenson. Transmission of a pulse of gas through an adsorber bed. Trans. Amer. Nucl. Soc., Vol. 5, 465 (1962).

¹ Schneider, P. and J. M. Smith. Adsorption rate constants from chromatography. AIChE J., Vol. 14, 762 (1968).

⁵ Bohart, G. S. and E. Q. Adams. Some aspects of the behavior of charcoal with respect to chlorine. J. of American Chemical Society, 42, 523 (1920).

flow in cm per unit time, z the bed depth in cm, C_b the first detectable trace concentration of vapor penetrating the adsorbent bed, k_1 a constant, and t_b the elapsed time in the bed for the vapor before C_b penetrated its depth.

A later work, Short and Pierce⁴⁸ suggested that the time to breakthrough could be represented by

$$t_b = \frac{N_o A_f}{C_o Q} \left[z - k_2 \left(\frac{1000Q}{A_b} \right)^n \ln \left(\frac{C_o}{C_b} \right) \right] \quad (2)$$

where A_f was the cross-sectional area of the adsorbent bed in cm^2 , A_b the baffle area (in most adsorbent holder designs $A_f = A_b$), Q the volumetric flow rate in liters per unit time, n and k_2 are constants depending on the adsorbate and adsorbent, respectively. The right side of the expression in brackets was identified as the critical bed depth, λ_c , or that portion of the total bed depth needed under the conditions of the test to reduce the inlet concentration C_o to the exit concentration C_b . The constant k_2 was a function of the granular size of the adsorbent

$$k_2 = d_p n_1 \quad (3)$$

where d_p was the particle or granule diameter in cm and n_1 a constant dependent upon the nature of the gas ranging between 0.68 and 0.83.

A more sophisticated treatment considered the critical bed depth to be made up of two parts

$$\lambda_c = \lambda_t + \lambda_r \quad (4)$$

where λ_t represented that portion of the critical bed depth due to the slowness of diffusion of gas from the air stream to the surface of the adsorbent, whereas λ_r is that portion of λ_c due to processes (e.g., adsorption) occurring within the adsorbent. Since the critical bed depth could be thought of as the distance which the gas might penetrate before

⁴⁸Short, O. A. and F. M. Pierce. MITMR Report Number 114 (1946).

its concentration was reduced to the break value, it seemed reasonable to expect a certain minimum value of λ_c . This limiting value of λ_c for a fixed set of conditions would be λ_t . Any critical bed depth above λ_t must be the contribution of the processes within the granule.

An earlier work of Mecklenburg⁴⁹ was modified by Klotz⁶. He assumed that only a negligible quantity of vapor penetrates the adsorbent bed at the breakthrough time. Using this approach the following could be written:

$$\text{amount of gas supplied} = \text{amount of gas adsorbed} \quad (5)$$

$$C_o Q t_b = N_o A_f z \quad (6)$$

However, since Mecklenburg had plotted t_b versus z and found that when t_b was zero, it resulted in critical bed depth, λ_c , representing that portion of the total adsorbent bed just sufficient to reduce the concentration to an arbitrarily chosen break value of C_b . By introducing the concept of an adsorption-ineffective portion of the bed, the effective portion became $z - \lambda_c$. Thus

$$t_b = \frac{N_o A_f}{C_o Q} (z - \lambda_c) \quad (7)$$

The critical bed depth λ_c could be expressed in terms of the Reynolds Number and Schmidt Number

$$\begin{aligned} \lambda_c &= \lambda_t + \lambda_r \\ &= \frac{2.303}{a} \left(\frac{d_p V_p}{u} \right)^{0.41} \left(\frac{\mu}{\rho D} \right)^{0.67} \ln \left(\frac{C_o}{C_b} \right) + k_v \ln \left(\frac{C_o}{C_b} \right) \end{aligned} \quad (8)$$

The breakthrough analysis up to this point was based upon a mass balance which stated that the quantity of gas sent into the adsorbent bed

⁴⁹Mecklenburg, W. Z. Electrochem, 31, 488 (1925).

⁶Klotz, I. M. The adsorption wave. Chemical Reviews, Vol. 39, 241 (1946).

could be equated with the quantity adsorbed by the bed. The only difference among the equations was the functional dependence ascribed to the critical bed depth. Underlying this mass balance concept were the following assumptions:

(a) That the adsorption wave progressed through a bed of carbon granules as a square wave front, each infinitesimal depth of bed, dz becoming saturated with the gas, under the conditions of relative pressure and temperature prevailing for the test, before the air-gas mixture moved to the next infinitesimal section of bed. As the bed became saturated with adsorbed gas, the section of bed furthest from the incoming gas, which was of a thickness just sufficient to reduce the incoming gas concentration C_0 to the arbitrarily chosen break concentration C_b became the critical bed depth.

(b) That the breakthrough concentration C_b was very small compared to C_0 .

(c) The adsorption was irreversible or its near equivalent in terms of driving force and equilibrium constant.

A new approach to the kinetics of gas adsorption by beds of adsorbent granules was made by Wheeler and Robell⁵⁰. For a bed initially clean (no previous exposure to a vapor adsorbate) the continuity equation of mass balance per unit area is:

$$\text{Weight of vapor flowed into bed} = \text{Weight of vapor adsorbed on bed} + \text{Weight of vapor flowed out of bed} \quad (9)$$

$$MC_0 V \alpha t_b = \rho_B \int_0^z W(z) dz + MV \alpha \int_0^{t_b} C(z, t) dt \quad (10)$$

where M is the molecular weight, ρ_B the bulk density, $W(z)$ the weight of vapor adsorbed per unit weight of adsorbent at point z . The form which the breakthrough equation took for the adsorbent bed was

⁵⁰Wheeler, A. and A. J. Robell. Performance of fixed-bed catalytic reactors with poison in the feed. J. Catalysis, Vol. 13, 299 (1969).

$$t_b = \frac{\rho_B W_e}{M C_o v \alpha} \left[z - \frac{V \alpha}{k_{ads}} \ln \left(K \frac{C_o}{C_b} \right) \right] \quad (11)$$

where K was a dimensionless constant which described the shape of the concentration-time breakthrough curve, and varied from 0.368 to 7.39. W_e was the saturation capacity of the adsorbent bed and k_{ads} the adsorption rate constant.

Wheeler's equation was modified by Jonas and Svirbely⁵¹ for greater applicability

$$t_b = \frac{W_e}{C_o Q} \left[W - \frac{\rho_B Q}{k_{ads}} \ln \left(\frac{C_o}{C_b} \right) \right] \quad (12)$$

where Q is the volumetric flow rate and W the total bed weight. This equation has been experimentally verified and is valid in the range

$$0 \leq \frac{C(Z,t)}{C_o} \leq 0.04.$$

⁵¹ Jonas, L. A. and W. J. Svirbely. The kinetics of adsorption of carbon tetrachloride and chloroform from air mixtures by activated carbon. J. of Catalysis, Vol. 24, 446-459 (1972).

EXPERIMENTAL

To accomplish the objectives of this study, three major pieces of equipment were designed and constructed:

- (a) Dynamic vapor test apparatus
- (b) Equilibrium vapor transport sorption-desorption apparatus
- (c) Sweat applicator

Adsorbent Material

The adsorbent material was developed by the U. S. Army Natick R&D Command for use as a protective overgarment to adsorb chemical agents, especially poisonous gases. It consists of a layer of polyurethane foam bonded to a nylon tricot and impregnated with activated carbon held on the material with a polymer latex binder. A detailed description of the adsorbent material has been given in the introduction. Samples of the carbon impregnated foam material were received as bolts of cloth.

Method of Conditioning the Carbon Impregnated Foam Material

A method of conditioning the samples was derived to improve consistency from sample to sample. The carbon impregnated foam material was cut by a carefully machined device to stamp out circles of cloth 5 1/4 inches in diameter. The circular samples were then soaked in distilled water for twenty-four hours, wrung out between rubber rollers, and allowed to equilibrate in a room maintained at 70°F and 65% relative humidity. Treatment with other solutions (e.g., sweat, lactic acid) was accomplished by following the water conditioning with treatment by the appropriate solution and again allowing the sample to equilibrate at 70°F and 65% relative humidity. Valid comparisons could then be made between different treatments and also among conditioned samples for different run conditions.

The adsorption bed was composed of either single or multiple layers of the carbon impregnated foam material. For this study, beds of one, two, and three layers were considered. In this manner the effects of different bed depths could be studied.

Measurement of Void Fraction

The cloth porosity, $\alpha = (1 - v_s/v)$, was determined for various bolts of carbon impregnated foam material. Material thickness was measured by placing a sample between two pieces of flat aluminum sheets and measuring the thickness of the sandwiched material with a micrometer gauge, accurate to 0.001 inch. Compression of the sample by the aluminum material and gauge was slight. The sample weight, W_f , and area, A , were determined and the sample was submerged in water with an attached dead weight of mass 5.00 g and volume 5.00 cm^3 . After air had been expelled from the sample the combined weight of the submerged sample and dead weight was determined with a McPherson balance. The porosity was then determined from the bouyant force, W_b , by the following equations:

$$W_b = (W_f + 5.00 \text{ g}) - \rho_{\text{H}_2\text{O}} (v_s + 5.00 \text{ cm}^3)$$

$$v_s = 5.00 \text{ cm}^3 + (W_b - W_f - 5.00 \text{ g})/\rho_{\text{H}_2\text{O}} \quad (13)$$

$$\alpha = 1 - v_s/v$$

Table 1. Physical Properties of the Adsorbent Material

Cloth Type	Cloth Thickness cm	Porosity α
Bolt 2	0.172	0.846
Bolt 3	0.183	0.813
Bolt 4	0.174	0.860
Pluton B-1	0.062	0.440
British Cloth A46C54	0.060	0.865
British Cloth P99	0.066	0.880

Dynamic Vapor Test Apparatus

A schematic of the apparatus for the study of the dynamics of carbon tetrachloride vapor adsorption by carbon impregnated foam material is shown in Figure 7 with a list of components in Table 2. The apparatus was designed to cover a range of vapor flow rates and carbon tetrachloride concentrations (Table 3). The apparatus was sufficiently flexible, however, that operation substantially outside these ranges are possible if necessary by minor modifications. In Table 3, concentrations and flow rates are shown

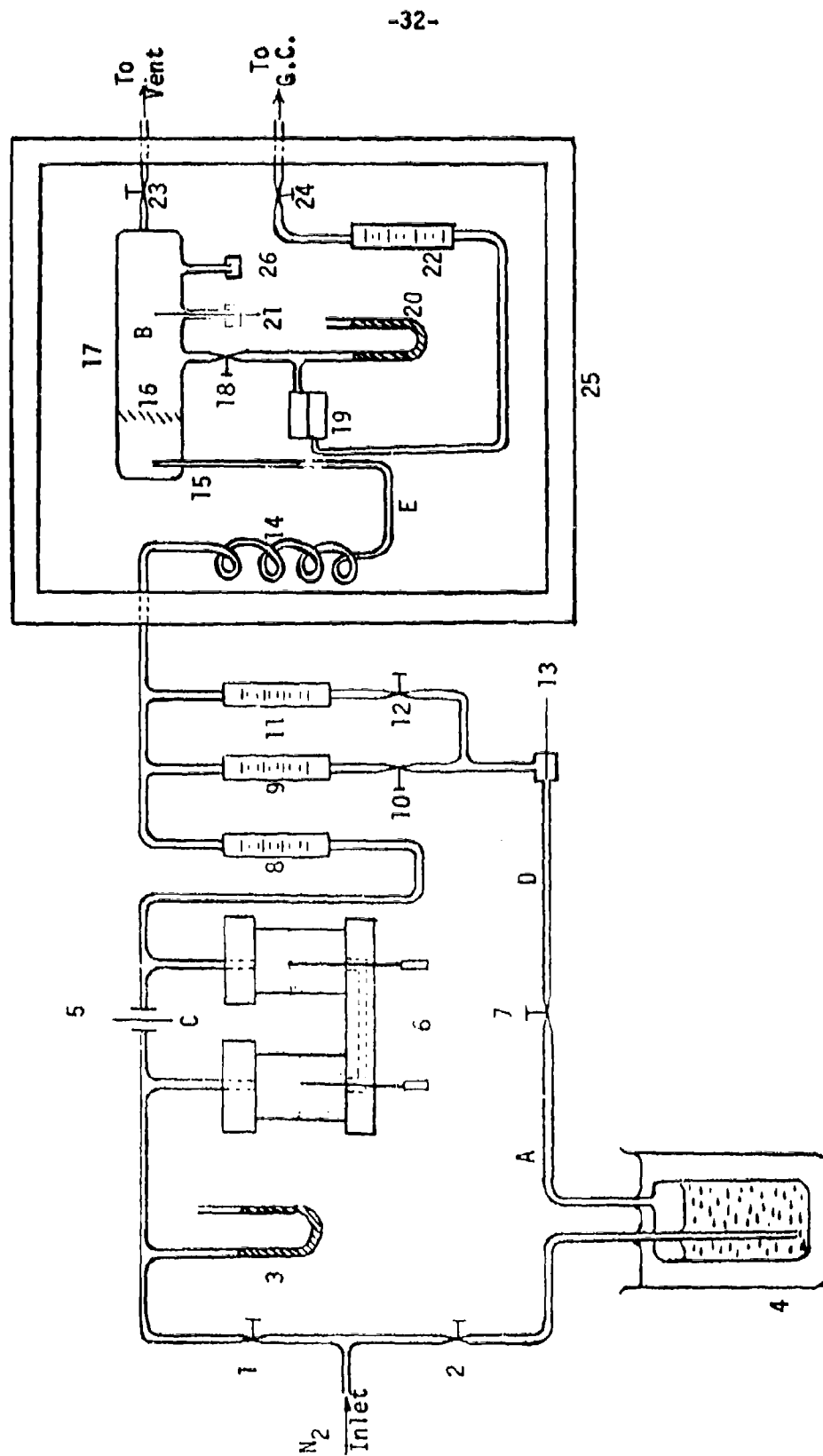


Figure 7. Schematic of vapor test apparatus

Table 2. Components as indicated in figure 7.

1. Control Valve size $C_v = 0.038$
2. Control Valve size $C_v = 0.00145$
3. U-tube Manometer
4. Carbon Tetrachloride Bubbler Chilled at 0°C
5. Orifice Meter
6. Hook-Gauge Manometer
7. Control Valve size $C_v = 0.15$
8. Rotameter
9. Rotameter
10. On-off Valve
11. Rotameter
12. On-off Valve
13. Thermocouple
14. Temperature Equilibrating Coil
15. Tangential Entry of gas into Manifold to Facilitate Mixing
16. Wire Mesh Obstruction to Improve Mixing
17. Stainless Steel Manifold
18. On-off Valve
19. Sample Holder
20. U-tube Manometer
21. Thermocouple
22. Rotameter
23. Control Valve size $C_v = 0.15$
24. Control Valve size $C_v = 0.15$
25. Plexiglass Compartment

A&B Conc. of CCl_4

C,D&E Flow rates

Table 3. Design Concentrations and Flow Rates

Concentration Mg CCl ₄ /liter		Flow Rate Liter/min		
A	B	C	D	E
283.6	1.0	9.965	0.035	10.0
283.6	2.0	9.93	0.07	10.0
283.6	5.0	9.825	0.175	10.0
283.6	7.0	9.755	0.245	10.0
283.6	10.0	9.65	0.35	10.0

at points identified on Figure 7. The apparatus has six functional features:

- (a) vapor generating device (4)
- (b) vapor mixing system (15, 16)
- (c) temperature equilibrating coil (14)
- (d) constant temperature box (25)
- (e) vapor adsorption chamber (19)
- (f) detection of penetrating adsorbate concentration
by gas chromatograph

This apparatus consisted of a flow system of 1/4 inch stainless steel tubing with an adsorption chamber encased in a plexiglass box for constant temperature control. A pure nitrogen stream from the nitrogen supply cylinder was split at the inlet and sent through lines (1) and (2). Nitrogen in line (2) flowed through carbon tetrachloride bubbler (4) immersed in an ice-bath to saturate the nitrogen stream with carbon tetrachloride vapor at 0°C. The pure nitrogen stream in line (1) flowed through an orifice (5) which had a Hook-Gauge manometer (6) in parallel and a rotameter in series. This pure nitrogen stream was mixed with the nitrogen-carbon tetrachloride mixture for dilution to the desired concentration. The pure nitrogen in line (1) was set roughly by the rotameter (8) and then adjusted by measuring the pressure drop across the orifice to one ten-thousandth of an inch of water with the Hook-Gauge manometer.

The diluted nitrogen-carbon tetrachloride mixture was sent into the constant temperature box (25) through a temperature equilibrating coil (14) and into a manifold (17). A vapor stream was drawn from the manifold at (18) and sent through the sample holder (19) at a flow rate set by rotameter (22). This sample holder consisted of two cups between which the foam material was sandwiched, tightened with a clamp, and sealed with wax. The top cup contained a perforated metal sheet to assure uniform gas flow through the sample. The vapor stream leaving the sample holder was sent through a gas collection coil on the chromatograph and the remainder of the vapor mixture entering the manifold was vented through an exhaust hood (23).

Analysis of the carbon tetrachloride concentration in the stream exiting the sample cup was made by a Perkin-Elmer gas chromatograph using a column of

silicone oil D.C. #200 (Perkin-Elmer Column C) with a thermal conductivity cell. The exit vapor flowed continuously through a 1 cm^3 sample loop, except when the sample was injected into the chromatograph. At each injection the vapor stream was diverted to a vent and the flow through the sample was readjusted due to the pressure change. The sample injection time was small enough that the gas concentration was essentially constant during this period. The required time for analysis in the chromatograph (resolution time) limited the injection frequency to one every three minutes. The apparatus was arranged and operated such that the transportation delay between the bed and the sample injection site and between the sample injection site and detector were minimized in order to reduce the disparity in moments of the bed from that of the observed moments.

A Moseley strip chart recorder monitored the chromatograph output. Reference peaks for the inlet concentration were obtained at the beginning and end of each adsorption run by taking a sample stream from the manifold at (26) and sending it through the chromatograph. From the recorded output (chromatographic curve), transmission or breakthrough curves of $C(z,t)/C_0$ versus time were generated.

Sample Holder

Photographs of the sample holder furnished by the Natick R&D Command are shown in Figure 8. While the inside diameter of the sample holder is 4 inches, the rounded edges at the flange which clamps the sample causes a large uncertainty in the flow area through the sample. For this holder the exposed sample area was estimated to be approximately 100 cm^2 .

To eliminate this uncertainty, and also to decrease the possibility of radial diffusion of vapor into the clamped area of the sample, a new sample holder was designed. Photographs of the new holder are shown in Figure 9. The inside diameter of the sample holder was kept at 4 inches, giving a well defined flow area of 81.1 cm^2 . The new sample holder has the following features:

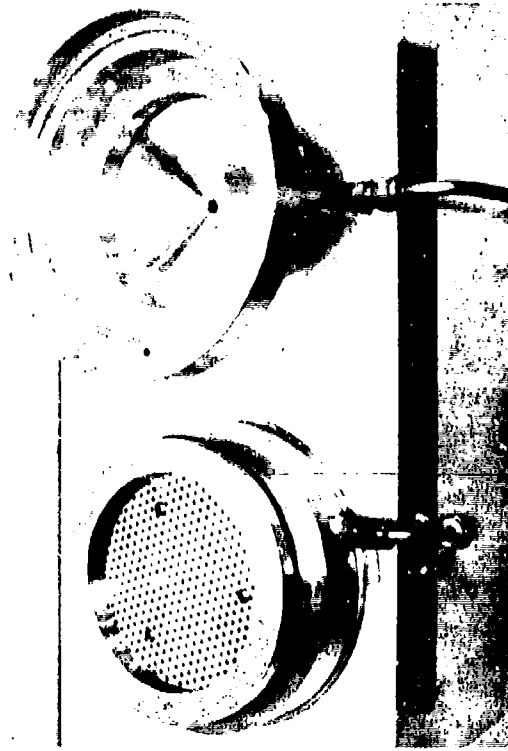


Figure 9. New Sample Holder



Figure 8. Old Sample Holder

- (a) Exact positioning of the top and bottom cups to greatly increase resistance to flow under the lips
- (b) Tangential entry of vapor for more uniform flow through the distributor
- (c) Conical geometry of the bottom cup to remove regions of dead space
- (d) Holder positioning pin for better consistency of fitting
- (e) Accurately defined flow area
- (f) O-Ring seal for preventing leaks
- (g) O-Clamp and wax sealing system

Figure 10 shows the difference in breakthrough curves for the new and old sample holder. The run conditions are $C_0 = 7.76 \text{ mg/l}$, $Q = 1.0 \text{ l/min}$ and $T = 32.5^\circ\text{C}$. It was observed that the total amount adsorbed in the new holder is less than that in the old one, primarily because of the reduced flow area in the new holder. A comparison of the runs made in the two sample holders is given in Table A-12.

Consistency and Reproducibility of the Vapor Test Apparatus

It is believed that some of the scatter observed in the data in experiments on various samples of foam material are due to the following uncertainties in the properties of the material:

- (a) amount of carbon in a sample
- (b) carbon particle size and distribution
- (c) nonuniform nature of flow through a foam matrix.

A series of runs was made on two layers of foam material to test experimental reproducibility of the two-layer samples. The samples were regenerated in the sample holder and the adsorption runs repeated. Regeneration was achieved by placing the sample holder with the samples still in place in an oven at 50°C and blowing air at 50°C through it for thirty minutes. The flow rate of air was approximately 1 CFM. This method was successful in regenerating the cloth without apparent damage. It was observed that the adsorptive capacity of the samples decreased somewhat between the first and successive runs. This is believed due to the presence of some active sites where the adsorption is irreversible. The remaining sites can be regenerated giving rise

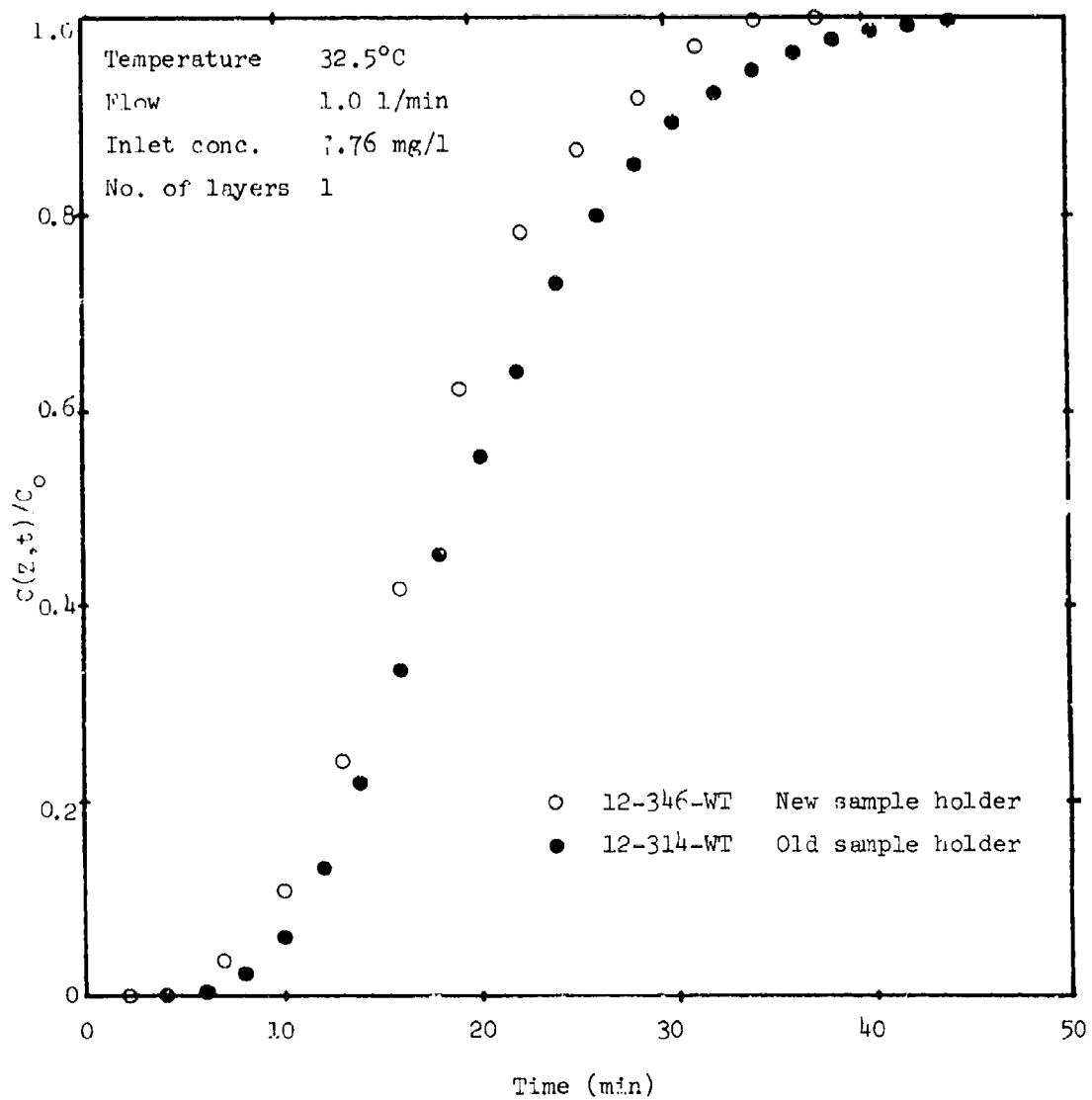


Figure 10. Breakthrough comparison between new and old sample holders

to identical transmission curves for runs two through three. Figures 11 and 12 illustrate the excellent reproducibility of the data from these runs and indicate the consistency of the apparatus and experimental procedure. Consistency of the apparatus refers to the ability of various experimental components (rotameters, manometers, thermocouples, etc.) to give the same output for identical conditions.

Equilibrium Vapor Transport Sorption-Desorption Apparatus

Quartz helical springs supplied by Worden Quartz Products, Inc., Houston, Texas, were used to measure the weight gain or loss in equilibrium adsorption experiments. The springs had a maximum extension of 150 millimeters for a load of 3.0 grams. The springs were calibrated by measuring the extension as a function of known load between 0.0026 grams and 1.5000 grams in a jacketed vessel at 31°C. A linear relationship between the spring extension and the load was found, with sensitivities of 49.7401 and 51.1761 millimeters per gram, for the two springs.

The extension of the quartz spring during the transient period of the sorption and desorption runs was monitored using a cathetometer having a range of 100 centimeters. The precision of the relative weight measurement, determined by the cathetometer was $\pm 200 \mu$ grams.

The vapor sorption-desorption experiments were conducted in two similar chambers connected to the same manifold, of which one is shown schematically in Figure 13. Both chambers were serviced by a high vacuum line equipped with a Cenco high vacuum mechanical pump and a liquid nitrogen cold trap to obtain pressures as low as 10^{-6} mmHg. Each system consisted of a thermostatted chamber in which the sorption experiment was conducted, a vapor supply source, a mercury manometer and a 10 liter vapor reservoir. Dissolved gases were removed from the liquid used in the vapor sorption studies by repeated freeze-thaw cycles under high vacuum.

After suspending the sample from the quartz pan held by a quartz spring, the entire system, vacuum manifold and spring case, was degassed for approximately 17 hours in a dynamic vacuum of about 10^{-6} mmHg. The spring case stopcock was then closed and carbon tetrachloride vapor was bled into the remainder of the system to provide the desired relative saturation for the total system when the stopcock was reopened. The stopcock was opened quickly

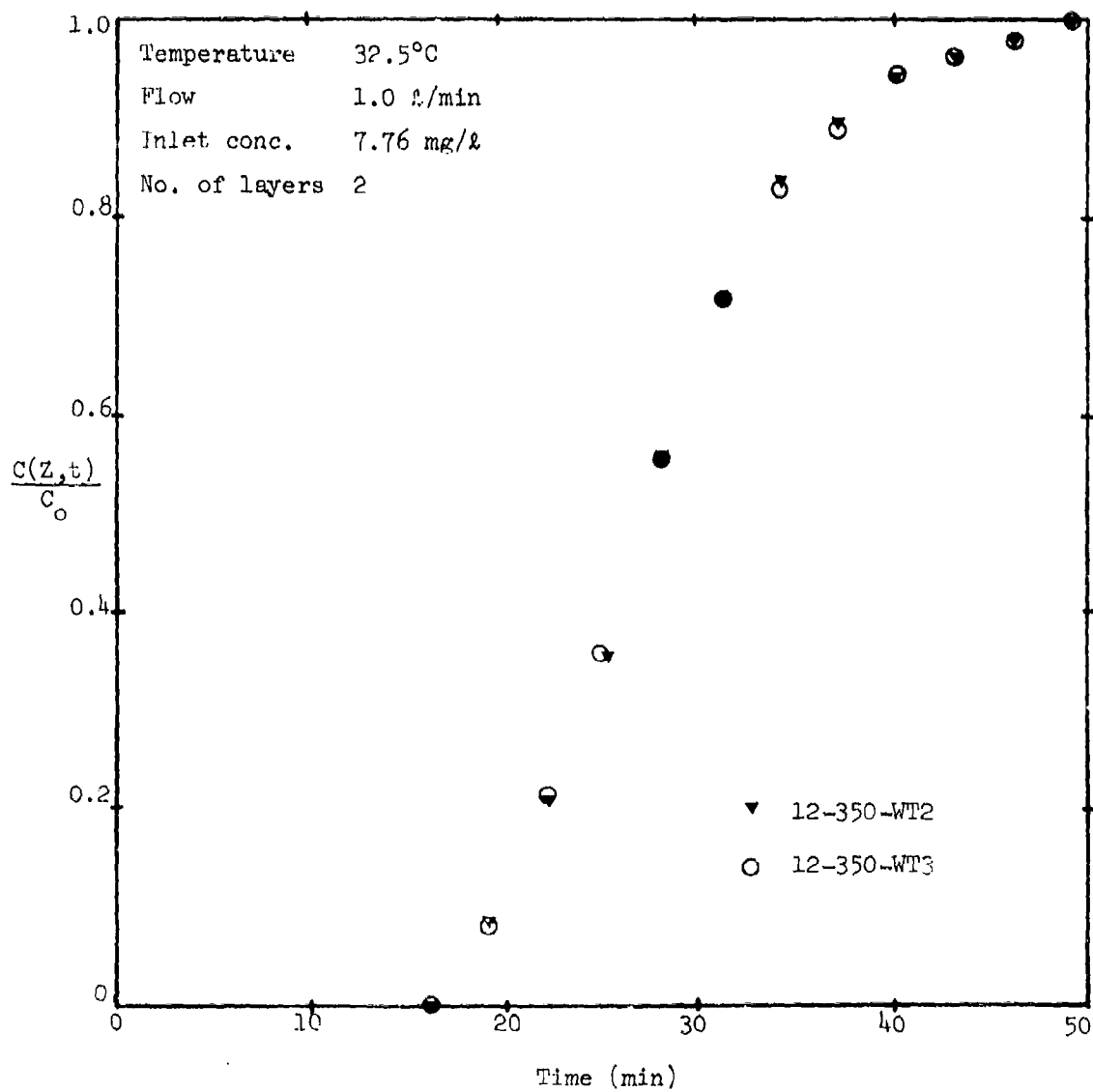


Figure 11. Reproducibility runs

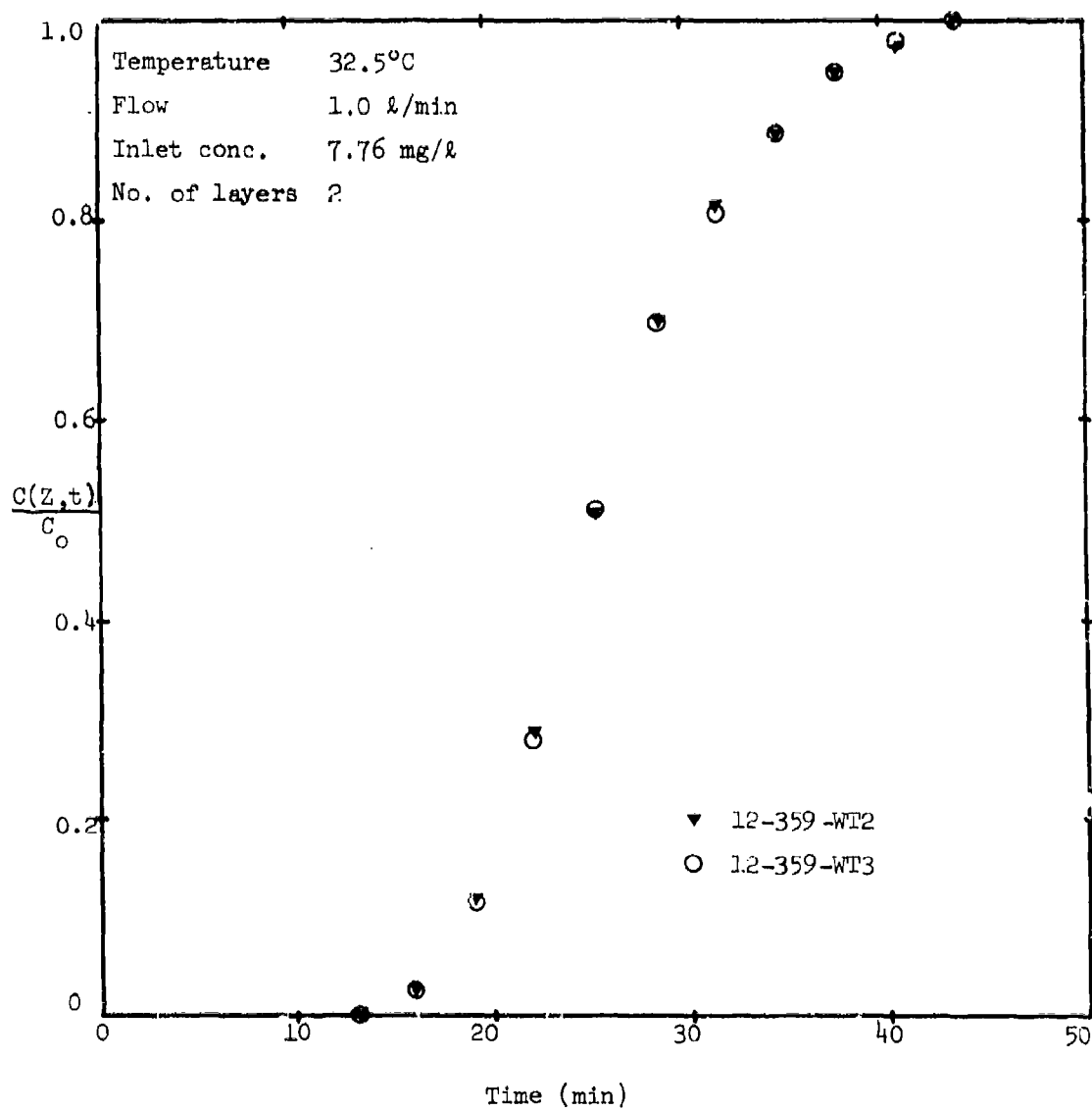


Figure 12. Reproducibility runs

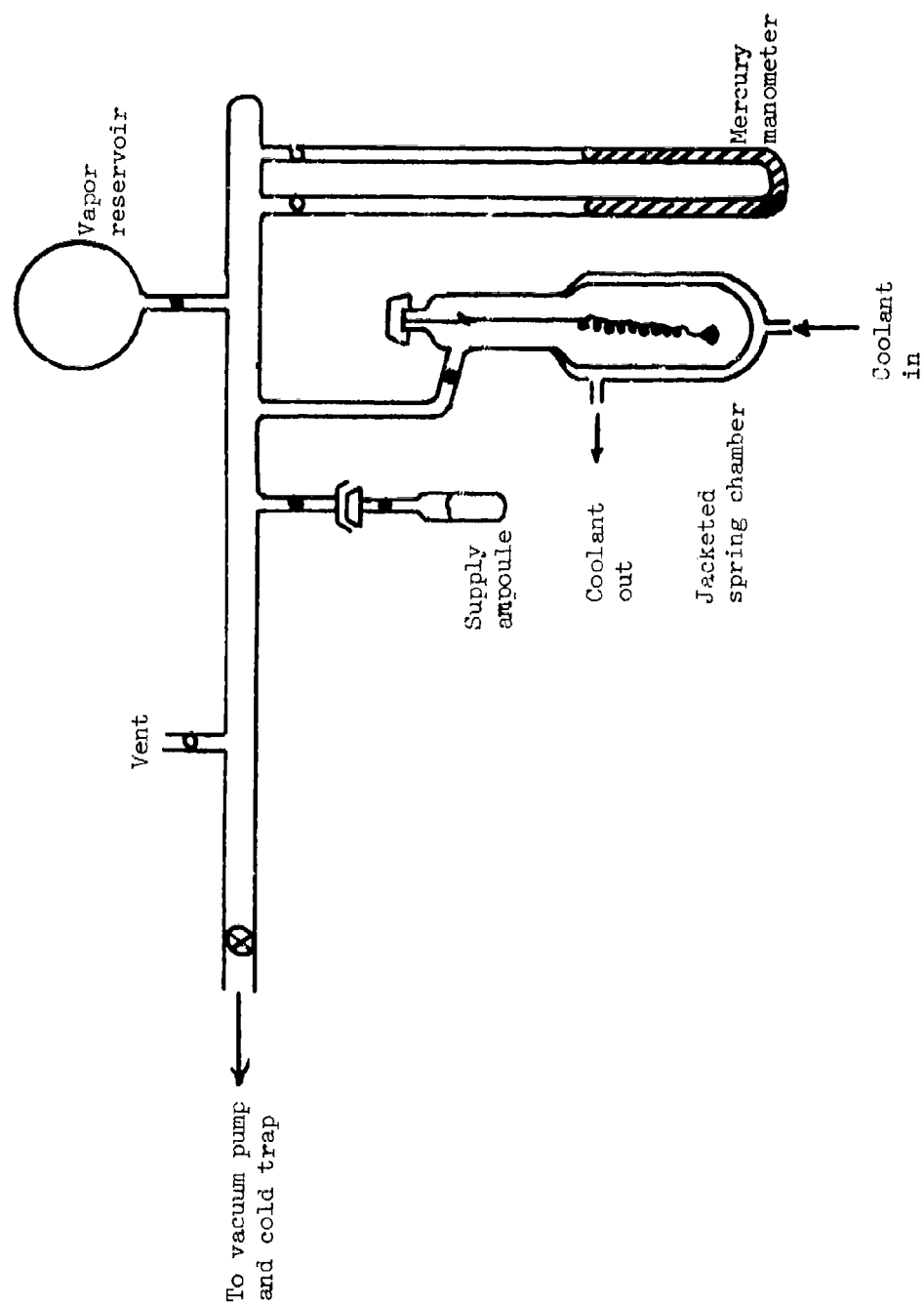


Figure 13. Schematic diagram of vapor sorption system

to make the change in vapor pressure appear a step change. To prevent damage to the spring, small pressure changes were introduced. The stopcock was closed following the admission of the vapor into the spring case. The weight gain of the sample was recorded as a function of time until equilibrium was reached.

Desorption was performed in a reverse manner. The vacuum manifold was evacuated with the stopcock closed. At time zero, the stockcock was opened to rapidly evacuate the spring case and begin the desorption process. The weight loss during desorption was recorded versus time until equilibrium was reached. For all experiments conducted, a new sample was introduced for each isotherm.

The spring case was water jacketed to control the temperature of the vapor and sample during the adsorption and desorption studies to $\pm 0.05^{\circ}\text{C}$. The entire chamber was not jacketed, thus introducing vapor circulation caused by a temperature gradient when the system was being controlled at high vapor pressures and temperatures differing from ambient conditions by $\pm 5^{\circ}\text{C}$. This was avoided by properly insulating the non-jacketed part of the spring case. A sufficient flow rate of water through the jacket was maintained to prevent a drop in temperature between the water bath and the spring case.

The vapor pressure in the system was measured with a closed end manometer. The vapor pressure in the spring case was checked periodically by opening the spring case to the vacuum manifold. The vapor pressure was found not to vary by more than ± 3 mmHg.

Apparatus for Sweat Application

Before beginning experiments on the development of an effective method of reducing sweat poisoning of a material, reproducible and realistic procedures for applying sweat and its constituents to the carbon impregnated foam material were devised. An applicator was designed and tested which provided for the application of sweat to the foam material from one side only, in a manner similar to the transfer of sweat from the human body to the material. The apparatus is shown in Figure 14.

The applicator consisted of a cylindrical vessel, six inches tall and five and one-half inches in diameter. The top was covered with a

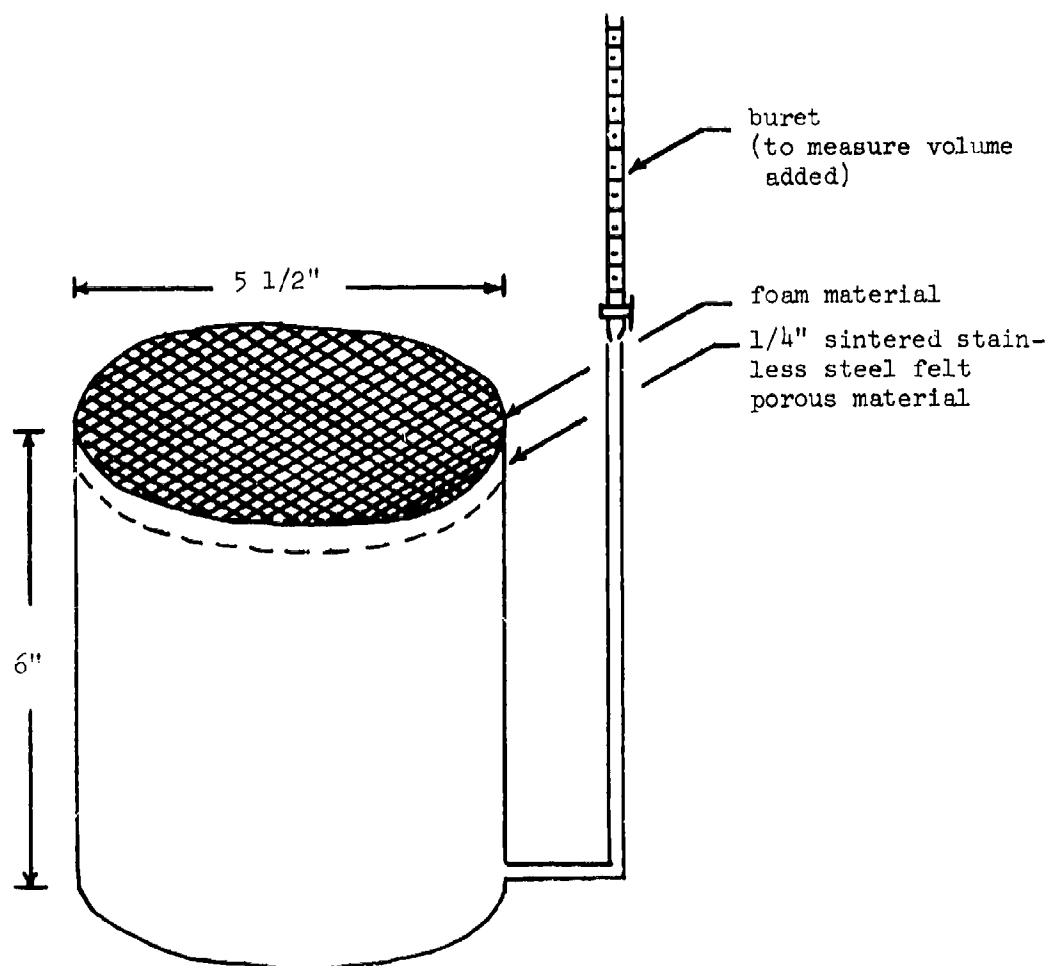


Figure 14. Sweat applicator

quarter-inch sintered stainless steel felt porous material. A fitting was connected to the bottom of the vessel through which the apparatus was filled with sweat or its constituents.

The application procedure consisted of laying the carbon impregnated foam sample, nylon side down, onto the felt porous material of the completely filled applicator. The sample was left on the applicator until no further decrease was recorded in the level of the attached observation leg. More sweat or its components were added depending on the amount required for treatment. The treated sample was removed, weighed and placed in the constant relative humidity and temperature room for equilibration. The total amount of sweat or its components adsorbed correspond to the initial amount adsorbed by capillary action plus the amount added subsequently.

With this device it was thus possible to apply sweat or its components in any desired amount to the material. It was also possible to apply the chemicals with an untreated or treated undershirt material between the carbon impregnated foam and the sintered stainless steel felt porous material of the applicator.

BREAKTHROUGH TIME ANALYSIS

For fixed bed adsorption processes the breakthrough time is of primary importance in most applications. This is especially so for the present study of the adsorption of vapors in protective clothing materials. For this study the breakthrough time was defined as the time when five percent of the inlet concentration ($\frac{C}{C_0} = 0.05$) appears in the exit flow stream.

It is possible to predict the breakthrough time from any of the fixed-bed adsorption models reviewed earlier in this report, when all of the model parameters have been evaluated. To predict the entire breakthrough curve for the carbon impregnated foam material, an overall adsorption coefficient model has been developed and is presented in Part II of this report.

The present analysis seeks to obtain equations governing the breakthrough phenomena and relate them to experimental measurements. The interrelation of the important variables, i.e., number of carbon impregnated foam layers (bed depth), gas flow rate, inlet gas concentration, residence time and temperature on the breakthrough time have been studied in detail to give an understanding of the factors governing the behavior of this system.

Development of the Breakthrough Time Model

For the present study, the adsorption bed was composed of carbon particles, assumed to be spherical, embedded in a matrix of urethane foam. The development of the breakthrough time model for this system was done by making a material balance over an elemental thickness of bed, which gave rise to the following equation. The symbols are defined in the list of symbols.

$$V \frac{\partial C}{\partial z} + \frac{\partial C}{\partial t} + \rho_p \frac{1-\epsilon}{\alpha} \frac{\partial C_{ads}}{\partial t} = 0 \quad (14)$$

If the controlling mechanism in the early part of a run is considered to be an irreversible adsorption reaction which is first order in active sites and adsorbate concentration, the local rate of removal can be expressed as:

$$\frac{\partial C_{ads}}{\partial t} = k C (N_0 - C_{ads}) \quad (15)$$

where k is the adsorption rate constant and N_0 the capacity of the adsorbent or the number of active centers of unit activity per unit weight of bed. Amundson^{25a} gives the solution to these two equations

$$\frac{C_0}{C} = 1 + \left[\exp \left(-\frac{ktC_0}{j} \right) \right] \left[\exp \left(\frac{kN_0 z}{V} \right) - 1 \right] \quad (16)$$

where

$$j = \frac{\delta \rho_m}{\alpha} = \rho_p \frac{1-\epsilon}{\alpha} \quad (17)$$

and

$$\frac{N_0}{C_{ads}} = 1 + \left[\exp \left(-\frac{kN_0 z}{V} \right) \right] \left[\exp \left(\frac{ktC_0}{j} \right) - 1 \right]^{-1} \quad (18)$$

If the breakthrough time t_b is defined as the time at which the concentration of the gas escaping the bed reaches some specified value

C_b , ($\frac{C_b}{C_0} = 0.05$), then by substituting $C = C_b$ at $t = t_b$ in Equation 16 and rearranging we arrive at the desired form:

$$t_b = \frac{j}{kC_0} \left[\ln \left(\exp \left(-\frac{kN_0 z}{V} \right) - 1 \right) - \ln \left(\frac{C_0}{C_b} - 1 \right) \right] \quad (19)$$

It should be mentioned that Equation 18 could also be rearranged in the same form as Equation 19 as shown below

$$\text{at } t = t_b, C_{ads} = M_b^* = \frac{C_0 Q t_b}{W_t} \quad (20)$$

hence

$$t_b = \frac{j}{kC_0} \left[\ln \left(\exp \left(-\frac{kN_0 z}{V} \right) + \left(\frac{N_0}{M_b^*} - 1 \right) \right) - \ln \left(\frac{N_0}{M_b^*} - 1 \right) \right] \quad (21)$$

^{25a}Amundson, N. R., A note on the mathematics of adsorption in beds. J. Phy. and Colloid Chem., 52, 1153-1157 (1950).

However, since C_{ads} is not a directly measured quantity but a calculated one, the breakthrough time analysis that follows will utilize Equation 19.

Effect of Measured Variables on the Breakthrough Time

To study the effect of measured variables on the breakthrough time, we can rewrite Equation 19 as

$$t_b + t_1 = \frac{j}{kC_0} \ln \left[\exp \left(\frac{kN_0 z}{V} \right) - 1 \right] \quad (22)$$

where

$$t_1 = \frac{j}{kC_0} \ln \left(\frac{C_0}{C_b} - 1 \right) \quad (23)$$

From the values of k and N_0 obtained, as shown in Table 4, it was possible to verify the following assumption

$$\exp \left(\frac{kN_0 z}{V} \right) \gg 1 \quad (24)$$

Hence, we may write

$$t_b + t_1 = \frac{N_0 j}{C_0 V} z \quad (25)$$

Now by defining residence time, τ , as

$$\tau = \frac{z}{V} \quad (26)$$

and substituting for the quantities defined earlier, we can write

$$\tau = \frac{W_t \alpha}{\rho_m Q} = \frac{z A_f \alpha}{Q} \quad (27)$$

Equation 25 can now be written as

$$t_b = \frac{N_0 j}{C_0} (\tau - \tau_f) = \frac{N_0 J}{C_0} \left(\frac{\alpha A_f z}{Q} - \tau_f \right) \quad (28)$$

Table 4. Breakthrough time model parameters

Cloth Type	$\frac{k}{j}$ ($\frac{1 \text{ gm particle}}{j \text{ mg CCl}_4\text{-min}}$) Values at $C_0 = 7.8 \text{ mg/l}$	$j N_0$			$k N_0$ gm particle- active centers of unit activity mg $\text{CCl}_4\text{-min-}$
		$j \frac{\text{mg CCl}_4}{\text{gm-particle}}$	$j \frac{\text{active centers of unit activity}}{\text{unit weight of bed}}$		
Bolt 2	0.064	14.08	120.66×10^{22}		8.36×10^{22}
Bolt 3	0.031	34.92	324.06×10^{22}		10.05×10^{22}
Bolt 4	0.031	7.04	65.33×10^{22}		2.03×10^{22}
Pluton B-1	0.037	55.72	517.08×10^{22}		19.13×10^{22}
British Cloth A46C54	0.047	74.32	689.69×10^{22}		32.42×10^{22}
British Cloth p99	0.010	6.73	62.45×10^{22}		0.63×10^{22}

where τ_f is a fictitious resident time, a feature of the model, below which the bed breaks down and is given by the relation

$$\tau_f = \frac{1}{N_0 k} \ln \left(\frac{C_0}{C_b} - 1 \right) \quad (29)$$

Equation 28 is a simple equation representing the breakthrough time. It suggests that the breakthrough time varies directly as the number of carbon impregnated foam layers, or bed depth, and inversely as the gas flow rate and inlet gas concentration (Figure 15). From Equation 28 and Equation 29 we observe that the value of N_0 was obtained from the slope of breakthrough time versus $\left(\frac{z}{C_0 Q}\right)$ graph, while k was determined from the intercept on the t_b axis of the same plot. The breakthrough time may now be written as

$$t_b = \bar{A} + \bar{B} \frac{z}{nC_0 Q} \quad (30)$$

where

$$\bar{A} = - \frac{j}{kC_0} \ln \left(\frac{C_0}{C_b} - 1 \right) \text{ and } \bar{B} = N_0 j A_f \alpha$$

Thus $\bar{A}$ and $\bar{B}$ are functions of model parameters k and N_0 , and n in Equation 30 is the sample weight normalizing factor given as the average sample weight divided by the real sample weight. This assumed that the adsorbent capacity, N_0 , was a linear function of the real weight of the sample. A statistical fit for the breakthrough time from the Central Composite Statistical Design (Appendix A) of experiments (50 runs) revealed the following:

$$t_b = - 5.87 + 1191.70 \frac{z}{nC_0 Q} \quad (31)$$

for

$$5.0 \text{ mg/l} \leq C_0 \leq 12.0 \text{ mg/l}$$

$$0.5 \text{ l/min} \leq Q \leq 1.5 \text{ l/min}$$

$$1, 2, \text{ or } 3 \text{ layers}$$

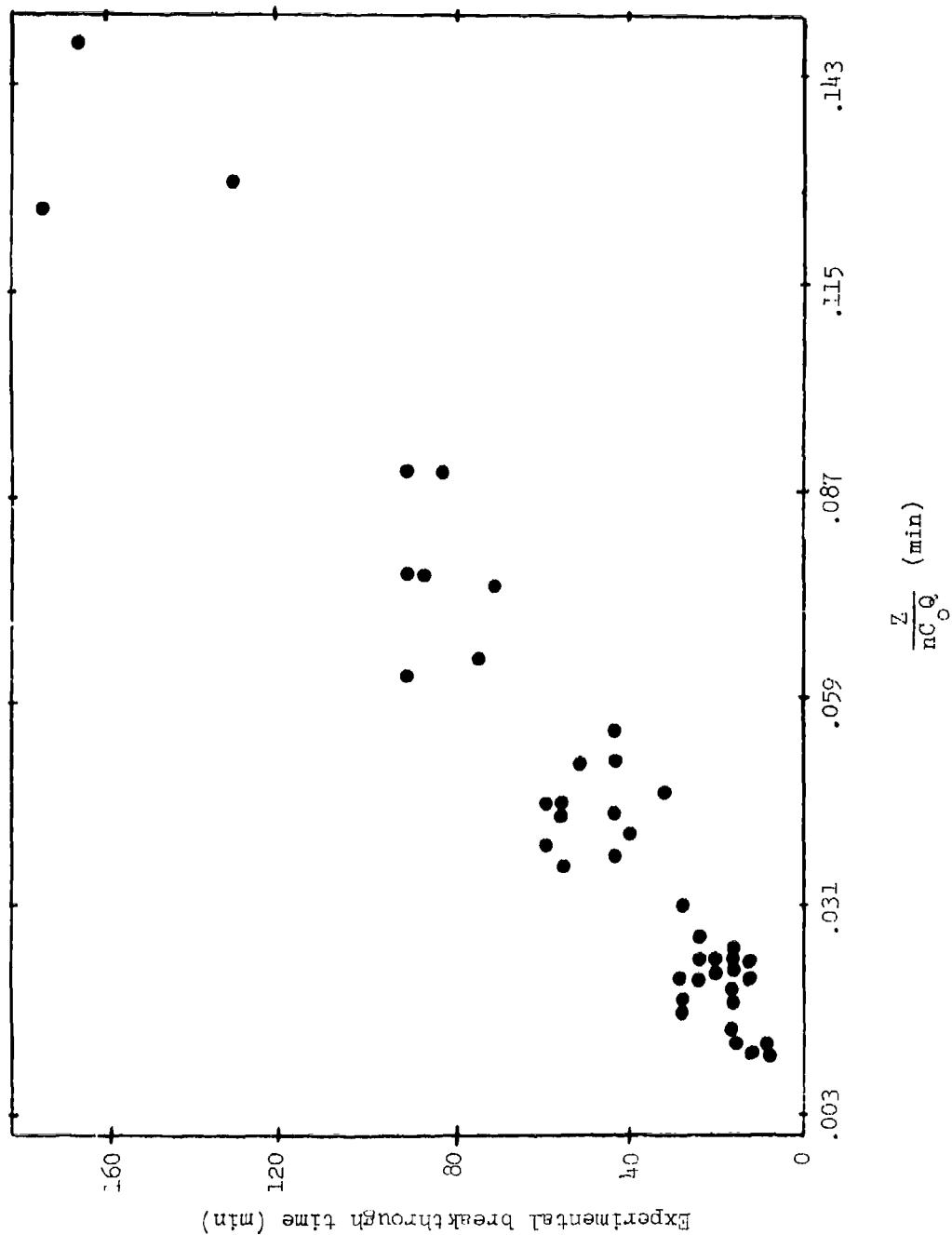


Figure 15. Plot of experimental breakthrough time versus $\frac{Z}{nC_o Q}$

The variation of breakthrough time with temperature, T , was not statistically significant; however, this was probably due to the small temperature range ($25^{\circ}\text{C} \leq T \leq 40^{\circ}\text{C}$) considered. Figure 16 compares the experimental values of the breakthrough time with the model values obtained from Equation 31.

An equation of the form

$$t_b (\text{Model}) = a + b t_b (\text{Experimental}) \quad (32)$$

was fit with a least square technique to the data; the results are shown in Table 5.

If the model is an accurate prediction of the breakthrough time, the

Table 5. Table of standard error

a (Standard Error)	b (Standard Error)	Number of Observations	F	R^2
2.9927 (2.2049)	0.9311 (0.0378)	47	608.25	0.9311

expected form of Equation 32 is

$$t_b (\text{Model}) = 0 + 1.0 t_b (\text{Experimental}) \quad (33)$$

The Student's t Test was used to compare statistically the best estimates of a and b against the expected value of zero and one. These tests, summarized in Table 6, show that none of the best-estimate values of a and b

Table 6. Table indicating significance at 95% confidence level

Value of t for a	Significant (at 95% Confidence level)	Value of t for b	Significant (at 95% Confidence level)
1.357	No	1.820	No

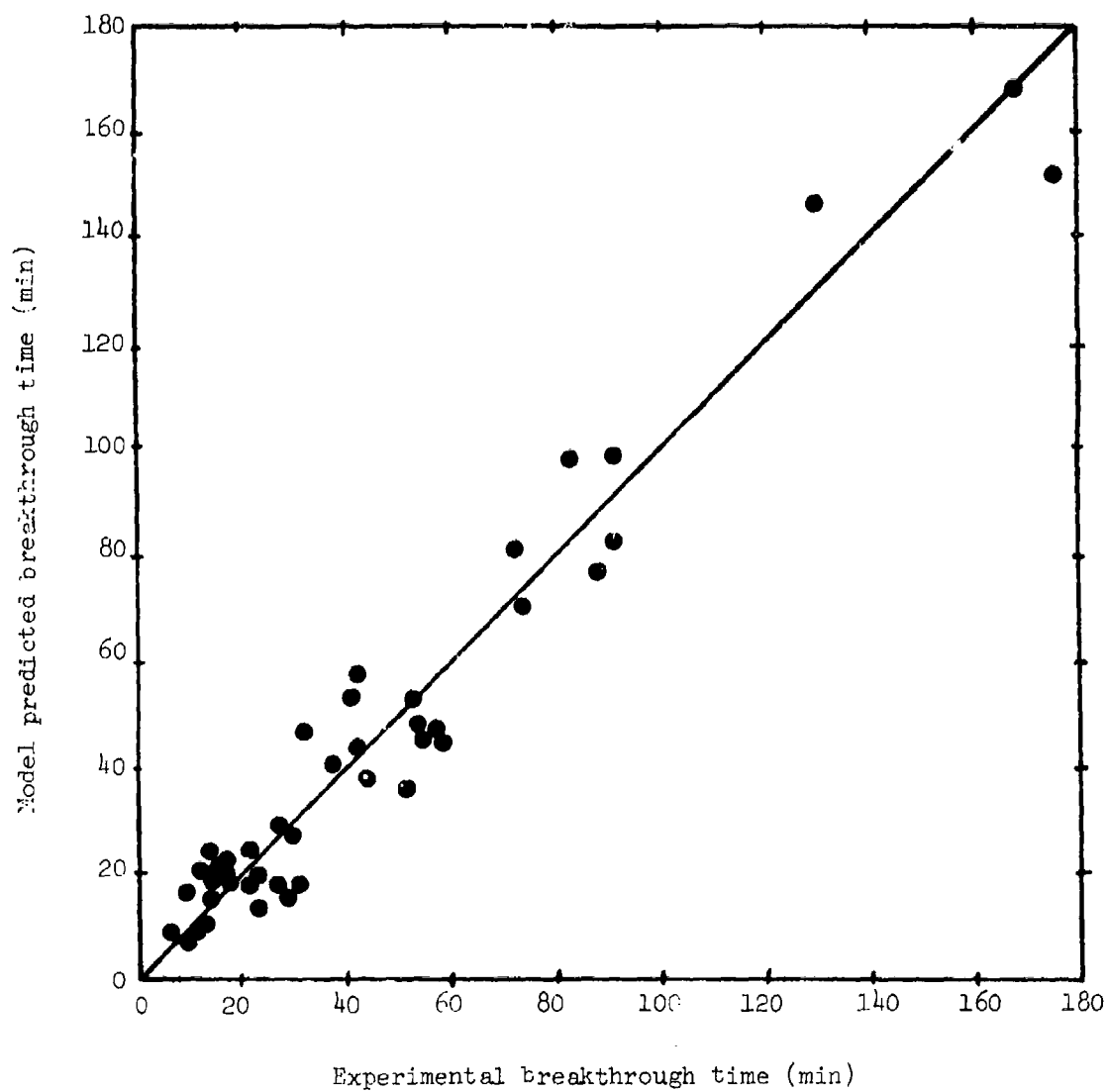


Figure 16. Comparison of experimental and predicted breakthrough time

were significantly different from the expected value at the 95% confidence level. That is, the calculated value of the breakthrough time is statistically the same as the experimental value. The scatter that does exist in Figure 16 is probably due to the following uncertainties inherent of the adsorbent;

- (a) amount of carbon in a sample
- (b) carbon particle size and distribution
- (c) nonuniform nature of flow through a foam matrix embedded with carbon

A justification for these uncertainties has already been given.

Generality of the Breakthrough Time Model

Figure 17 shows the breakthrough curves for one and two layer runs on conditioned samples of Bolt 2 material as determined from the Breakthrough Model and the Overall Adsorption Coefficient Model described in Part II. The model predictions are shown as solid lines and the experimental data are plotted as symbols. Figure 18 shows the comparison for two and three layer runs. An excellent agreement of the overall adsorption coefficient model and experimental results are seen for the complete breakthrough. It was observed, from the figures, that the breakthrough model follows the experimental curve up to $C/C_0 = 0.08$. The values of parameters k and N_0 determined from the breakthrough model with $\frac{C}{C_0} \leq 0.08$ were in excellent agreement with the analysis postulated thus far. For $\frac{C}{C_0} \geq 0.08$, the breakthrough model does not hold.

Effect of Model Parameters on the Shape and Size of the Breakthrough Curve

Both the Breakthrough Time Model and the Overall Adsorption Coefficient Model are two parameter models. A test of the sensitivity of the Breakthrough Time Model to changes in the parameters k and N_0 is shown in Figure 19 and Figure 20. While the former demonstrates the prediction of the breakthrough curves when k is changed by 25%, the latter shows the sensitivity to a 25% change in N_0 . It was observed that the area under the $(1 - \frac{C}{C_0})$ versus time curve remains the same by a variation in k and the model is not very sensitive to changes in k . This indicates that some of

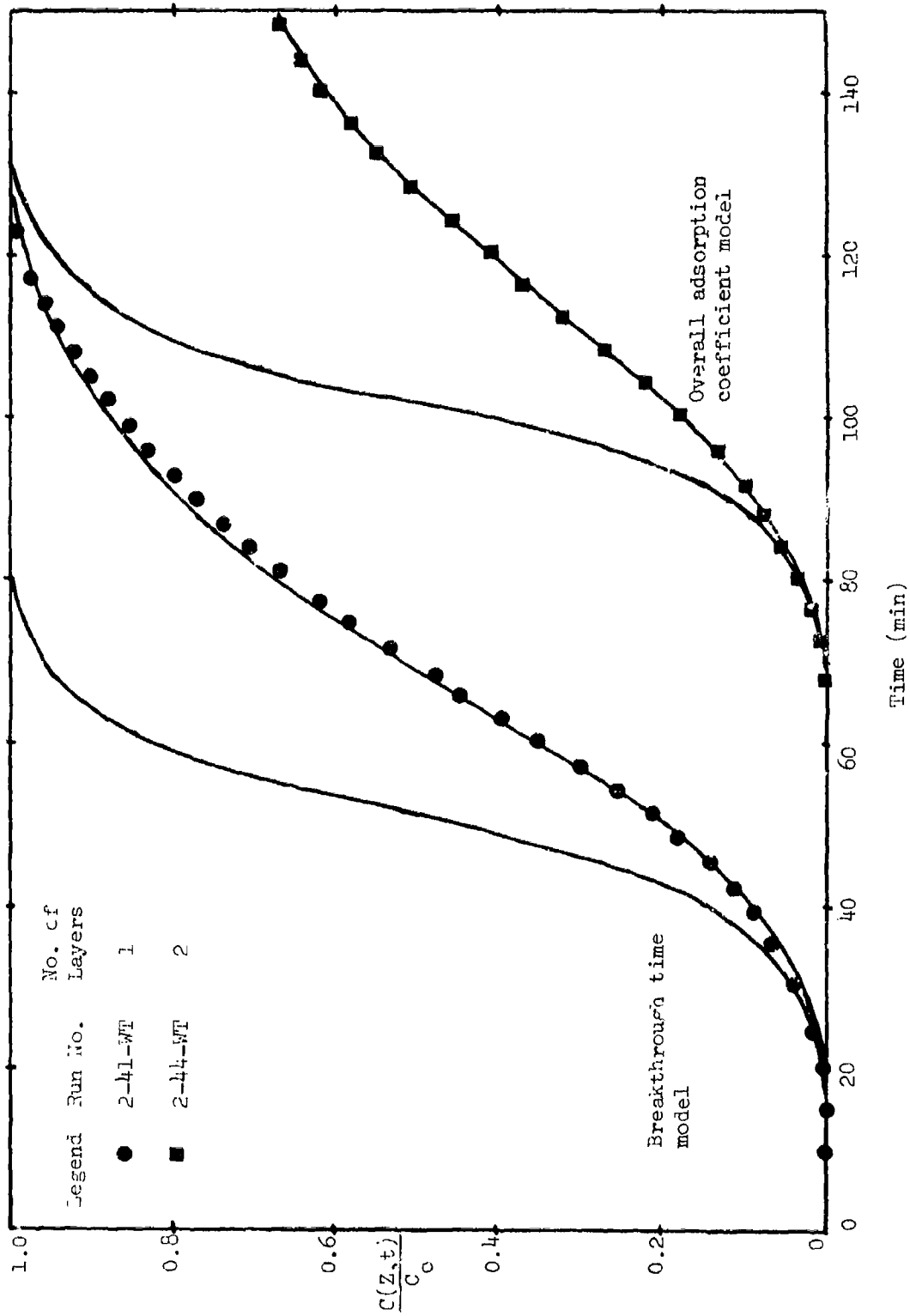


Figure 17. Model prediction and experimental data for one and two layer runs

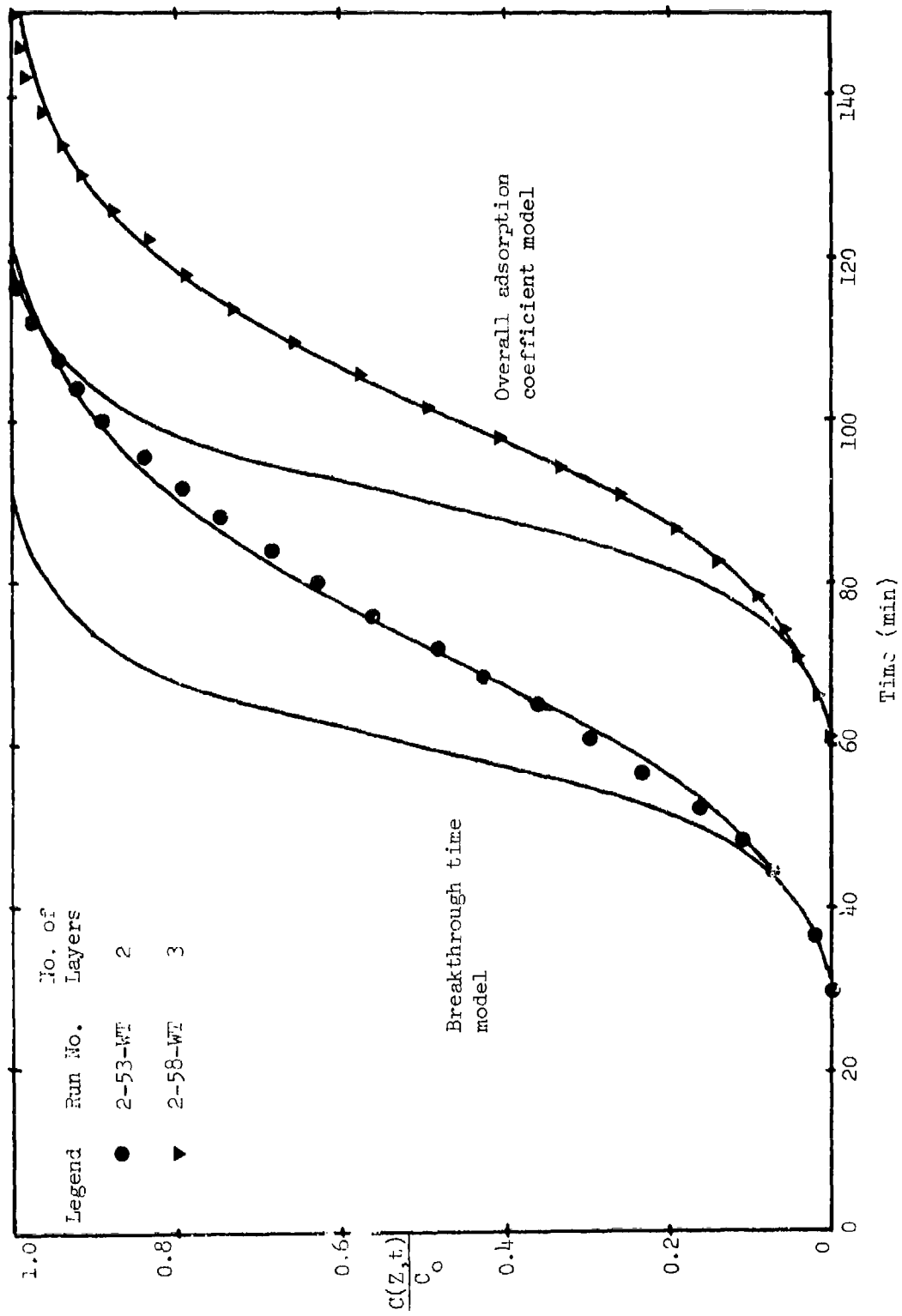


Figure 18. Model prediction and experimental data for two and three layer runs

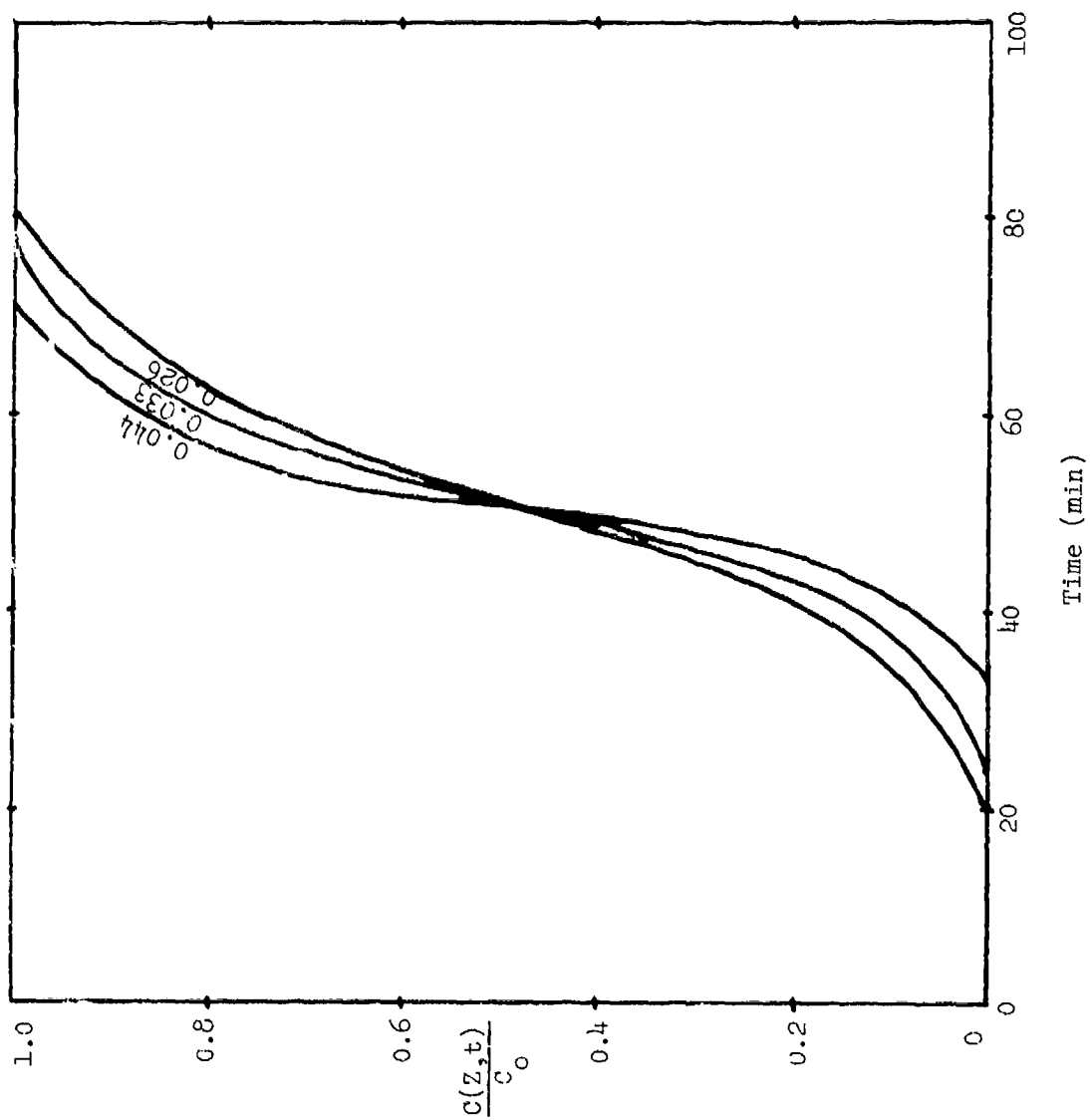


Figure 19. Effect of changing k/j 25% as predicted by breakthrough time model

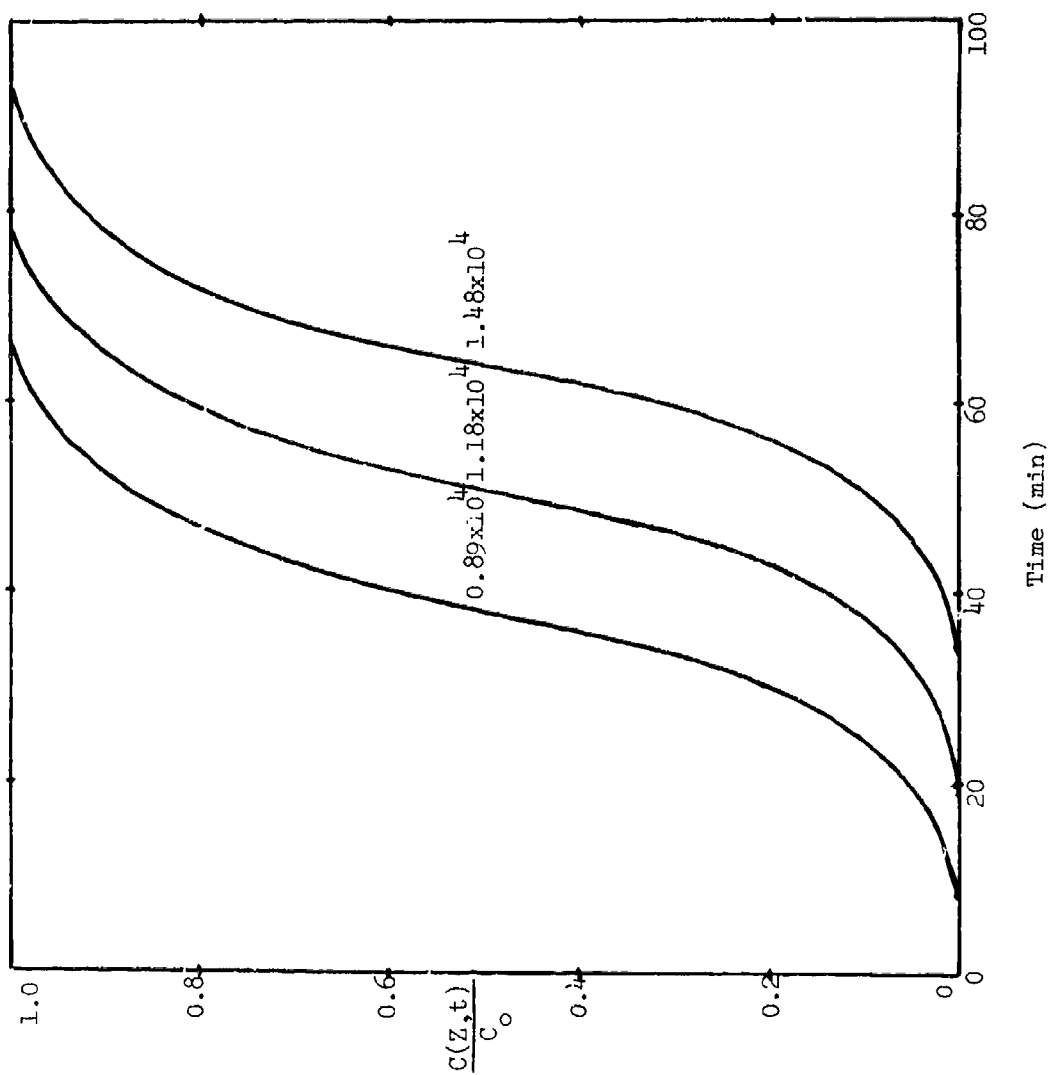


Figure 20. Effect of changing $j N_0$ 25% as predicted by the breakthrough time model

the scatter in experimental values of this parameter is not significant. Figure 20 shows the effect of changing the adsorbent capacity parameter, N_0 , as predicted by the model. The characteristic shape of the curve is the same but the area under the $(1 - \frac{C}{C_0})$ versus time curve is different. This reflects a change in the total amount adsorbed. The variation in N_0 also affects the most critical zone of interest ($0 \leq \frac{C}{C_0} \leq 0.08$) from the point of view of breakthrough time.

It may also be pointed out that a change similar to k is observed by altering UA , while N_0 is analogous to K_A of the Overall Adsorption Coefficient Model.

While the use of the breakthrough time model is not limited to a complex adsorption system like carbon impregnated foam material, its chief advantage lies in the simple approach to modeling. It is, however, possible to predict the breakthrough time from any of the fixed-bed adsorption models that have been proposed when all the model parameters have been evaluated. Using these methods for predicting breakthrough time is somewhat time consuming since the breakthrough time must be found by numerical integration of the model solution. The breakthrough time model proposed herein is an alternate, simple approach to the study of the phenomena of breakthrough time.

The model works well for the carbon impregnated foam material for the range of inlet concentration, flow, and bed depth used in this study. Some of the coefficients may be a function of temperature, but due to the small range considered, the effect of temperature on the model parameters was not statistically significant.

INVESTIGATION OF SWEAT INDUCED DIMINUTION OF THE EFFECTIVE CAPACITY OF PROTECTIVE CLOTHING

Protective clothing containing charcoal may be exposed during storage or wear to a variety of materials which could be detrimental to the adsorptive ability of the charcoal and to its function as a chemical warfare agent barrier. Poisoning of charcoal during wear has been attributed to sweat. Although carbon impregnated foam material has been in existence for some years, there is little definitive work on the effects of sweat on these materials. It has been established that in most cases the loss of protection is caused by poisoning rather than by loss of impregnant. There has been no systematic study of the constituents of sweat responsible for poisoning of charcoal impregnated foam responsible for poisoning of charcoal impregnated foam material. The quantitative data available on the extent of exposure to sweat required for a given degree of poisoning is inadequate.

Formulation of Simulated Sweat and Comparison with Real Sweat

Simulated sweat containing the principal organic and inorganic substances known to be present in whole sweat has the following composition:

Simulated Sweat	
Sodium chloride	8.0 g
Potassium sulphate	0.5 g
Sodium sulphate	0.1 g
Magnesium sulphate	1.02 g
Calcium chloride	0.04 g
Urea	0.5 g
Glucose	0.15 g
Lactic acid	1.0 g
Pyruvic acid	0.03 g
Ammonium hydroxide to	pH 7.5
Water to	1 liter

One difference between real and simulated sweat is in surface tension. The surface tension of the simulated sweat is close to that of distilled water, 75 dynes/cm, while for several samples of real sweat, it has been

measured to within the range of 42.5 to 44.0 dynes/cm, indicating the presence of some surface active material. Other differences also exist. Simulated sweat, for example, is colorless, clear and practically odorless and when evaporated, leaves a colorless crystalline residue while real sweat is generally yellow brown in color, slightly turbid and has a distinct odor. When evaporated, the residue is brown and contains crystals together with some amorphous material. Except where indicated, the results reported here were obtained using simulated sweat.

Equilibrium Adsorptive Capacity of Carbon Impregnated Foam Material

Equilibrium adsorptive capacity of untreated carbon impregnated foam material was obtained in the McBain Balance as a reference for comparison with different types of treatments. The method of treatment of carbon impregnated foam material with sweat or its constituents was accomplished by following the water conditioning with a treatment by the appropriate solution and again allowing the sample to equilibrate at 70°F and 65% relative humidity. The samples were then used to obtain carbon tetrachloride equilibrium adsorption isotherms.

Figure 21 shows the poisoning effect of whole sweat on carbon impregnated foam material. It is of interest to note that water conditioning reduces the capacity of the sample when compared to unconditioned foam material. Examination of the various treatments shown in Figure 21, indicates that the capacity of the material is reduced by about 50% by sweat treatment.

The adsorption isotherm of water on conditioned carbon impregnated foam material is shown in Figure 22. Figure 23 shows the adsorption isotherms of carbon tetrachloride on conditioned foam material. The adsorption is linear up to a concentration of about 7.5 mg/l, and the slope is K_A .

The Effect of Individual Constituents of Sweat on the Adsorptive Capacity of Carbon Impregnated Foam Material

A number of substances were selected as representative of the principal constituents of sweat, and their effect upon the carbon tetrachloride capacity

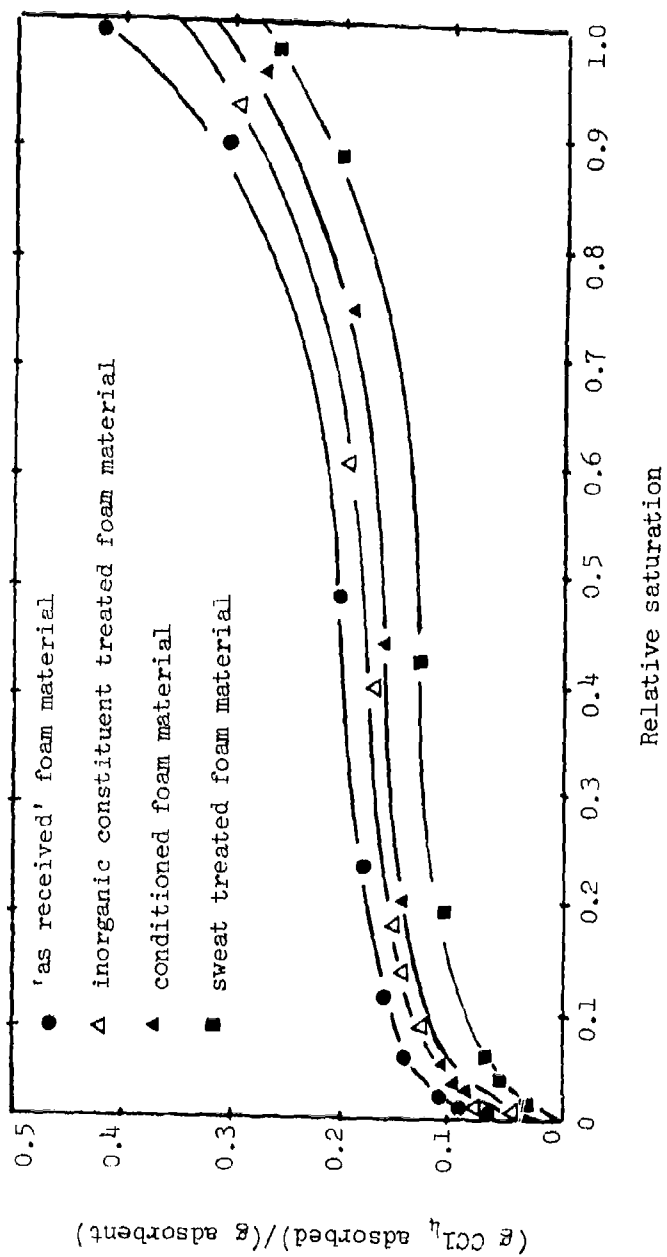


Figure 21. Adsorption isotherm of CCl_4 on treated Bolt-3 carbon impregnated foam material at 25°C

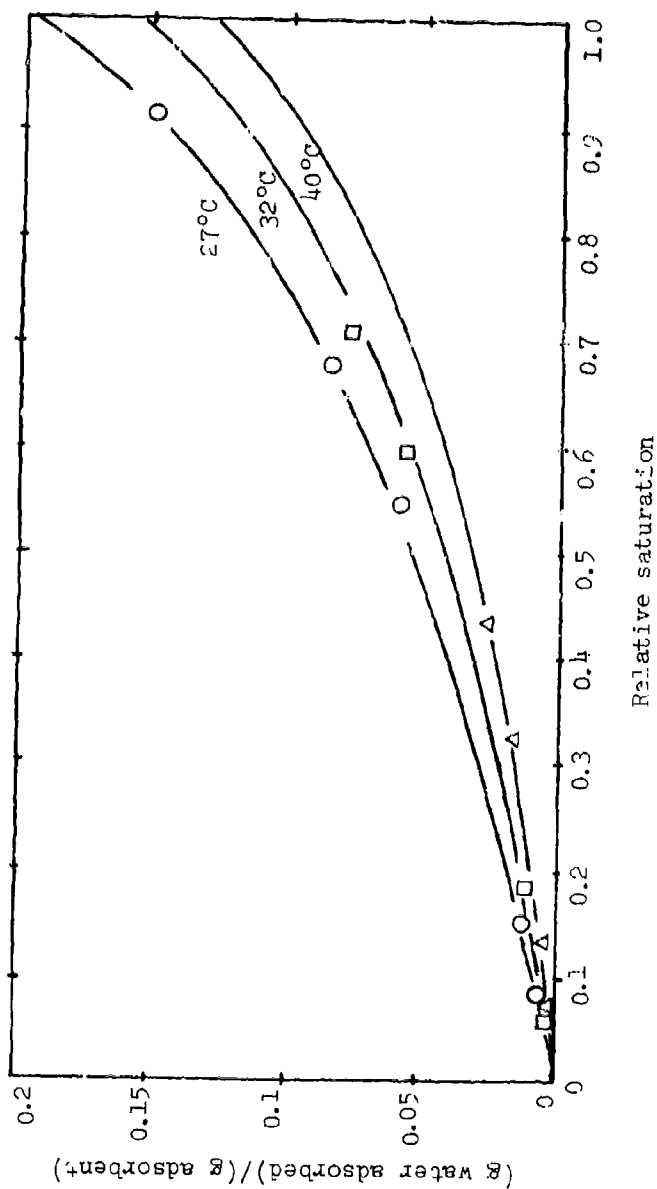


Figure 22. Adsorption isotherm of water on Bolt-3 conditioned carbon impregnated foam material

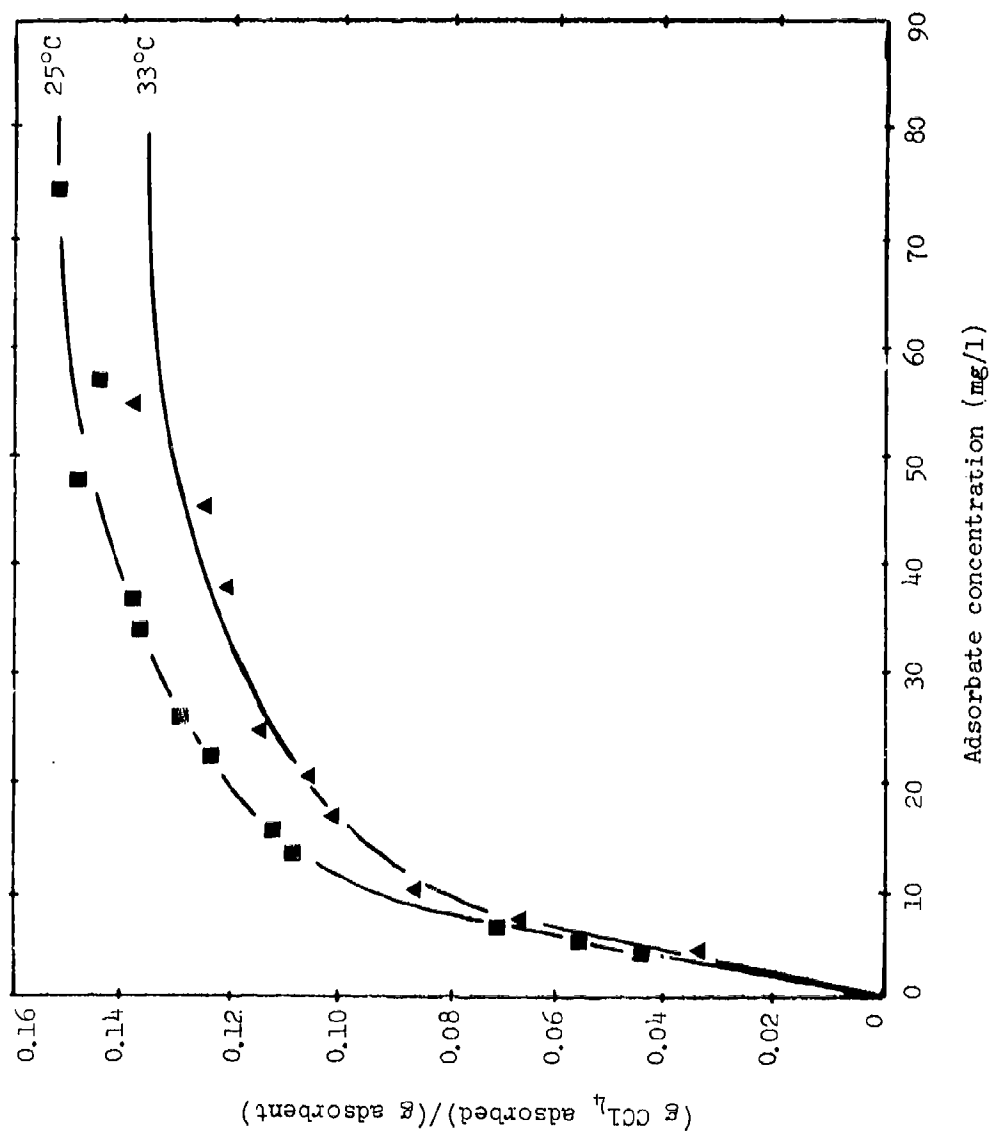


Figure 23. Adsorption isotherm of CCl_4 on conditioned Bolt-3 carbon impregnated foam material

of carbon-impregnated foam material was determined. The procedure was similar to that used for determining the effects of whole sweat. Water was used as solvent for the sweat constituents. The selection of the substances to be examined was based upon the reviews of the chemical composition of sweat by Robinson and Robinson⁵². Since the data shown in Figure 21 indicated that the organic constituents of sweat poison the cloth most severely, this work concentrated on those constituents. In Figures 24 through 26, the data obtained for lactic acid, urea and glucose treatment (these being the principal constituents of sweat), are shown. The concentration of each of these reagents in their respective solutions was the same as that reported for whole sweat: lactic acid - 1 g/l, urea - 0.5 g/l, and glucose 0.15 g/l. A comparison of the poisoning by these components shows (Figure 27) that lactic acid is most severe in inhibiting the total amount of carbon tetrachloride adsorbed and reduces the capacity of the cloth by 10% with respect to conditioned material and 38.6% when compared to untreated sample. Glucose and urea treatment, surprisingly enhance the capacity when compared to a conditioned sample.

The Effect of Sweat and its Constituents Upon the Dynamic Adsorptive Capacity of Carbon Impregnated Foam Material on Complete Saturation

Breakthrough curves were obtained at different experimental conditions for as received (AR), conditioned and dried (D), conditioned (WT), sweat-treated (ST), lactic acid (LA), urea (U), and real sweat treated (RST) foam material samples. Data for these runs are compiled in Table A-7. Conditioning consists of soaking the sample in distilled water and then allowing the samples to reach equilibrium in a constant temperature (70°F) and relative humidity (65%) room. Dried samples were obtained by placing conditioned samples in a desiccator for at least three days before using. The weights used in normalizing the amount adsorbed were weights recorded after removal from the constant humidity room. The samples labeled as received were not conditioned and their recorded weights were increased by 10% for consistency

⁵²Robinson, S. and A. H. Robinson. Chemical composition of sweat. Physiological Reviews, 202-220 (1954).

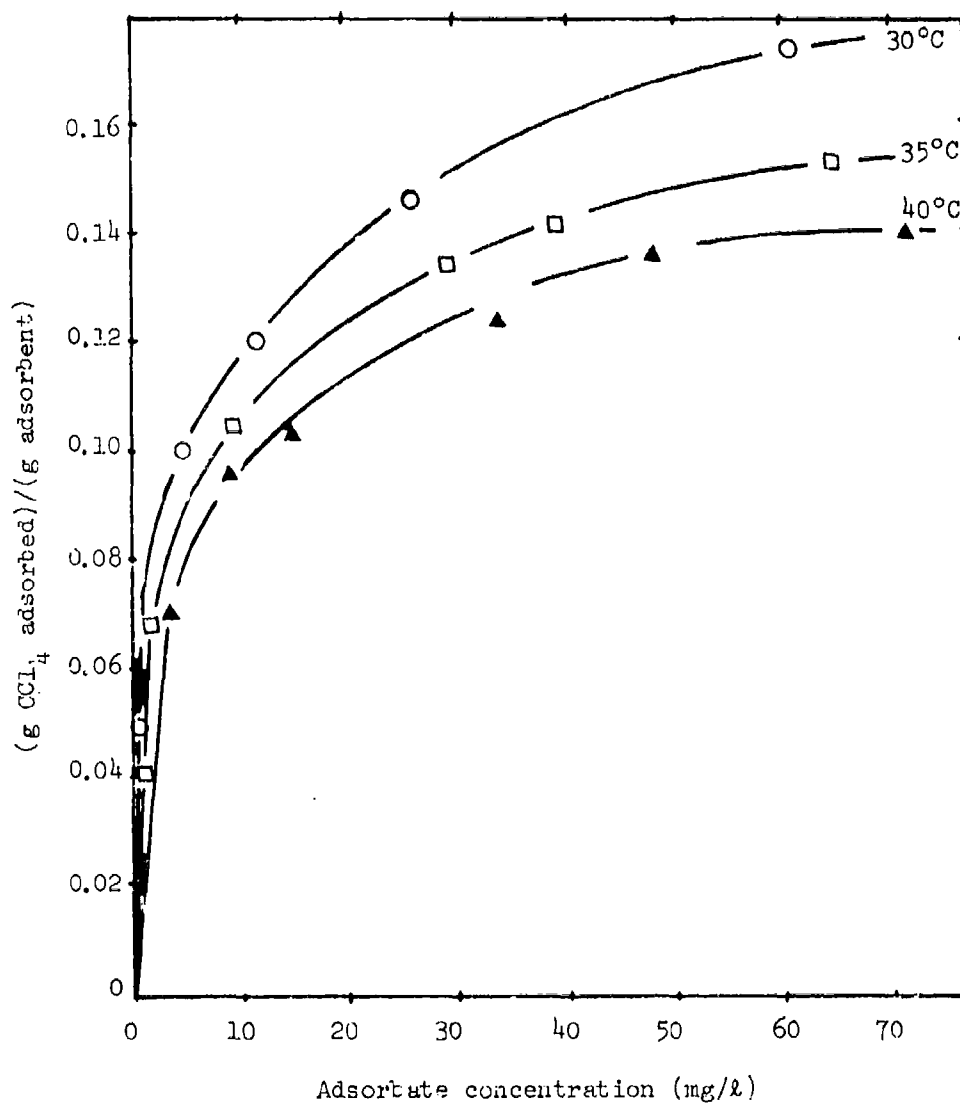


Figure 24. Adsorption isotherm of CCl_4 on lactic acid treated Bclt-3 carbon impregnated foam material.

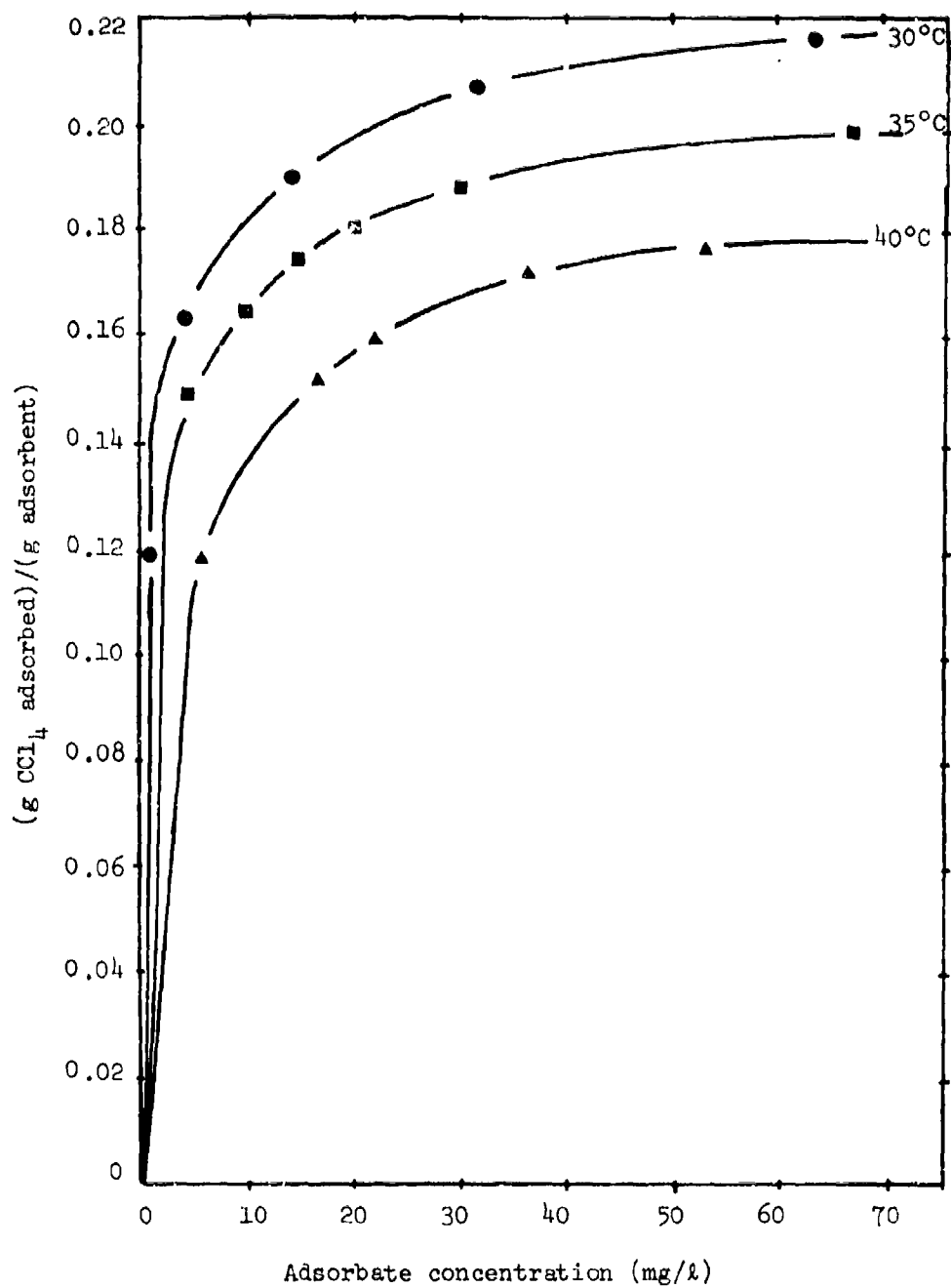


Figure 25. Adsorption isotherm of CCl₄ on urea treated Bolt-3 carbon impregnated foam material

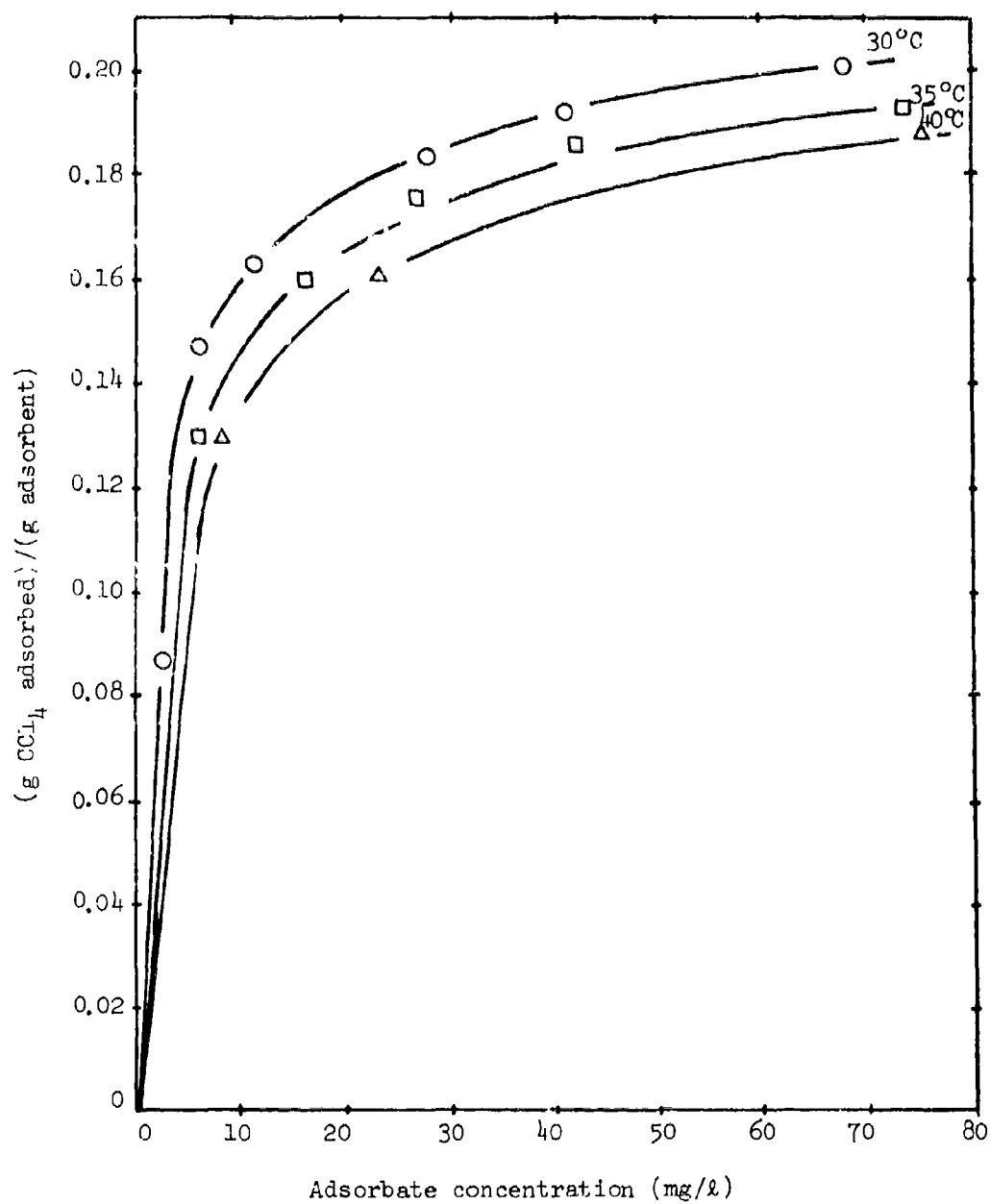


Figure 26. Adsorption isotherm of CCl_4 on glucose treated Bolt-3 carbon impregnated foam material

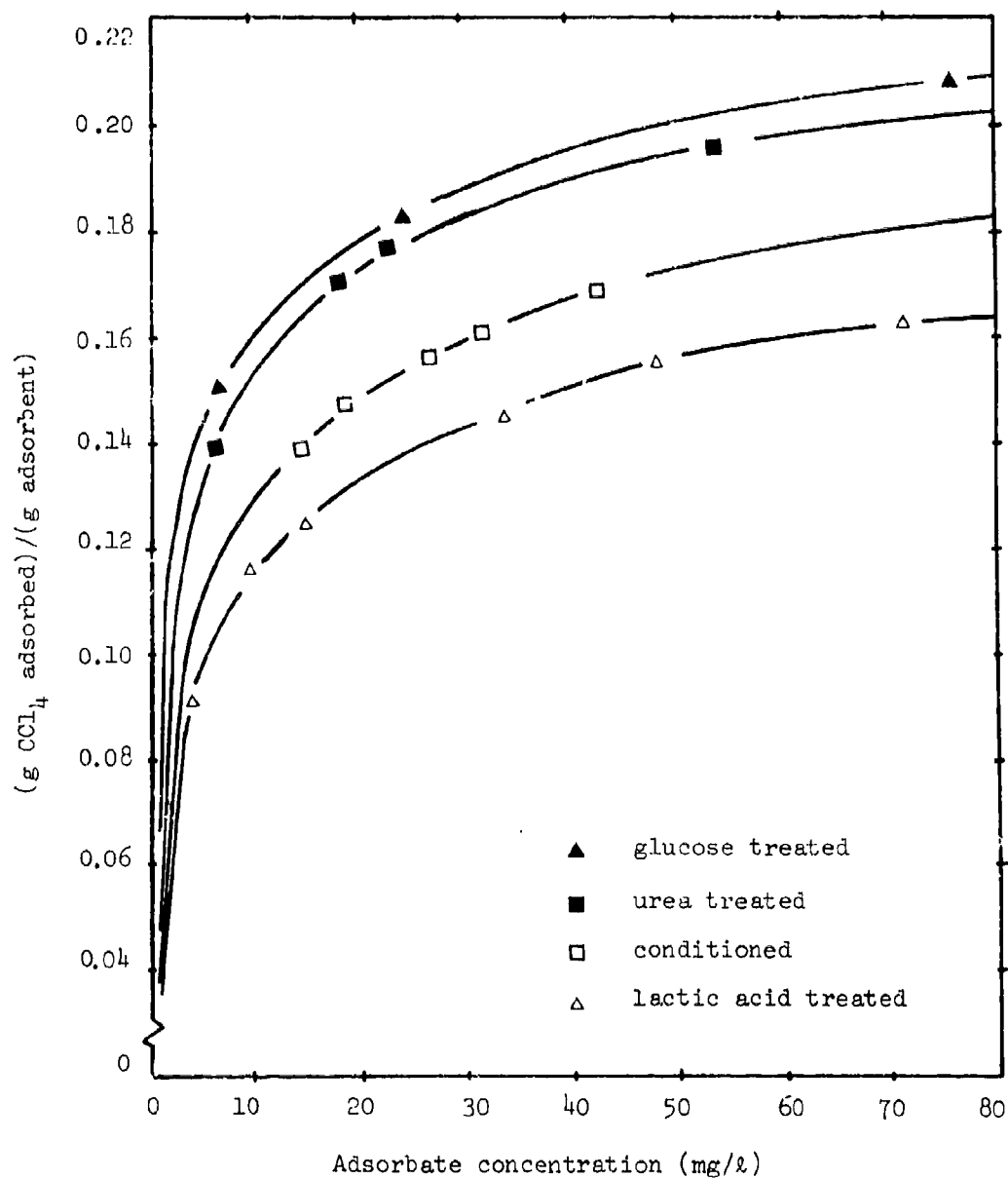


Figure 27. Adsorption isotherm of CCl_4 on treated Bolt-3 carbon impregnated foam material at 40°C

in the normalizing procedure as the cloth increased 10% in weight after conditioning due to adsorbed water.

1. Sweat Poisoning of Charcoal Impregnated Foam Material

Samples were sweat treated by soaking nine samples in 18 liters of simulated sweat overnight and then placing in a room maintained at a constant condition of temperature (70°F) and relative humidity (65%). A large volume of simulated sweat was used to assure that the initial concentration of sweat components would be approximately equal to the equilibrium concentration and thus provide consistency in the total amount of these components adsorbed for future comparisons. Figures 28 through 31 show a comparison of various types of treatment as a percent deviation from the conditioned samples at two different run conditions for 1 and 3 layers. The properties considered were the breakthrough time, t_b , amount adsorbed at breakthrough per unit weight of sample, M_b^* , total amount adsorbed per unit weight of sample, M_t^* , and adsorption equilibrium constant, K_A .

Drying the cloth in a desiccator after conditioning increased t_b and the amount adsorbed to break, M_b^* , for 1 layer, but had little effect on M_b^* for 3 layers. The total amount adsorbed, M_t^* , does not seem to be affected by drying.

Samples used as received had an M_t^* slightly less than that of conditioned material but an M_b^* that was much less for 3 layer runs.

Sweat treatment consistently decreased the total amount adsorbed by about 10%, but effected M_b^* according to run conditions. At a temperature of 32.5°C, flow of 1.0 l/min and inlet concentration of 7.87 mg/l, M_b^* is decreased by about 5%; however, at a temperature of 37.0°C, flow of 1.3 l/min, and inlet concentration of 10.47 mg/l, M_b^* is decreased by about 20%.

Values of K_A showed no significant variation except for sweat-treated samples for which K_A was consistently about 10% lower than that of conditioned samples.

2. Poisoning of Charcoal Impregnated Foam Material by Sweat Components

To investigate the influence of sweat components on the breakthrough curves, samples of Bolt 3 charcoal impregnated foam material were conditioned

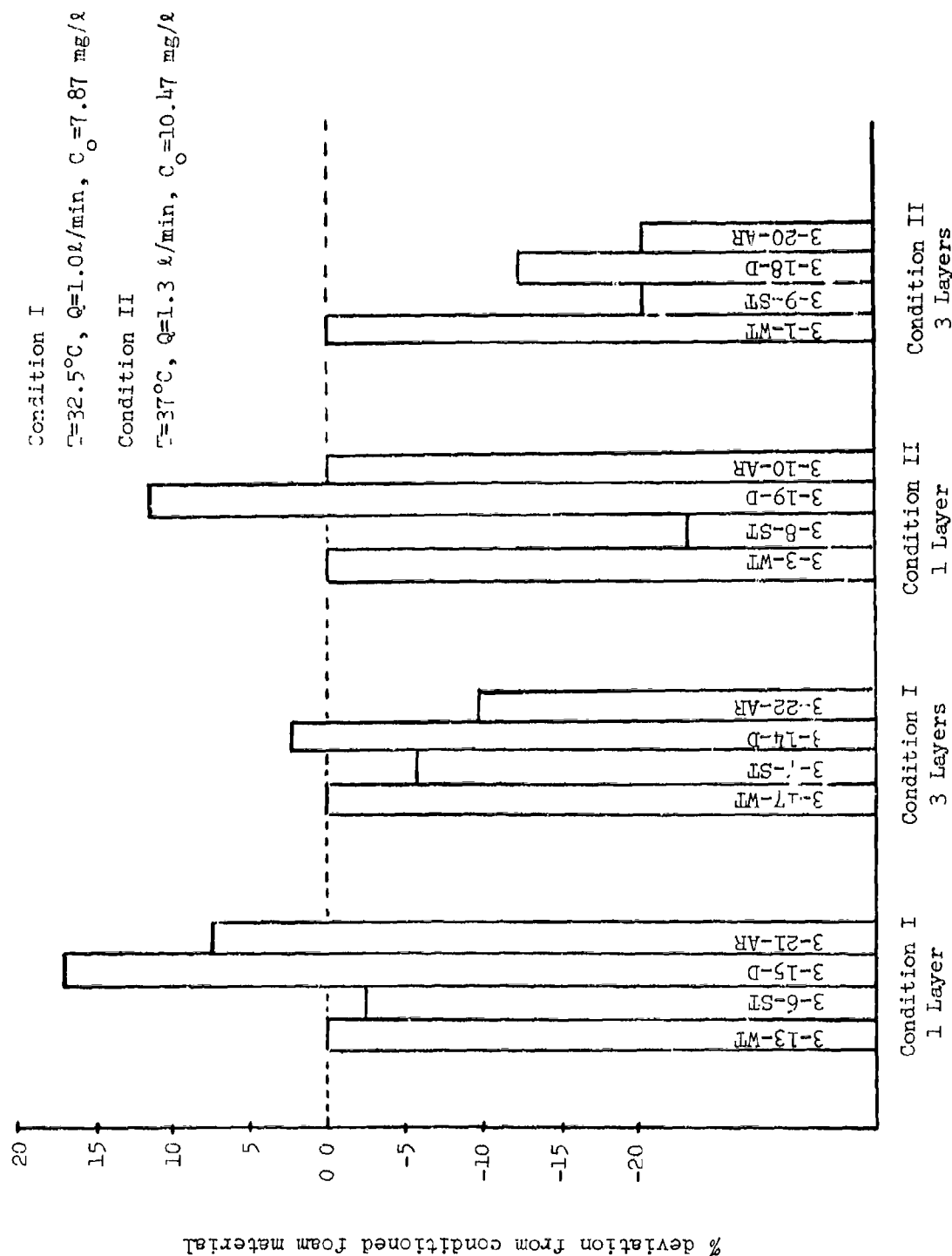


Figure 28. Evaluation of sweat poisoning comparison of breakthrough time (for run conditions specified inside the bars refer to Table A-7)

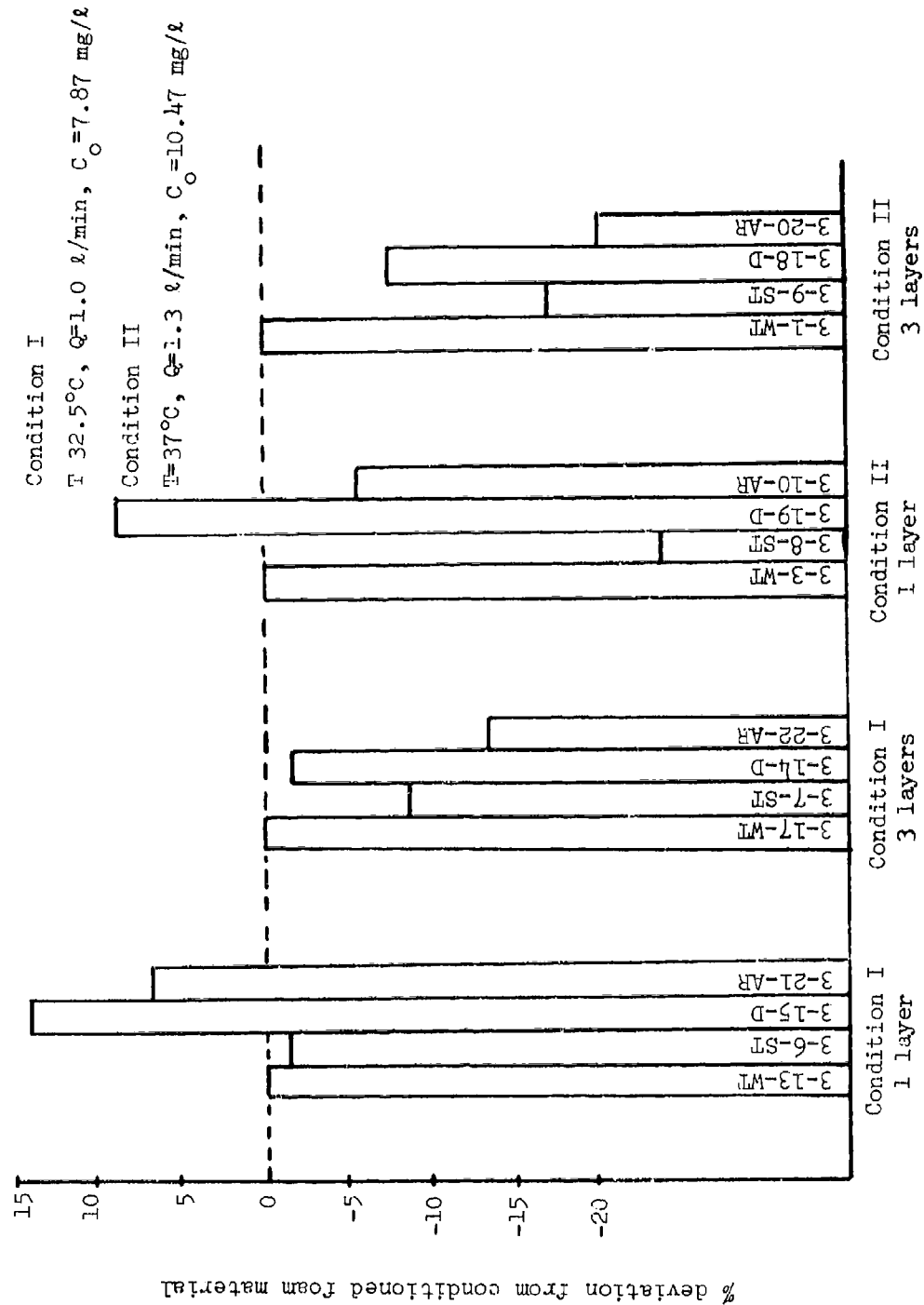


Figure 29. Evaluation of sweat poisoning comparison of M_b*
(for run conditions specified inside the bars, refer to Table A-7)

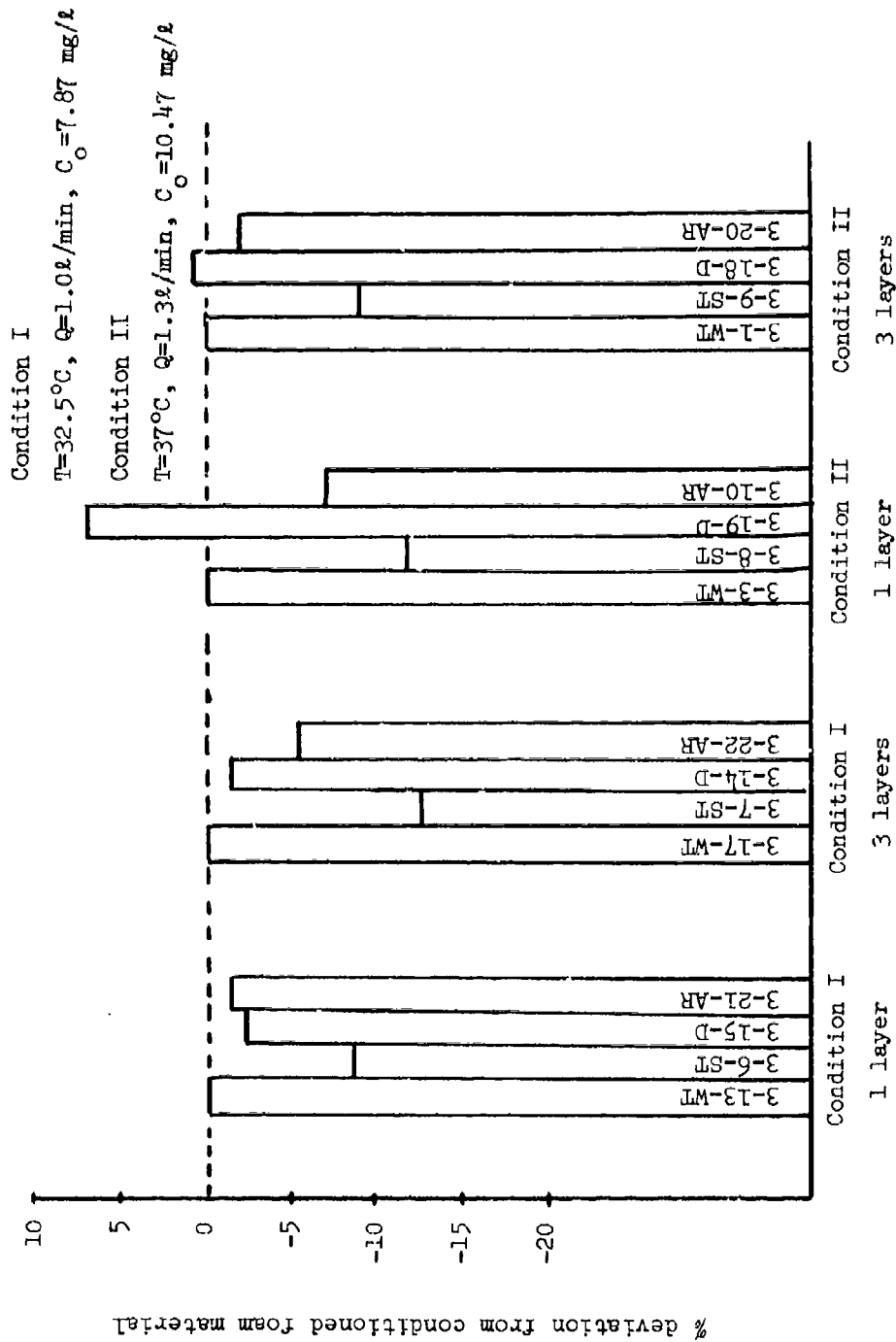


Figure 30. Evaluation of sweat poisoning comparison of M_t^*
 (for run conditions specified inside the bars, refer to Table A-7)

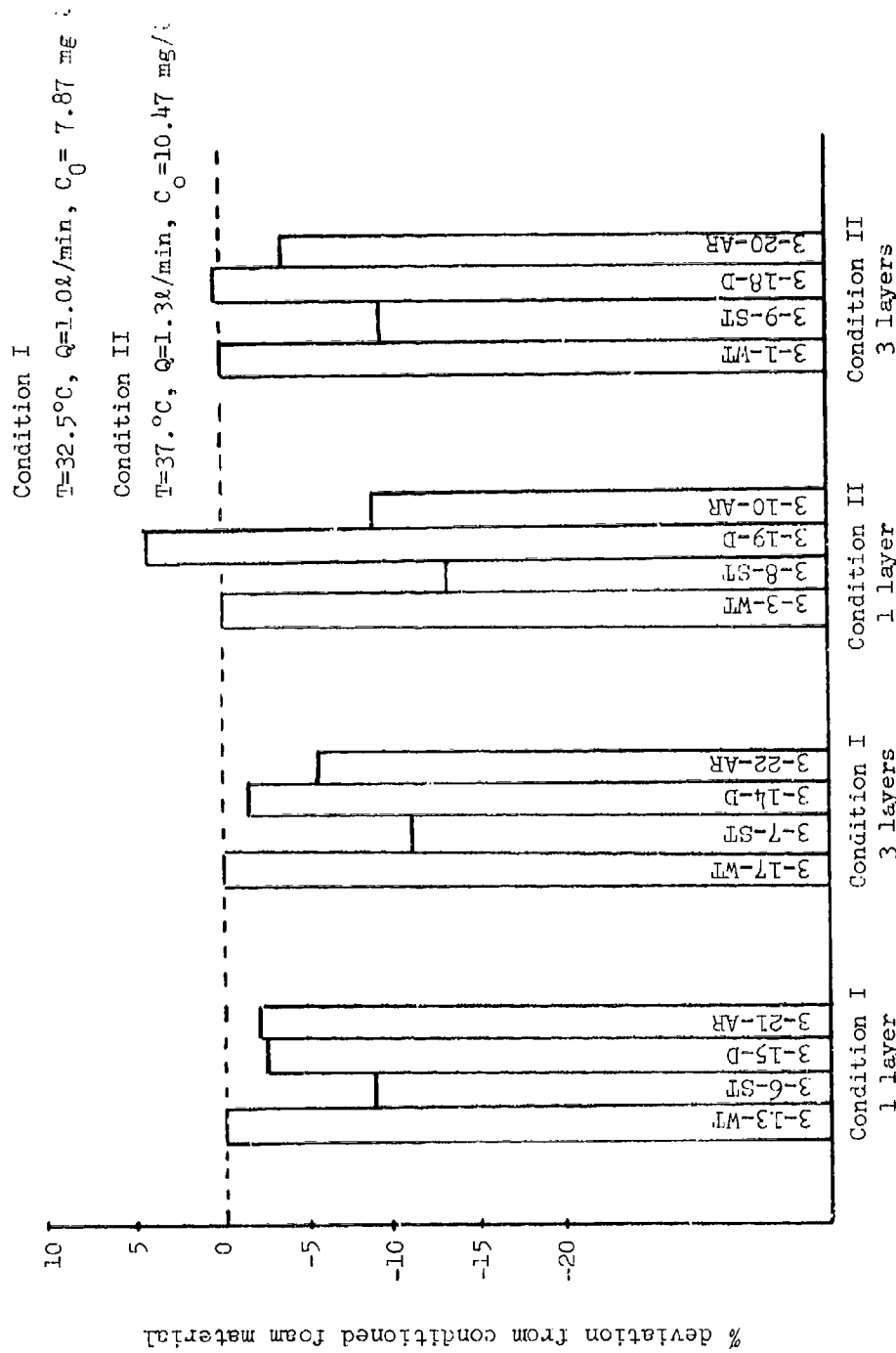


Figure 31. Evaluation of sweat poisoning comparison of K_A
 (for run conditions specified inside the bars, refer to Table A-7)

and treated with the solution of the appropriate component. Data for these experiments are tabulated in Table A-8. Breakthrough curves were then obtained and evaluated as discussed in the previous section. Figures 32 through 35 facilitate a comparison of the effects of sweat and its components on the significant properties of the foam material, namely M_t^* , M_b^* , t_b and K_A .

Examination of Figures 32 through 35 indicates that lactic acid most adversely affects the adsorption of carbon tetrachloride. Urea has no poisoning effect on the adsorption for one-layer runs and shows only a slight effect for three layer runs. Poisoning is sharply increased by changing Condition I ($T = 32.5^\circ\text{C}$, $Q = 1.9$ ℓ/min and $C_0 = 7.87$ mg/ℓ) to Condition II ($T = 37^\circ\text{C}$, $Q = 1.3$ ℓ/min and $C_0 = 10.4$ mg/ℓ).

At Condition I, sweat and sweat components decreased the total amount adsorbed, M_t^* , and amount adsorbed to break, M_b^* , by 5 - 15% of that of a conditioned sample. At Condition II, M_b^* decreased by 15% for three-layer runs and by 20 to 25% for one-layer runs by the addition of real sweat, lactic acid, high concentration of urea, and simulated sweat. The poisoning effect on t_b and M_b^* was a strong function of run conditions, but K_A and M_t^* did not show a strong dependence on run conditions.

Drying the samples soaked in high concentrations of lactic acid and urea did not improve t_b or M_b^* , but did increase K_A and M_t^* when these quantities were compared to non-dried samples treated with similar solutions. This seems to indicate that the adsorbed poisons are responsible for decreasing t_b and M_b^* , while the presence of water is partially responsible for the decrease in K_A and M_t^* for one-layer runs.

3. Effect of Sweat Treatment of Carbon Impregnated Foam Material on the Overall Adsorption Coefficient Model Parameters

It is of interest to observe the effect of sweat treatment on the overall adsorption coefficient model parameters (Part II). Figures 36, 37 and 38 show comparisons for nine runs and show the effect of sweat treated material, conditioned and dried material (Table A-9). The model prediction is shown as a solid line and the experimental data are plotted as symbols. All of these runs were on Bolt-3 material. Except for somewhat

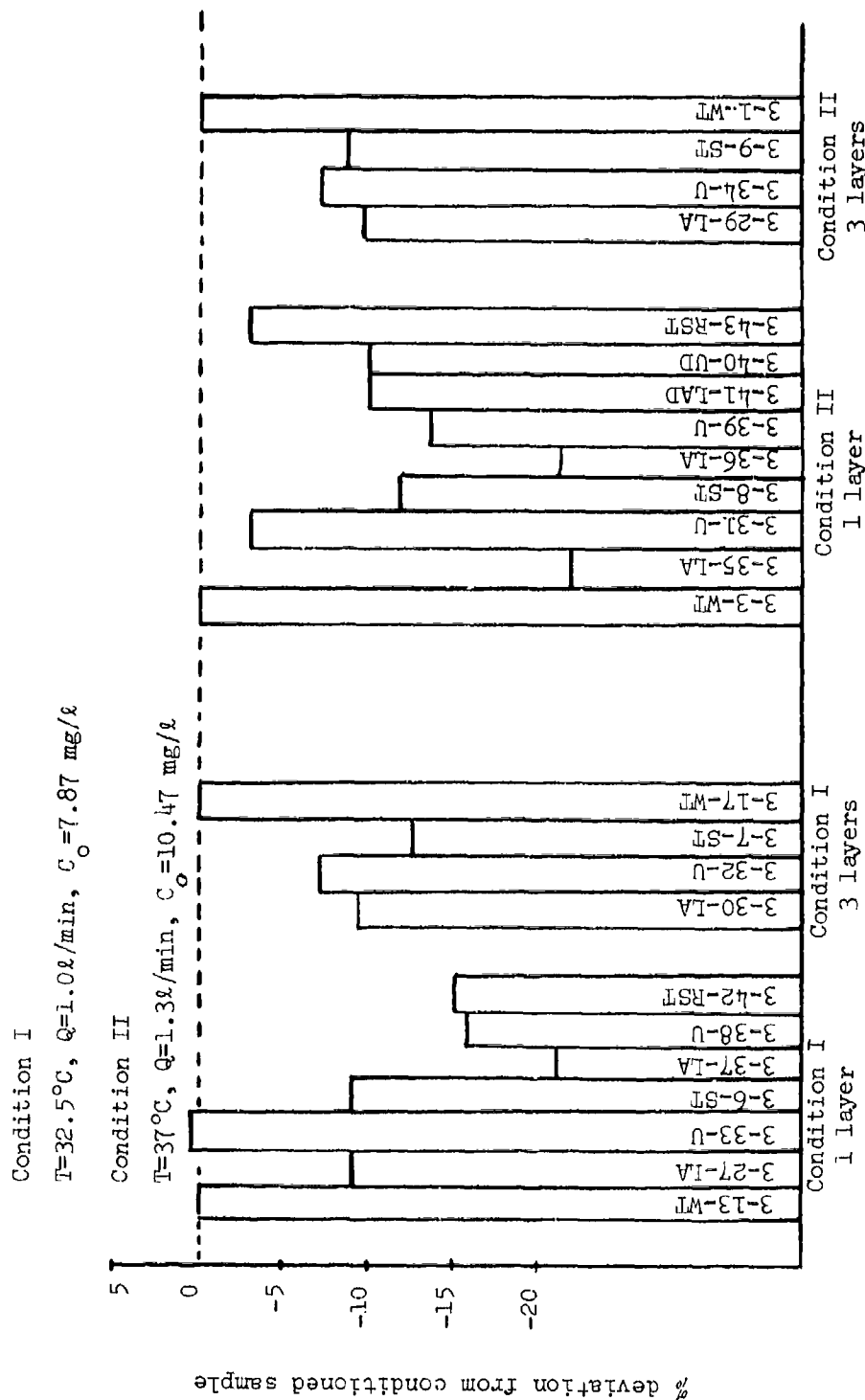


Figure 32. Evaluation of sweat poisoning comparison of M_t^*
 (for run conditions specified inside the bars, refer to Table A-8)

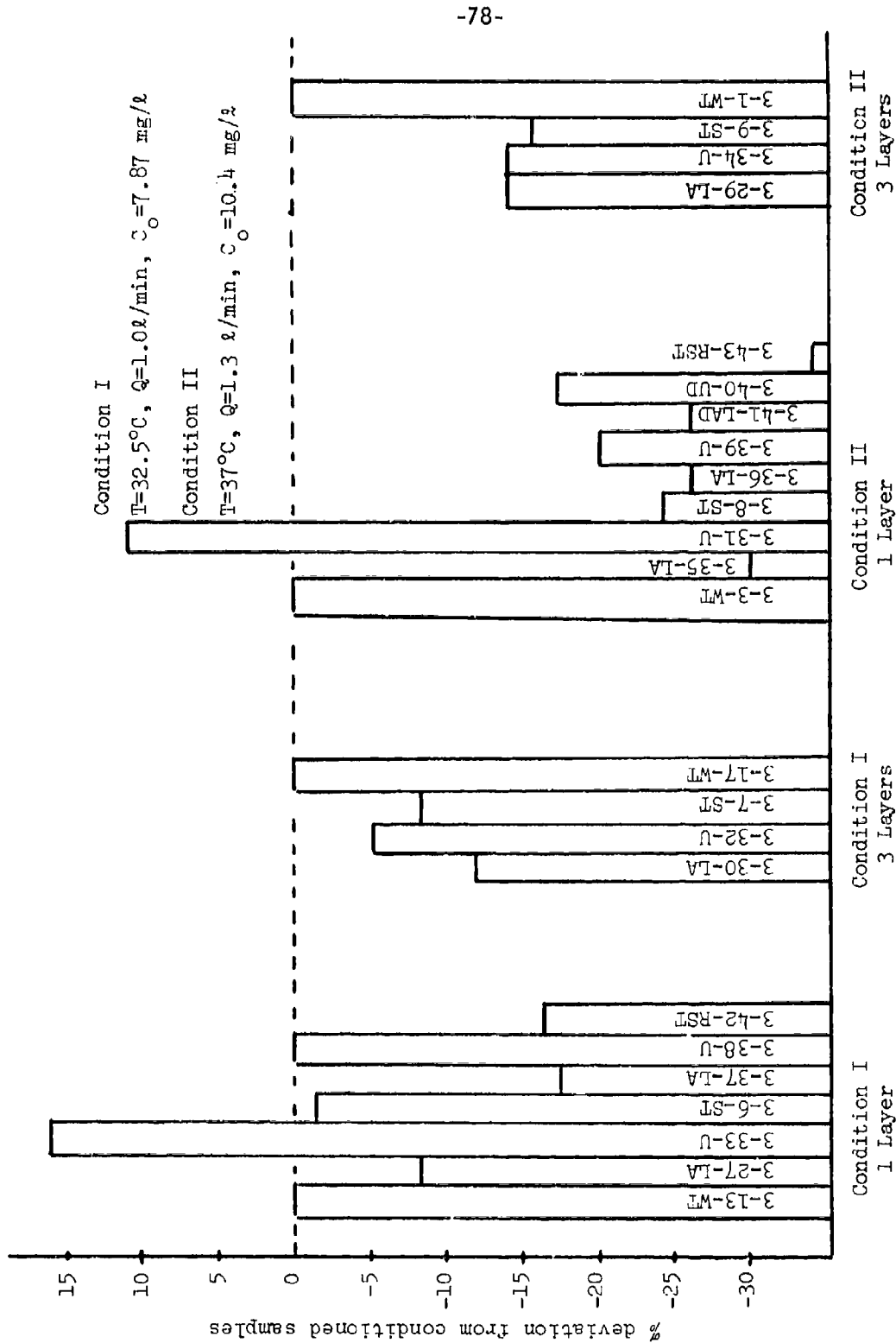


Figure 33. Evaluation of sweat poisoning, M_b^* (for run conditions specified inside the bars refer to Table A-8)

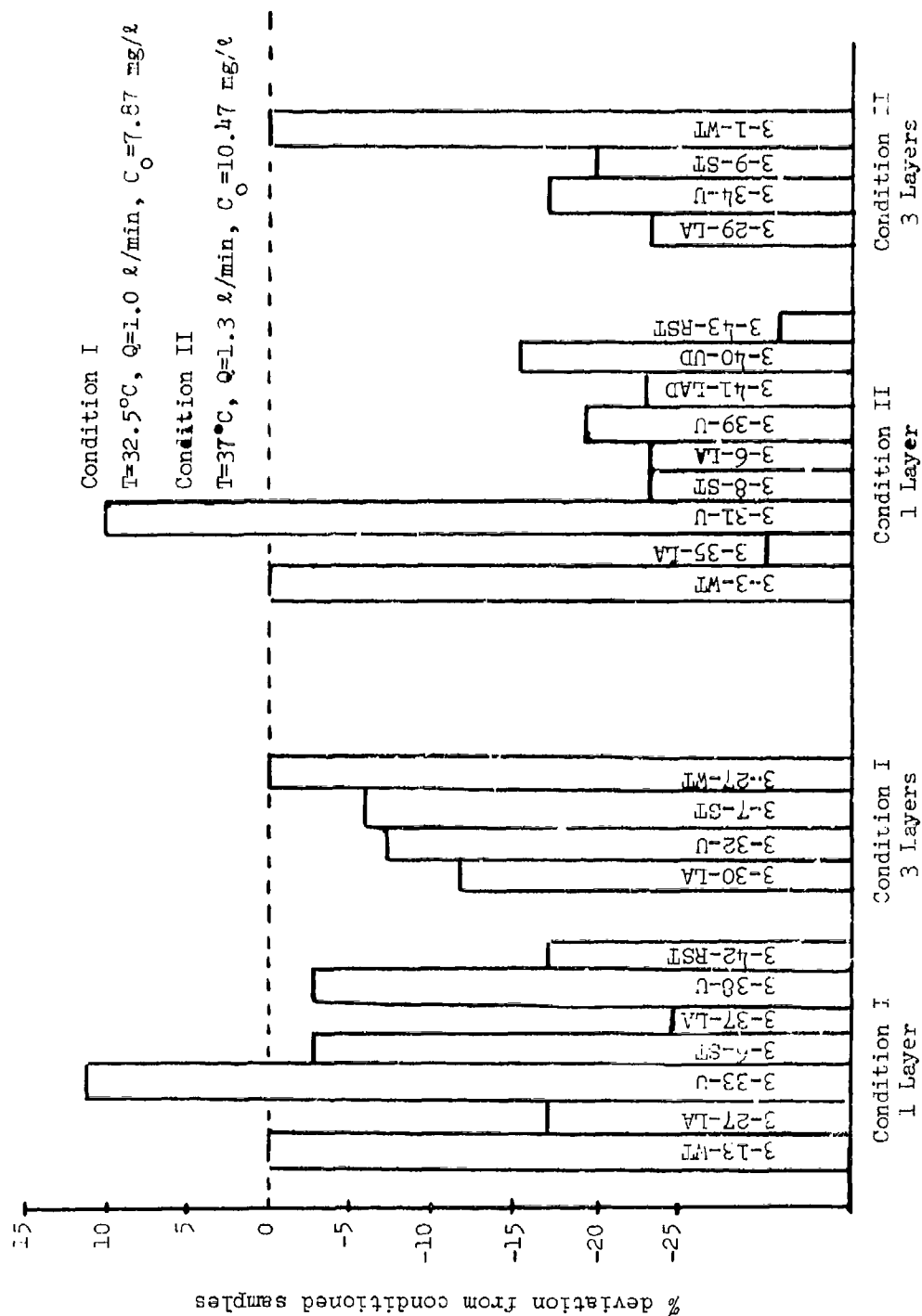


Figure 34. Evaluation of sweat poisoning comparison of t_b
(for run conditions specified inside the bars refer to Table A-8)

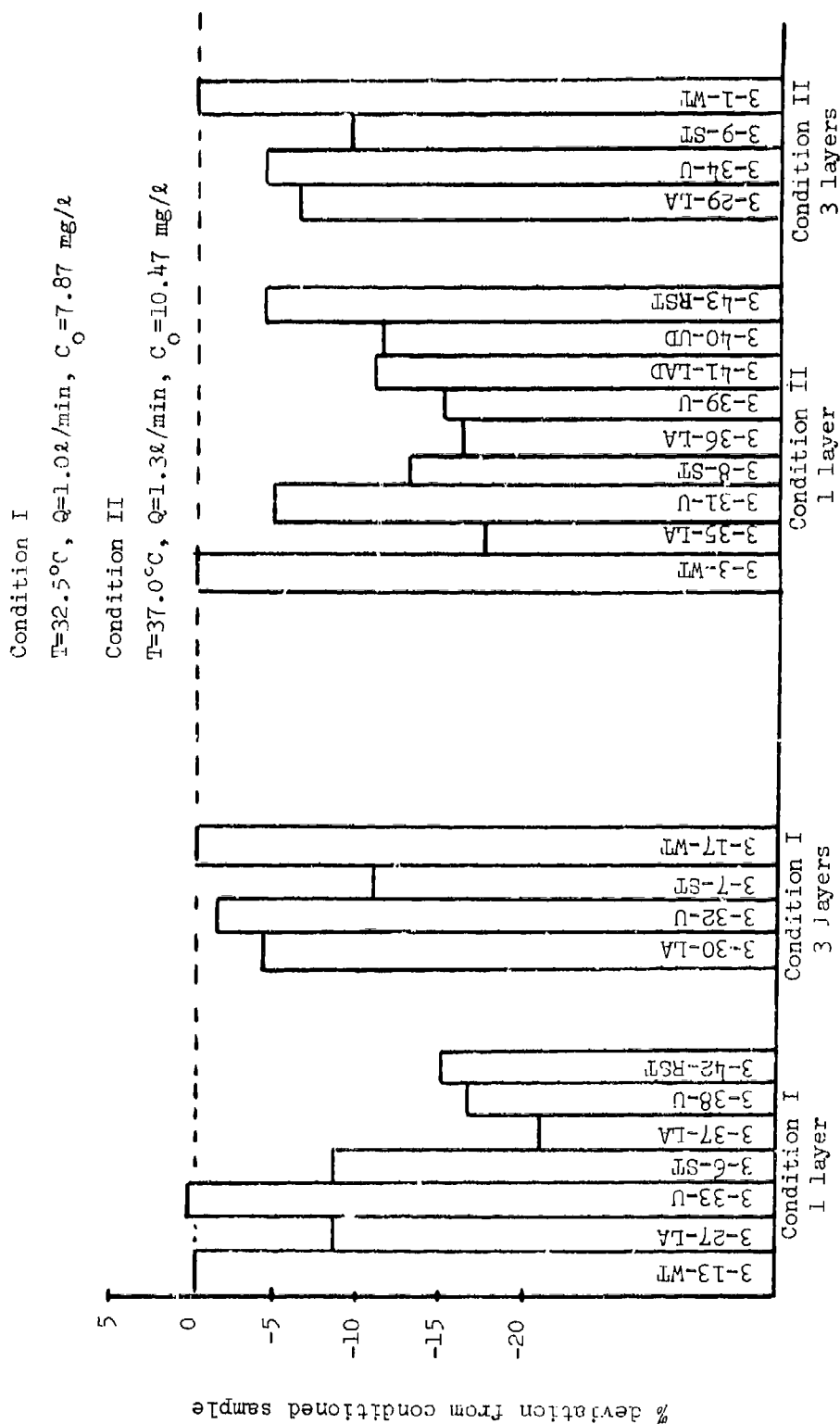


Figure 35. Evaluation of sweat poisoning comparison of K_A
 (for run conditions specified inside the bars, refer to Table A-8)

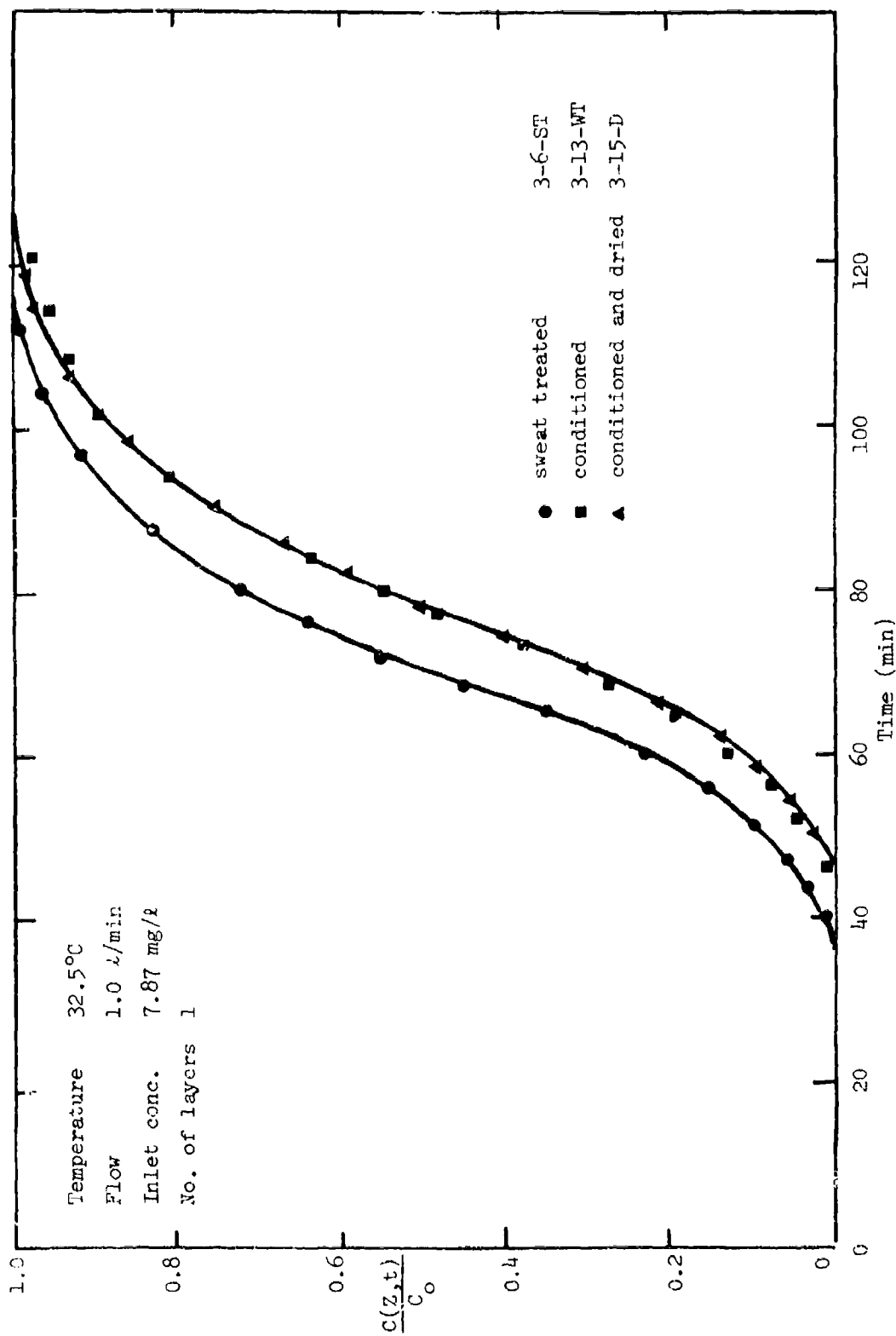


Figure 36. Overall adsorption coefficient model and experimental data for different conditionings

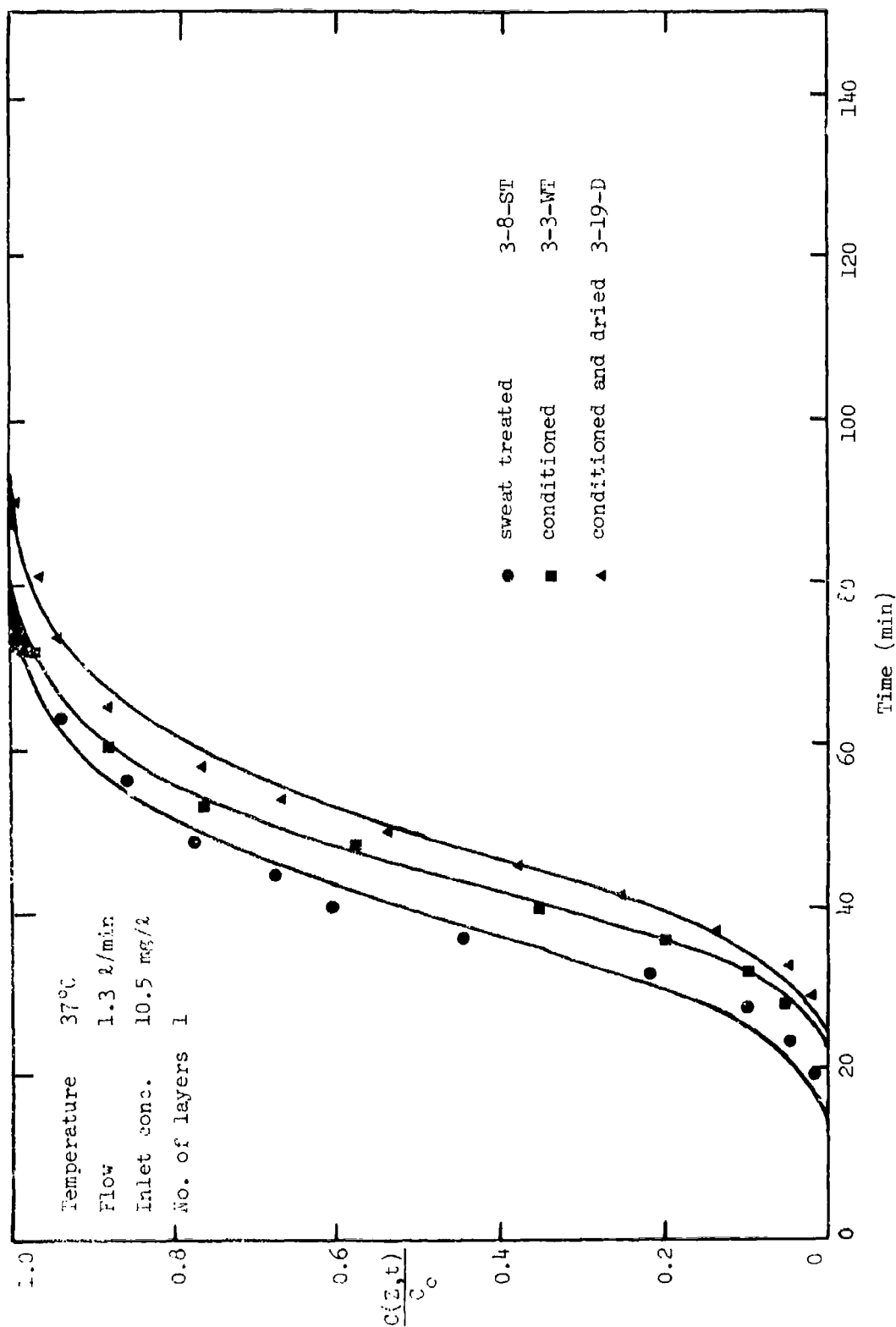


Figure 37. Overall adsorption coefficient model and experimental data for different conditionings

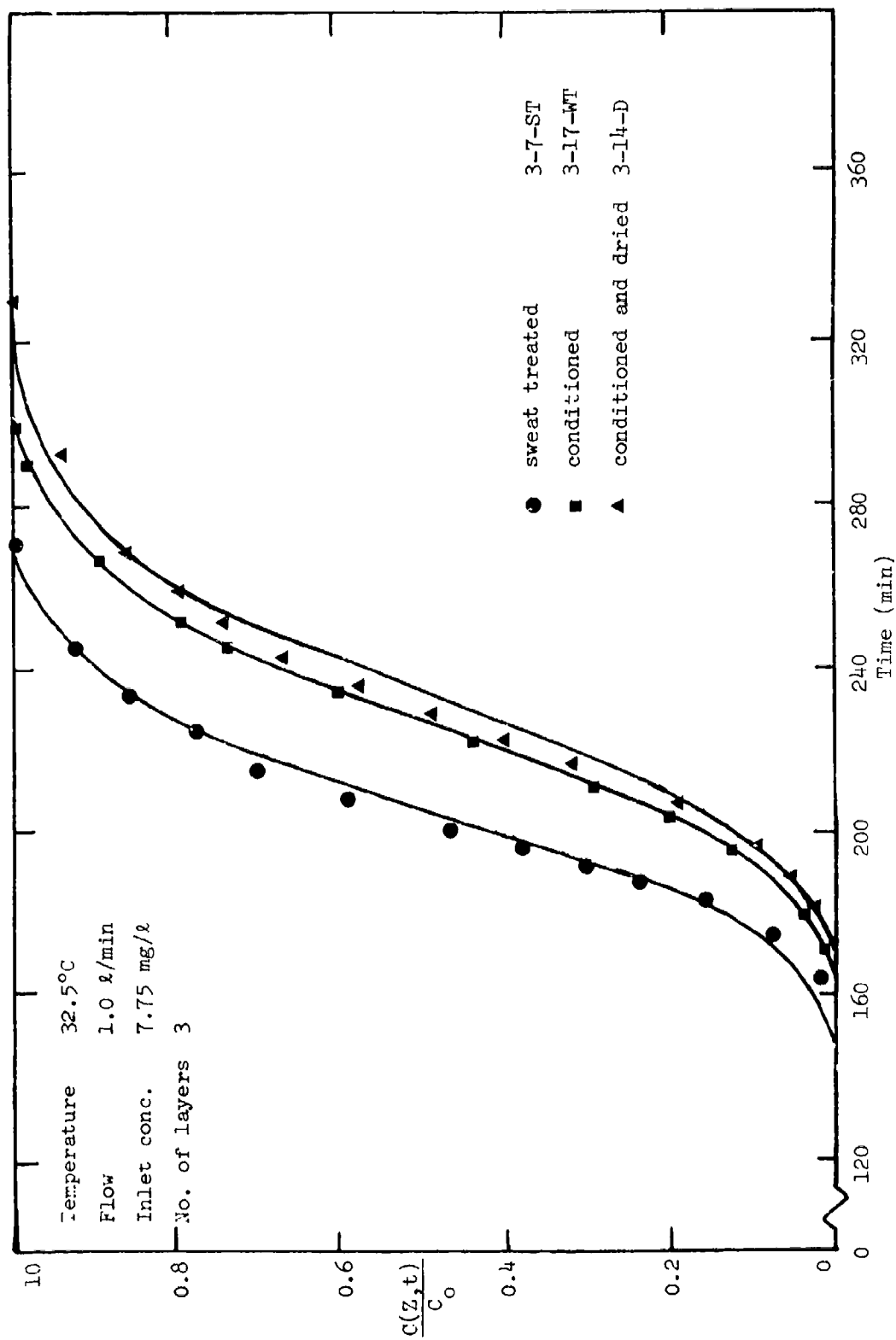


Figure 38. Overall adsorption coefficient model and experimental data for different conditionings

scattered data in Figure 37, the data fit is excellent. These results indicate that the model is adequate for correlating breakthrough curves in cases when the foam material's adsorptive capacity may have been altered by sweat poisoning, addition of water or removal of water. The run conditions in Figure 37 represent the upper range of flow rate and concentration used in this investigation, and the experimental scatter is probably due to the very rapid rise of the breakthrough curve coupled with limited sampling frequency. Since K_A and the rate parameter UA are calculated from the experimental data, the poor fit by the model in Figure 37 may be due to either inaccurate data or differences introduced due to various treatments. The model is helpful even with scattered data as it fits a smooth continuous curve through the experimental points. On changing the equilibrium adsorption constant, K_A , the characteristic shape of the curve is the same but the area under the $1 - \frac{C(z,t)}{C_0}$ versus t curve is different. This reflects a change in the total amount⁰ adsorbed, M_t^* , which is proportional to the area under the $1 - \frac{C(z,t)}{C_0}$ versus t curve and proportional to K_A . However, on changing UA the curve's characteristic shape is changed, but the area under the $1 - \frac{C(z,t)}{C_0}$ curve is unaltered. From these figures we observe that sweat treatment⁰ does not change the rate parameter UA , but significantly effects the equilibrium adsorption constant K_A and the total adsorption capacity.

The Effect of Sweat and its Constituents on the Dynamic Adsorptive Capacity of Carbon Impregnated Foam Material Upon Treatment Through an Applicator

Before beginning experiments on the development of an effective method of reducing sweat-poisoning of carbon impregnated foam material, a reproducible procedure for simulating the uptake of sweat by a garment from a wearer was devised. A discussion of the sweat applicator appears above.

Table A-10 includes data demonstrating that sweat treatment on the applicator reduces the total amount of CCl_4 adsorbed, M_t^* , by about 24% and the amount adsorbed to break, M_b^* , by about 50% when compared to conditioned cloth. For those runs the amount of sweat applied was not recorded. However, all samples were treated such that they were completely soaked with sweat. Drying the conditioned samples only slightly increased M_t^* but increased M_b^*

by 10%. These comparative results were consistent with previous runs on samples from other bolts of cloth.

Table A-11 includes data on tests resulting from other methods of sweat application. Carbon impregnated foam material was sweat treated on the applicator with a stream of air blowing over it to simulate a more realistic physical situation. The total amount of CCl_4 adsorbed, M_t^* , was reduced by 23.93% and the amount adsorbed to break, M_b^* , by 10.64% when compared to conditioned cloth. Samples were also treated with real sweat by placing samples on the human body (Table A-8). At a temperature of 32.5°C , flow of 1.0 ℓ/min and inlet concentration of 7.76 mg/ℓ , M_b^* , decreased by 16.55% and M_t^* decreased by 15.71%; however at a temperature of 37°C , flow of 1.3 ℓ/min and inlet concentration of 10.3 mg/ℓ , M_b^* , decreased by 33.89% while the decrease in M_t^* was about 5% when compared to conditioned cloth.

An extensive study of sweat and its constituent poisoning on the carbon impregnated foam material was done and the results are given in the next section as a comparative basis for control of sweat poisoning.

CONTROL OF SWEAT POISONING

The extent to which a garment can be affected by sweat depends upon a variety of factors including the level and duration of activity, environmental conditions of temperature, humidity, wind, and sun, as well as upon the type of clothing worn. Garments worn in direct contact with the skin may be expected to become soiled by sweat more rapidly and more completely than those which are separated from the skin by other layers of clothing.

With some understanding of the mechanisms involved in the poisoning of charcoal by skin secretion, it seems possible that a means of complete or partial prevention of sweat poisoning might be devised. The prospect of increasing the adsorptive capacity of the carbon impregnated foam material by some physical treatment (radiation) is a distinct possibility. A case of special interest, however, is that of a garment which, when worn under the carbon impregnated foam material, provides a shield against all but prolonged copious sweating. The loss of protective capability of the carbon impregnated foam material during wear in this situation is favored by the physical separation between the overgarment and the skin by an undergarment.

Increasing the Adsorptive Capacity of Carbon Impregnated Foam Material by Radiation Treatment

There has been some evidence that radiation treatment increases the adsorptive capacity of carbon. Experiments to test this hypothesis were planned and conducted for the carbon impregnated foam material. The results are shown in Table A-13. For these experiments, conditioned carbon impregnated foam material samples were used. The samples were irradiated in a cobalt-60 source at a rate of 0.43 megarads per hour for various lengths of time - 12, 24, and 72 hours. It was observed that both M_b^* and M_t^* increased up to the 24-hour irradiation exposure (total dose of 10.32 megarads) and then began to decrease (Figure 39). It is believed that the increase in M_b^* and M_t^* was due to the drying of the cloth caused by heat generated in exposure of the cloth to radiation. This was evident from a very small chromatographic water peak obtained when the treated cloth was used in break-

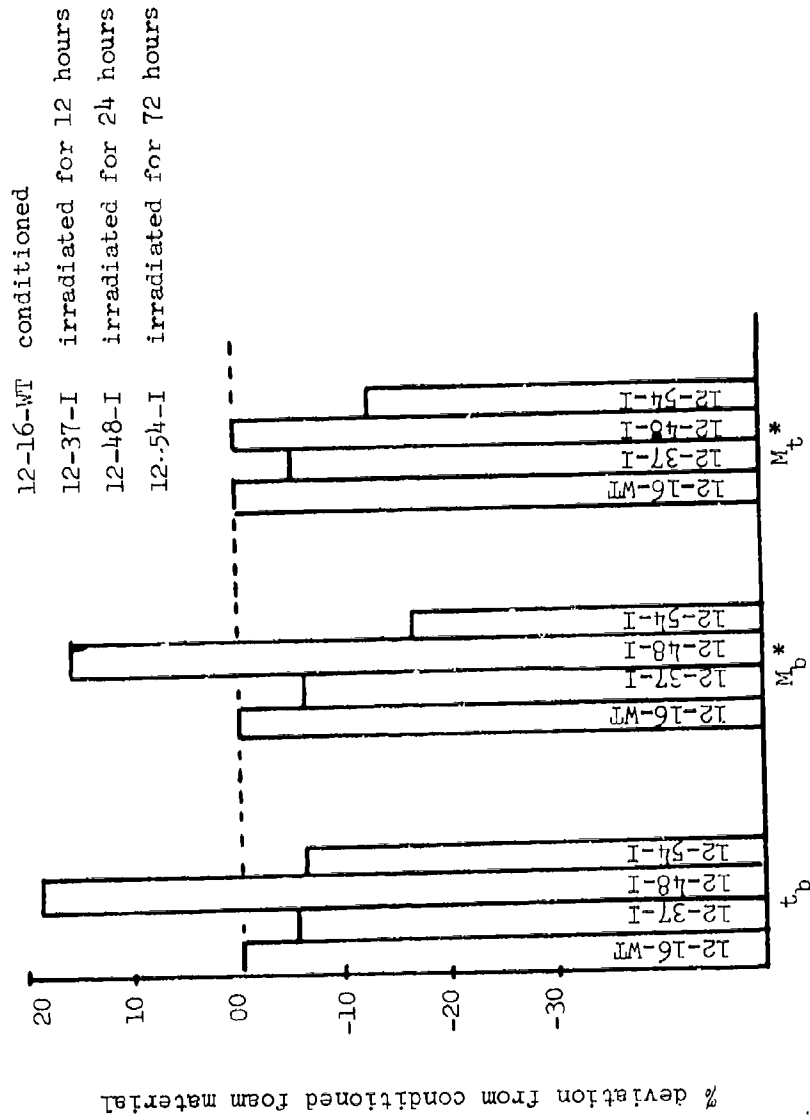


Figure 39. Comparison of irradiated conditioned foam samples (for run conditions specified inside the bars, refer to Table A-13)

through runs. The decrease in capacity after 24 hours of irradiation was attributed either to an alteration of sample structure, which adversely affects the adsorptive capacity, or to a degradation gas released from the foam which was then adsorbed by the active charcoal. There was no obvious change in the appearance of carbon impregnated foam material upon irradiation, however, after the 72 hours irradiation, the physical strength of the cloth was greatly reduced.

Development of an Undergarment for Selective Removal of the Primary Poisoning Agent in Sweat

The selective removal of the primary poisoning agent (lactic acid) in sweat was achieved by chemically modifying an undershirt material made from cotton cellulose through which the sweat must pass before it comes into contact with the carbon impregnated foam material. The cellulose fibers of the undershirt were given an ion exchange capability by grafting amino substituent groups (Hartman, 53) onto the cellulose molecule. The fabric structure was retained in the process and the chemically modified cellulose was an insoluble polymer having anion exchange functionality. In this form enormous surface for ion exchange is achieved^{54,55}.

The undershirt cotton fabric was chemically modified first by preparing diethyl aminoethyl cellulose. This was achieved by wetting the undershirt cotton fabric with a 10% aqueous solution of β -chloroethyldiethylamine: HCl, drying, and then mercerizing with a 25% solution of sodium hydroxide overnight at room temperature. The fabric was then thoroughly washed. The final form of modified fabric (a quaternary aminized cellulose and a Lewis base) was prepared by submerging diethyl aminoethyl cellulose in a boiling 10% solution of methyl iodide in absolute ethanol under reflux for two hours

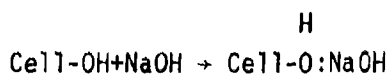
⁵³Hartman, M., Cellulose ethers and process of making, U. S. Patent 1, 77 77, 970 (1930).

⁵⁴Hoffpauir, C. L. and Guthrie. Ion-exchange characteristics of chemically modified cotton fabrics. Textile Research Journal, Vol. 20, No. 9, 617-620 (1950).

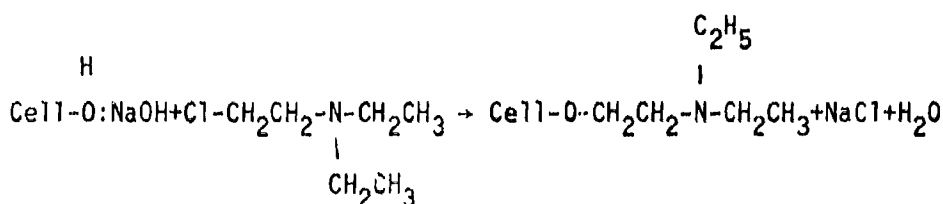
⁵⁵Reeves, W. A. and J. D. Guthrie. Aminization of Cotton. Textile Research Journal, Vol. 23, No. 8, 522-527 (1953).

following a procedure recommended by Jakubovic and Brooks⁵⁶ and McKelvey and Benerito⁵⁷. The mechanism for the formation of triethyl aminoethyl cellulose is shown below:

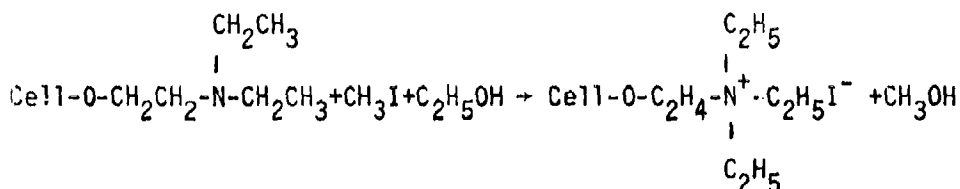
Step 1. Swelling and Mercerizing



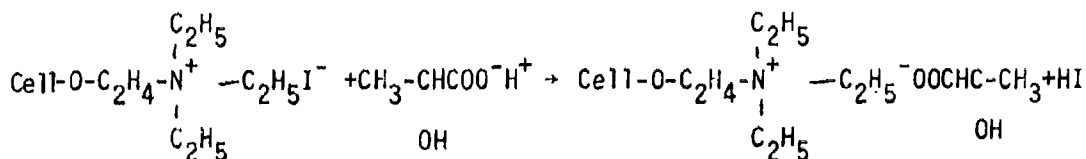
Step 2. DEAE-Cellulose Formation



Step 3. TEAE-Cellulose Formation



The ion exchange reaction which occurs between TEAE cellulose and lactic acid is



TEAE = Cellulose
(Lewis Base)

Lactic Acid
(Lewis Acid)

⁵⁶ Jakubovic, A. O. and B. N. Brooks. Anion exchangers based on cellulose: 1. Preparation and general properties. Polymer, Vol. 2, 19 (1961).

⁵⁷ McKelvey, J. B. and R. R. Benerito. Epichlorohydrin-triethanolamine reaction in the preparation of quaternary cellulose anion exchangers. J. of Applied Science, Vol. II, 1693-1701 (1967).

A series of runs was conducted to study the control of sweat poisoning by the chemically modified undergarment. The initial set of experiments consisted of one layer runs. All samples of carbon impregnated foam material were conditioned before being treated with lactic acid or simulated sweat. Both the lactic acid and sweat application of the carbon impregnated foam material samples were carried out on the applicator. Application consisted of either:

- (a) treating the carbon impregnated foam material by placing it directly on the applicator surface
- (b) treating the carbon impregnated foam material by placing an unmodified undershirt material between the applicator surface and the foam material sample
- (c) treating the carbon impregnated foam material by placing a modified (TEAE-cellulose) undershirt material between the applicator surface and the foam material sample.

Results of these experiments are shown in Figure 40 with data tabulated in Table A-14. All comparisons are made with respect to conditioned cloth. It can be seen that there was a substantial improvement in the breakthrough time of the carbon impregnated foam material treated with lactic acid with modified undergarment as compared with unmodified undergarment in place. An even more significant improvement in the breakthrough time was observed for the corresponding two cases with sweat treatment. Similar behavior is observed for M_b^* and M_t^* .

Two-layer runs of carbon impregnated foam material were also made (Figure 41). For this case, the treatment of the carbon impregnated foam with lactic acid or simulated sweat was done individually on each layer as described earlier. The two identically treated carbon impregnated foam samples were run together in the vapor test apparatus. All comparisons were made with two layers of conditioned cloth. Resulting data are shown in Table A-15. For the case of sweat treated carbon impregnated foam sample, the breakthrough time was considerably improved when modified undershirt material was used. A similar observation was made for M_b^* and M_t^* .

For the above analysis carbon impregnated foam samples were treated on the applicator with 100 ml of either a 1.0 g/l lactic acid solution or simulated sweat solution. The modified undergarment material had been



Figure 40. Evaluation of sweat poisoning for 1 layer runs (for run conditions specified inside the bars, refer to Table A-14)

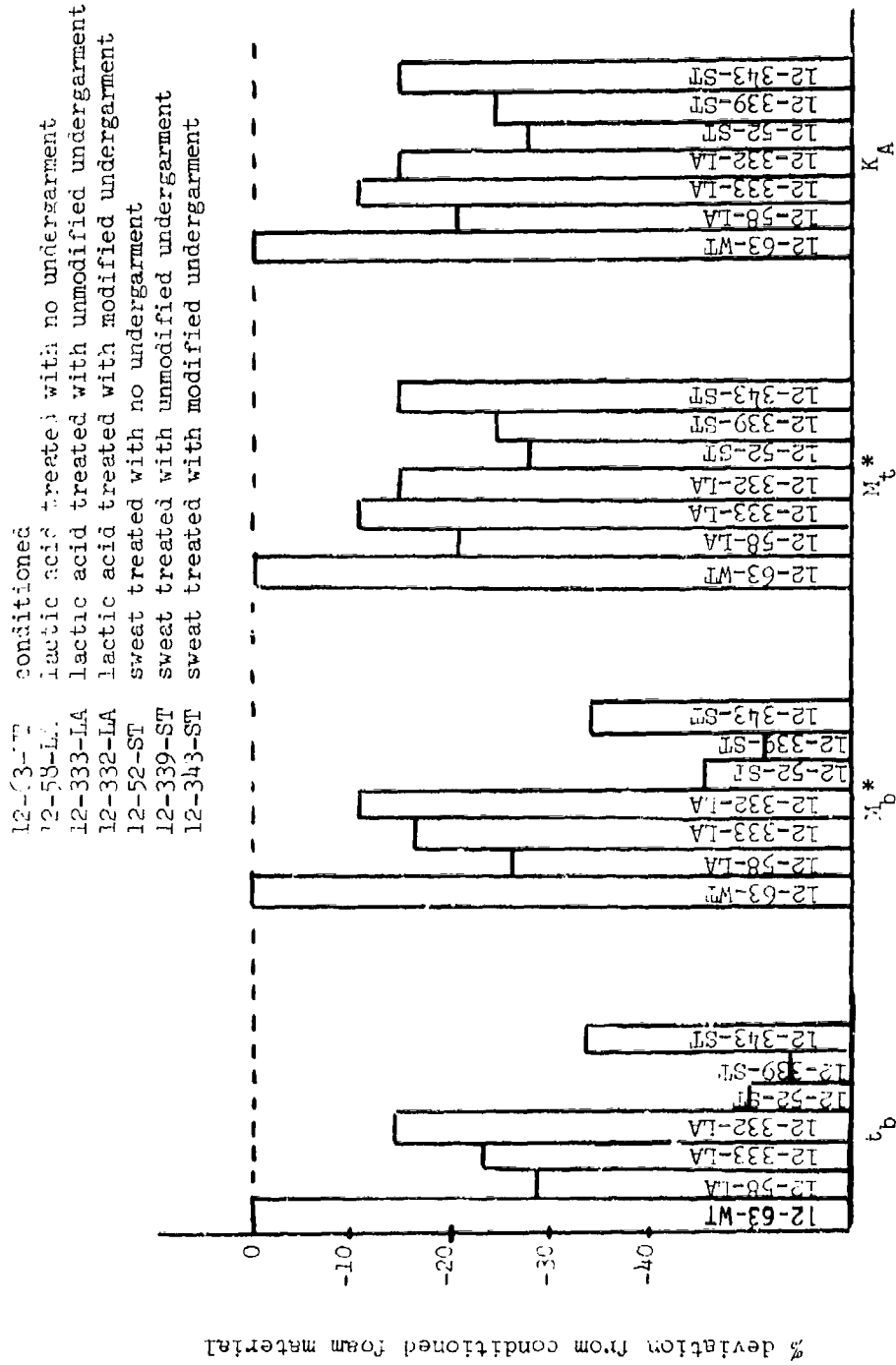


Figure 41. Evaluation of sweat poisoning for 2 layer runs
(for run conditions specified inside the bars, refer to Table A-15)

prepared as described earlier. The weight gain of the starting material was used to calculate the degree of substitution (number of substituent groups per monomer unit of cellulose) at the end of the aminization reaction to be 0.21; using the weight gain during the quaternization step, it was determined that 30.9% ($D.Q=0.309$) of the substituent groups were quaternized. Assuming only the quaternized amine groups are capable of removing lactic acid, the ion exchange capacity of the material is 0.34 meg/g material. With this capacity 4.5 g of the material should be able to remove all of the lactic acid in 138 ml of a 1.0 g/l solution of lactic acid. Samples of the material placed between the carbon impregnated foam and the sweat applicator weighed approximately 4.5 g. Samples of these calculation are given in Appendix B.

To obtain more conclusive results for the selective poisoning removal phenomena, a series of runs was conducted on two layers of carbon impregnated foam material. The new procedure involved the following:

Two layers of carbon impregnated foam material were conditioned, dried and run in the dynamic vapor test apparatus using the new sample holder. The two layers were then degassed by placing the sample holder in an oven at 50°C and blowing air for thirty minutes at 50°C through it. Another run was performed and the samples degassed. This procedure was continued until two successive runs were identical. The carbon impregnated foam samples were taken out of the sample-holder and treated on the applicator with either lactic acid or simulated sweat solution and run again in the dynamic vapor test apparatus. This method had the advantage of each treatment having its own independent reference.

In addition to the modification in procedure described in the preceding paragraph, the degree of substitution of the cotton cellulose undergarment was also improved by incorporating the following two changes in the synthesis procedure.

- (i) cotton cellulose was soaked in a 20% solution of NaOH overnight for swelling
- (ii) the concentration of methyl iodide in absolute ethanol was increased to 20% for the quaternizing step.

The degree of substitution on the undergarment fabric was 0.345 moles of amine substituent/mole of cellulose monomer unit; the degree of quaternization was 0.365 moles of quaternized amine/mole of total amine.

Again assuming only the quaternized amine to be effective in lactic acid removal, this material was calculated to have a capacity of 0.58 meq/g of material.

To work with what seemed like more realistic conditions, the total amount of sweat passed through the applicator was reduced from 100 ml to 20 ml. A summary of the results obtained is shown in Table A-16 which also includes the independent reference for each type of treatment. Figure 42 facilitates a comparison of the effects of lactic acid and sweat treatment on the significant dynamic properties of the carbon impregnated foam material, namely t_b , M_b^* and M_t^* . These adsorptive properties were improved for both lactic acid and sweat application to the carbon impregnated foam material sample when modified undergarment was used. For sweat treated carbon impregnated foam samples the breakthrough times were 90%, 70%, and 55% of sweat-free values when the application was done with modified undergarment, unmodified undergarment, and no undergarment, respectively. For lactic acid treated carbon impregnated foam samples, the breakthrough times were 90%, 80%, and 60% of sweat-free values when the application was done with modified undergarment, unmodified undergarment, and no undergarment, respectively. A similar increase in M_b^* for sweat and lactic acid treatment was observed. The total amounts of CCl_4 adsorbed, M_t^* , were 97%, 70%, and 65% of the sweat-free quantity when sweat application was done with modified undergarment, unmodified undergarment, and no undergarment, respectively.

For lactic acid treatment, M_t^* was 90%, 85% and 80% of the sweat-free value when treatment was through modified undergarment, unmodified undergarment, and no undergarment, respectively.

During the synthesis of the aminized cellulose there was considerable shrinkage of the undergarment material. This meant appreciable variation in the mass of material placed between the sweat applicator and carbon impregnated foam when comparing modified and unmodified material. It is unclear, therefore, whether modified material improved the adsorptive properties by the ion exchange mechanism or by a simple increase in moisture retention.

12-XXX-WT3 independent reference for each sample
 12-351-LA lactic acid treated with no undergarment
 12-353-LA lactic acid treated with unmodified undergarment
 12-355-LA lactic acid treated with modified undergarment
 12-357-ST sweat treated with no undergarment
 12-350-ST sweat treated with unmodified undergarment
 12-358-ST sweat treated with modified undergarment

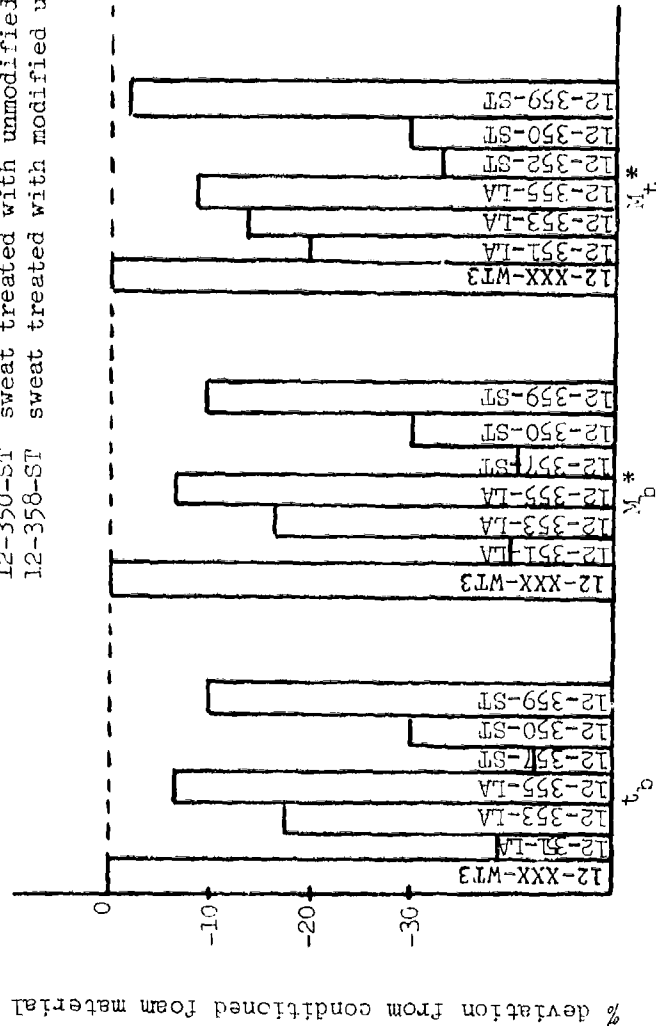


Figure 42. Evaluation of sweat poisoning for 2 layer runs each with its own independent reference (for run conditions specified inside the bars, refer to Table A-16)

CONCLUSIONS AND RESULTS

This report presents a study of the adsorption of carbon tetrachloride vapor by several different protective clothing materials both alone and in the presence of simulated sweat and the various components of sweat. A carbon impregnated foam material was used for most of the work, however, several other materials were tested and compared for breakthrough and adsorptive capacity and these are discussed in Appendix A. A mathematical model for the breakthrough time was developed.

While the breakthrough time model is not limited to a complex adsorption system - like the carbon impregnated foam - its chief advantage is that it is simple and reasonably accurate. Even though it is possible to predict the breakthrough time from several of the fixed-bed adsorption models that have been proposed, it is necessary that all model parameters be evaluated experimentally; using these models for predicting breakthrough time is somewhat time consuming because the breakthrough time must be found by numerical integration of the model.

The proposed model suggests that the breakthrough time varies directly as the number of carbon impregnated foam layers or bed depth and indirectly as the gas flow rate and inlet gas concentration. It works well for the carbon-impregnated foam in the ranges of inlet adsorbate concentration, flow rate and bed depth used. Some of the model parameters almost certainly are functions of temperature but, due to the small temperature range examined experimentally, statistically significant variations of the parameters with temperature were not observed.

Extension of this model to systems using well defined spherical adsorbents should be no problem. By setting up a few experiments, one can determine the model parameters for a given adsorbate-adsorbent system. With this information one can make predictions as to what will happen to the breakthrough time on varying the inlet adsorbate concentration, flow rate and bed depth. Hence with this simple approach, the dynamics of adsorption up to the breakthrough time can be characterized mathematically.

Laboratory experiments were conducted to examine the influence of sweat and sweat components on the adsorptive properties of carbon impregnated foam. A number of substances were selected as representative of the principal constituents of sweat and the effect of each upon the capacity

of the foam to adsorb carbon tetrachloride was determined by addition to the sample. The organic constituents of sweat were shown to be mainly responsible for poisoning. A comparison of poisoning by the individual components of simulated sweat showed that lactic acid was most severe in reducing the total amount of carbon tetrachloride adsorbed under both equilibrium and dynamic conditions.

The following results are a comparison with conditioned samples at $T = 32.5^{\circ}\text{C}$, $Q = 1.0 \text{ l/min}$ and $C_o = 7.87 \text{ mg/l}$. For foam samples soaked in various solutions overnight, sweat treatment consistently decreased the total amount adsorbed by about 10% but affected M_b^* according to run conditions. For lactic acid treatment, the total amount adsorbed, M_t^* , and the amount adsorbed to break, M_b^* , were reduced by 10 - 15%. When the solution application was done through an applicator, the total amount adsorbed, M_t^* , and the amount adsorbed to break, M_b^* , were reduced by 12% and 24% for lactic acid treatment, while for sweat treatment, the reduction was 22% and 45%, respectively. For experiments where each two-layer run had its own independent conditioned reference, the total amount adsorbed, M_t^* , and the amount adsorbed to break, M_b^* , were both reduced by 20% and 39% for lactic acid treatment and 33% and 40% for sweat treatment.

Information was also obtained by treating samples with real sweat. This was achieved by placing samples on the human body until they were well soaked in sweat. The results indicated a slightly more severe poisoning effect than simulated sweat.

To reduce the deleterious effects of sweat on the adsorptive capacity of the foam, two processes were considered:

- (a) Increasing the capacity of the existing foam by radiation treatment. Results of these experiments were inconclusive.
- (b) Selective removal of the primary poisoning agent in sweat (lactic acid). This was achieved by chemically modifying a cotton cellulose undershirt material, through which sweat must pass before coming in contact with the foam, to give it ion exchange properties. The modification consisted of grafting basic substituents (amine groups) to the cellulose molecule of the undershirt material under such conditions that the fabric structure was retained. The cellulose, thus chemically modified, functioned as an anion-exchanger.

The results of these experiments are very encouraging. The adsorptive properties of the foam were greatly improved when sweat treatment was done through a modified undergarment rather than an unmodified undergarment. For sweat treated carbon impregnated foam samples the breakthrough times were 90%, 70% and 55% of the sweat-free value when the application was done with modified undergarment, unmodified undergarment, and no undergarment, respectively. For lactic acid treated carbon impregnated foam samples, the breakthrough times were 90%, 80% and 60% of the sweat-free value when the application was done with modified undergarment, unmodified undergarment, and no undergarment, respectively. A similar rise in M_b^* for sweat and lactic acid treatment was observed. The total amount of CCl_4 adsorbed, M_t^* , was 97%, 70%, and 65% of the sweat-free amount when sweat application was through modified undergarment, unmodified undergarment, and no undergarment, respectively. For lactic acid treatment, M_t^* was 90%, 85%, and 80% of the sweat-free quantity with modified undergarment, unmodified undergarment, and no undergarment, respectively.

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LIST OF SYMBOLS

$\bar{A}$	constant defined as $-\frac{j}{kC_0} \ln \left(\frac{C_0}{C_b} - 1 \right)$, min
A_f	flow area of foam sample, cm^2
$\bar{B}$	constant defined as $N_0 j A_f \alpha$, mg/cm
C	concentration of adsorbable gas in the interparticle space, mg/l
C_{ads}	concentration of adsorbed gas per unit weight of adsorbent, mg CCl_4 /g particle
C_b	breakthrough time concentration ($\frac{C_b}{C_0} = 0.05$), mg/l
C_0	inlet concentration of adsorbate, mg/l
j	defined as $\delta \rho_m / \alpha$ or $\rho_p \frac{1-\epsilon}{\alpha}$
k	adsorption rate constant of breakthrough time model, g particle/(mg CCl_4 -min)
K_A	adsorption equilibrium constant, ml/g foam material
M_b	amount of CCl_4 adsorbed to break, mg CCl_4
M_b^*	amount of CCl_4 adsorbed to break per unit weight of sample, mg/g
M_0	zeroth moment of t vs. $(1 - \frac{C}{C_0})$ curve, min
M_T	total weight of CCl_4 adsorbed, mg CCl_4
M_T^*	total weight of CCl_4 adsorbed per unit weight of sample, mg/g
M_1	first moment, min^2
M_2	second moment, min^3
N_0	capacity of adsorbent, mg CCl_4 /g particle or the number of active centers of unit activity per unitweight of sample
n	sample weight normalizing factor Equation 30, g/g
Q	flow rate through sample, l/min
T	temperature of sample and adsorbate, $^{\circ}\text{C}$
t	time, min

t_b	breakthrough time, time when the exit concentration reached five percent of that at the inlet, min
t_1	defined by Equation 23, min
$\frac{1}{UA}$	overall adsorption coefficient, cc CCl_4 /g foam-min
V	interstitial velocity, cm/min
v	volume of sample
v_s	volume of solids in sample
W_f	dry weight of sample
W_t	sample weight after conditioning, g
z	length coordinate of the bed of adsorbent, cm

Greek Letters

α	cloth porosity (void volume/total volume)
δ	weight of particles per unit weight of foam material
c	void fraction representing the bed volume not occupied by carbon particles divided by the total volume
ρ_m	apparent density of foam material g solids/cc total volume
ρ_p	apparent particle density, g carbon/cc carbon
τ	residence time, Equation 26, min
τ_f	fictitious residence time, Equation 29, min

APPENDIX A

Data on Various Types of Adsorbent

Experimental evaluation of the adsorptive properties of several samples of cloth presented by the Natick R & D Command is reported and discussed in this section. The three independent variables which influence CCl_4 adsorption are temperature (T), concentration of the CCl_4 in the inlet gas stream (C_0), and flow rate through the sample (Q). A central composite statistical design of experiments was set up to determine quantitatively the effects of these variables on both adsorption kinetics and equilibrium. The design is illustrated in Figure A-1 which shows the approximate levels of each variable investigated. The data from these experiments (Bolt-2) was used to correlate the breakthrough time with the measurable parameters T, C_0 , Q and number of carbon impregnated foam layers. All the data used in the statistical analysis are summarized in Tables A-3 through A-5.

The characteristics of the Bolt-4 carbon impregnated foam material had lower breakthrough time and capacity than Bolt-3 material (Table A-6). The characteristics of Bolt-4 material were evaluated in several runs which are summarized in Table A-7. This bolt of cloth was primarily used for studying the removal of sweat poisoning, while Bolt-3 was used for isolating the constituent of sweat that poisoned the carbon impregnated foam material. Bolt 1 was used in testing the experimental apparatus.

Of the various other cloth samples tested (carbon fiber and carbon impregnated fabric), after being conditioned, only the British cloth seemed to compare favorably with the charcoal impregnated foam material. The two types of British cloth, P99 and A46C54, adsorbed approximately the same amount of CCl_4 per layer as the foam material (Figure A-2), and on a weight basis the British cloth adsorbed more than twice as much CCl_4 as the foam material (Figure A-3).

One-layer runs of British cloth had much faster breakthrough than the foam material, but the cloth compared favorably with the foam material on breakthrough time (Figure A-4) for three-layer runs.

Pluton B-1 and Nomex-Cotton-Carbon composite were the most promising of the other fabrics tested, although neither compared favorably with the foam material or British cloth. The quilted fabric (VEE 3098) showed very little adsorptive capacity with immediate breakthrough for both one- and three-layer runs.

A complete summary of the results on this material is given in Table A-15.

$$Y = f(T, C, Q)$$

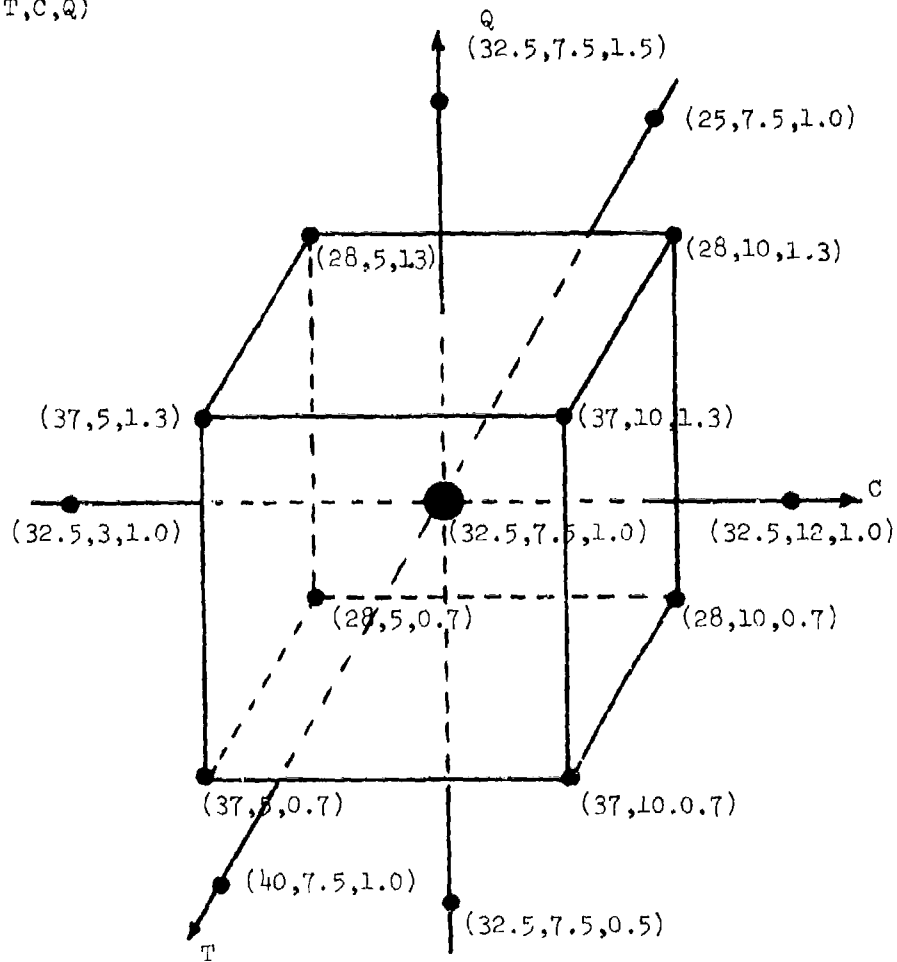


Figure A-1. Central composite statistical experiment design

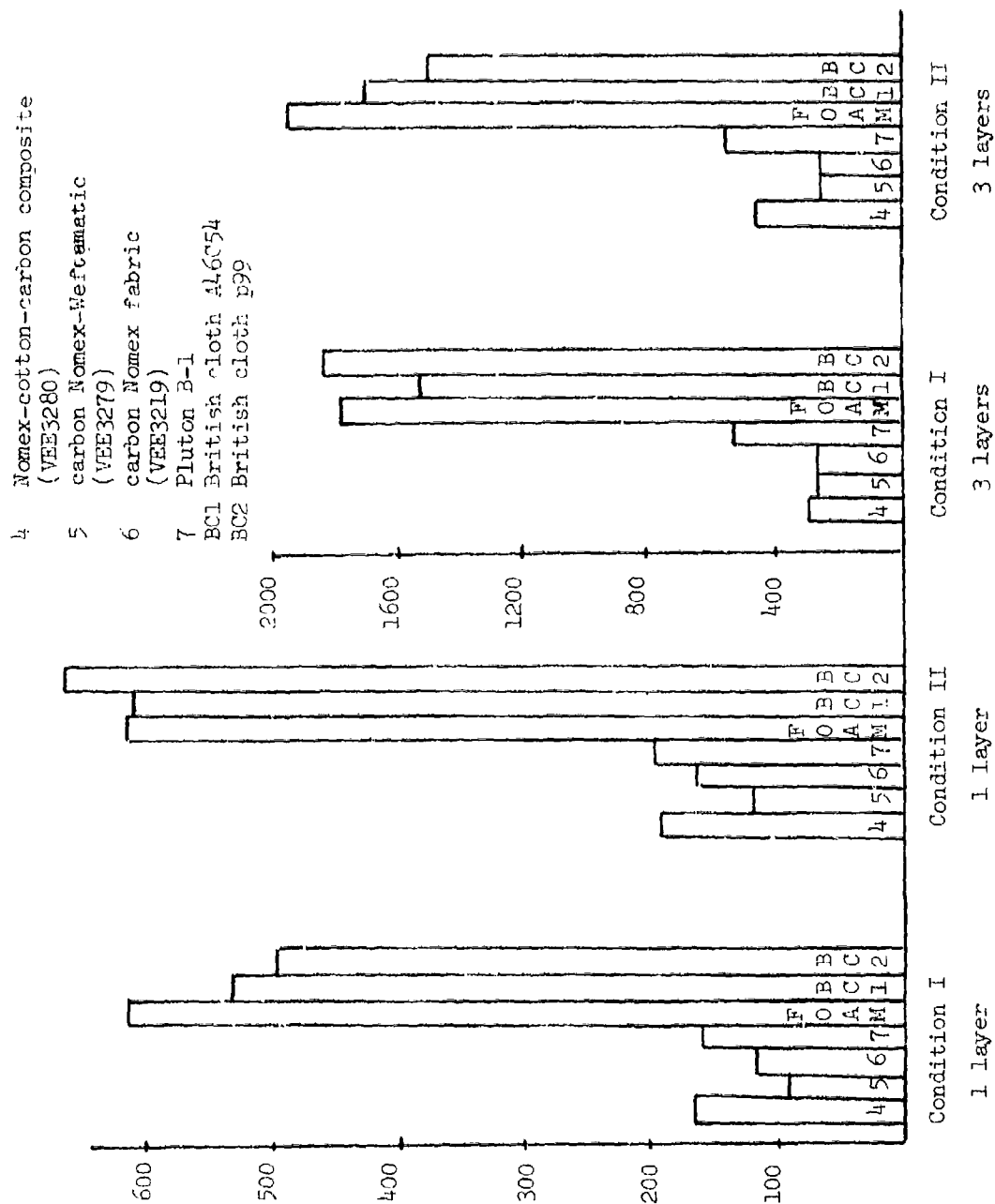


Figure A-2. Comparison of mg CCl_4 adsorbed for various fabrics (for run conditions specified inside the bars, refer to Table A-17)

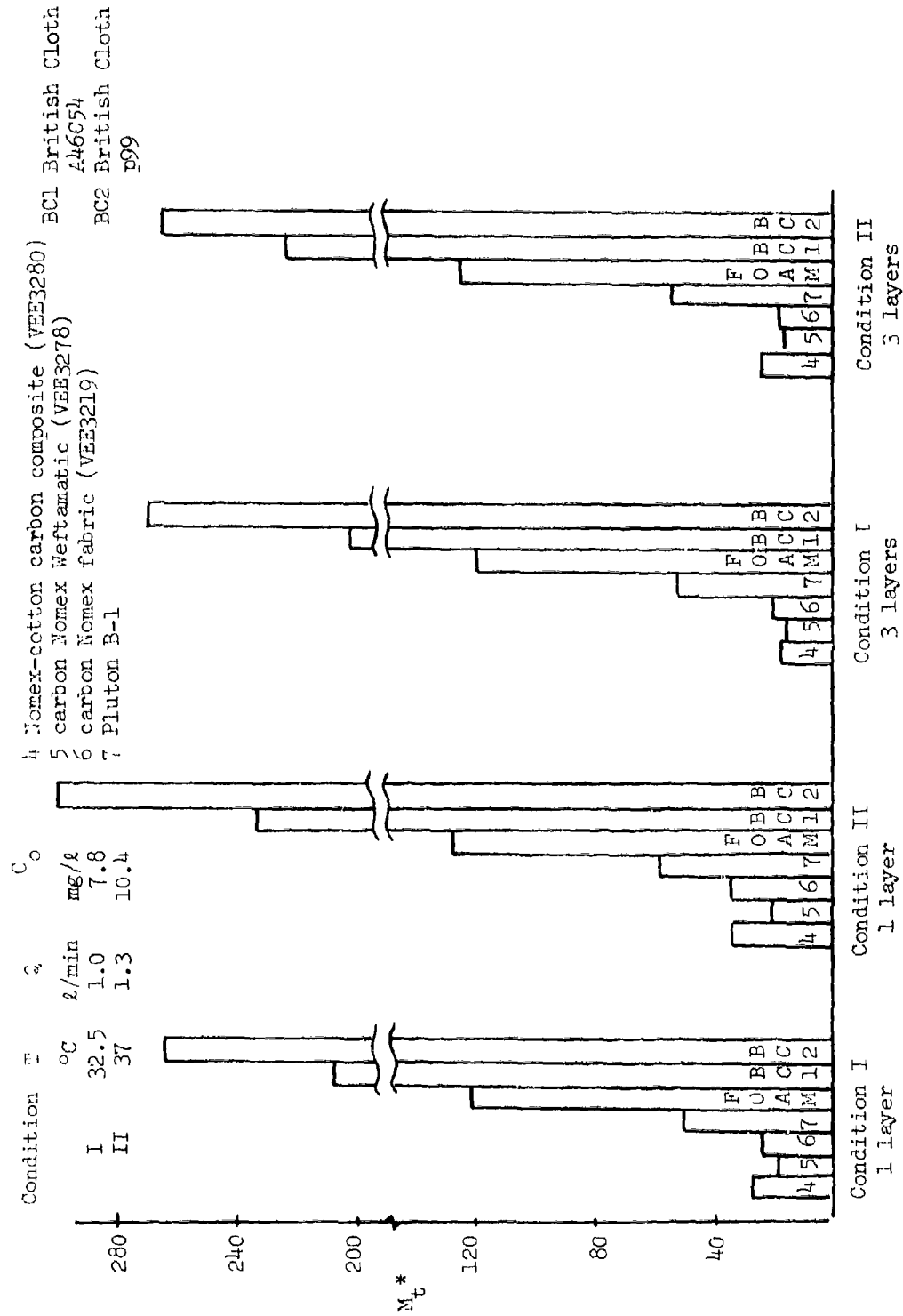


Figure A-3. Comparison of M_t^* for various fabrics
 (for run conditions specified inside the bars, refer to Table A-17)

Figure A-4. Comparison of breakthrough time for various fabrics (for run conditions specified inside the bars, refer to Table A-17)

Table A-1. Summary of Results for Bolt-1 Material

Run No.	No. of Layers	Cloth Type	Flow l/mir.	Co mg/l	t _b Min.	M _b mg	M _t mg	Wt. of Cloth Sample g	$\frac{M_b^*}{\text{mg CCl}_4}$ g cloth	$\frac{M_t^*}{\text{mg CCl}_4}$ g cloth
1-34-2	1	as rec'd	0.58	10	28	162.5	321	5.19	31.3	62
1-34-3	2	as rec'd	0.58	10	60	348	536	9.09	38.3	59.1
1-34-4	3	as rec'd	0.58	10	88	510	775	13.62	37.4	56.9
1-35-3	1	conditioned	1.0	10	7.5	75	322	4.69	16.0	68.7
1-35-2	2	conditioned	1.0	10	33	330	640	9.77	33.8	65.5
1-35-6	3	conditioned	1.0	10	82	820	1100	14.76	55.5	75.0
1-35-5	1	conditioned dried	1.0	10	18.5	185	354	5.07	36.5	69.5
1-35-4	2	as rec'd	1.0	10	36	360	648	9.54	38.7	68.0
1-35-1	2	conditioned	0.58	10	50	290	570	9.62	30.1	59.3

NOTE: M_b = amount adsorbed to breakthrough (mg CCl₄)M_t = total adsorbed (mg CCl₄)M_b^{*} = amount adsorbed to breakthrough (mg CCl₄/g cloth)M_t^{*} = total amount adsorbed (mg CCl₄/g cloth)

Table A-2. Comparisons for Bolt-1 Material.

Effect of Flow in Conditioned Cloth

<u>Run No.</u>	<u>Layers</u>	<u>Flow</u>	<u>M_b</u>	<u>M_t</u>	<u>M_b[*]</u>	<u>M_t[*]</u>
1-35-1	2	0.58	290 mg	570	30.1	59.3
1-35-2	2	1l/min	330 mg	640	33.8	65.5

Effect of Flow on Cloth as received

<u>Run No.</u>	<u>Layers</u>	<u>Flow</u>	<u>M_b</u>	<u>M_t</u>	<u>M_b[*]</u>	<u>M_t[*]</u>
1-34-3	2	0.58	348	536	38.3	59.1
1-35-4	2	1l/min	360	648	38.7	68.0

Effect of Conditioning

<u>Run No.</u>	<u>Layers</u>	<u>Flow</u>	<u>M_b (mg)</u>	<u>M_t</u>	<u>M_b[*]</u>	<u>M_t[*]</u>	<u>Treatment</u>
1-35-4	2	1l/min	360	648	38.7	68.0	as rec'd.
1-35-2	2	1	330	640	33.8	65.5	cond.
1-34-3	2	0.58	348	536	38.3	59.1	as rec'd.
1-35-1	2	0.58	290	570	30.1	59.3	cond.

Effect of drying cond. cloth

<u>Run No.</u>	<u>Layers</u>	<u>Flow</u>	<u>M_b</u>	<u>M_t</u>	<u>M_b[*]</u>	<u>M_t[*]</u>	<u>Treatment</u>
1-35-5	1	1	185	354	36.5	69.5	cond. dried
1-35-3	1	1	75	322	16.0	68.7	cond.

Table A-3 One Layer Runs, Second Bolt of Foam Material

Pur. No.	W_t (grams)	T (°C)	Q (g/min)	C_o (mg/l)	t_b (min)	M_b^* (mg/gr)	t ^a b	M_o (min)	M_t^* (mg/gr)	K_A (l/z)	UA	Comments
2-68*	4.5780	25	0.98	7.75	6	9.95	16.5	50.93	83.01	10.71	2.592	Box temp. varied 1°C
2-31*	4.5072	25	0.98	7.90	6	10.31	14.5	29.91	51.41	6.51	3.708	
2-79*	4.0509	25	1.27	5.15	7	11.30	12.0	41.18	66.32	12.92	3.711	Box temp. varied 1°C
2-71*	4.2840	25	1.27	5.15	6	9.23	14.0	41.16	63.31	12.29	3.465	Box temp. varied 1.5°C
2-42	4.1212	28	0.69	5.19	22	19.01	32.5	70.17	60.63	11.68	3.075	
2-43*	4.4228	28	0.69	11.98	8	15.55	21.6	47.60	88.43	7.38	2.885	
2-48*	4.3964	28	1.30	5.19	10	15.35	17.0	39.66	60.86	11.73		
2-47*	4.0358	28	1.30	12.08	4	13.72	7.0	23.26	78.63	6.93	3.011	
2-46*	4.5946	28	1.47	5.19	8	13.28	15.0	34.59	57.45	11.07	5.607	
2-35*	4.4467	32.5	0.50	7.75	29	25.27	42.0	82.30	71.73	9.26	2.181	
2-63*	4.6410	32.5	1.00	3.15	40	27.19	42.0	89.63	60.98	19.36	4.493	
2-24	4.2963	32.5	0.99	3.15	32	23.22	36.5	61.84	44.87	14.25	4.493	
2-26*	4.2377	32.5	0.99	7.87	5	9.19	8.5	24.58	45.19	5.74	4.079	Starting time incorrect
2-61*	4.6476	32.5	0.99	7.87	8	13.41	17.0	45.16	75.73	9.62	2.369	Starting time incorrect
2-28*	4.2630	32.5	0.99	12.57	6	17.52	12.4	32.82	95.82	7.62	2.108	
2-36*	4.6565	32.5	0.99	12.57	8	21.38	13.5	26.59	71.02	5.65	7.077	Bad run; trouble with ice bath
2-34*	4.9365	32.5	1.49	7.91	4	11.92	6.0	23.48	70.01	8.85	3.410	
2-41*	4.1945	37	0.70	5.19	22	17.78	32.0	71.25	57.58	11.10	2.789	
2-36*	4.5427	37	0.70	7.81	20	24.23	26.5	53.07	64.29	9.23	3.183	
2-37*	4.6688	37	0.70	12.08	17	30.79	25.5	46.86	84.90	7.03	3.383	CO ₂ -N ₂ Rotameter fluctuated
2-50*	4.6018	37	1.30	5.28	10	14.92	13.6	36.30	54.16	10.26	3.428	
2-54*	4.5400	37	1.30	11.98	5	17.15	9.5	26.98	92.51	7.72	2.199	
2-59	4.0819	40	1.00	7.75	10	18.97	14.0	38.83	67.97	8.77	2.564	
2-33*	5.0100	40	1.00	7.91	17	26.52	20.0	41.52	64.78	8.19	2.843	
2-6*	4.6937	32.5	1.00	9.44	8.50	17.09	14.10	33.00	66.36	7.031	2.793	
2-8*	4.5728	32.5	0.94	9.98	18.50	42.44	24.50	42.77	87.71	8.792	3.609	
2-12*	4.9859	32.5	0.99	9.78	7.50	14.52	14.50	38.35	74.46	7.615	2.447	
2-15*	4.6030	32.5	0.99	10.24	20.0	44.00	24.50					
2-21*	5.3308	32.5	0.495	10.07	21.0	19.54	38.00	63.25	58.92	5.851	2.825	

* used in statistical analysis of Chapter 5

Table A-4 Two Layer Runs, Second Bolt of Foam Material

Run No.	W_t (grams)	T (°C)	Q (t/min)	C_o (mg/g)	t_b (min)	V_b^* (mg/gr)	t_o^+	N_o (min)	M_o^* (mg/gr)	K_A (l/gr)	UA	Comments
2-51*	8.9090	28	0.70	5.25	76	3.53	31.0	123.33	51.19	9.70	1.220	CCl ₄ -N ₂ rotameter unstable run interrupted, restarted
2-52*	9.1092	28	0.70	12.17	50	47.61	58.5	91.73	87.73	7.04	2.103	
2-61*	8.9581	28.5	1.28	5.28	17	35.46	51.5	83.54	61.64	11.67	5.043	
2-56*	7.1527	28	1.30	12.57	17	30.35	22.5	113.71	76.11	6.21	3.452	CCl ₄ -N ₂ rotameter unstable
2-44*	8.8097	37	0.70	5.19	64	26.39	82.5	135.05	55.69	10.73	2.046	
2-65*	8.6425	37	0.69	10.35	42	34.71	32.5	90.75	74.99	7.24	2.472	
2-45*	10.0740	37	0.69	12.47	49	41.55	53.5	77.96	66.11	5.30	2.739	CCl ₄ -N ₂ rotameter unstable
2-53*	9.0997	37	1.30	5.15	36	26.49	41.0	73.44	54.03	10.49	3.734	
2-52*	8.7649	37	1.30	12.37	17	31.19	26.5	38.04	69.79	5.64	7.694	
2-7*	9.5433	32.5	1.00	9.50	37.50	37.37	43.70	65.10	64.86	6.82	3.192	CCl ₄ -N ₂ rotameter unstable
2-11	10.1927	32.5	0.99	10.24	50.0	48.36	58.50	82.27	79.18	7.76	4.637	
2-14	9.3243	32.5	0.99	10.10	45.00	48.30	50.05	73.88	79.19	7.84	4.352	
2-16	10.0036	32.5	0.99	10.24	45.00	45.62	52.50	73.71	76.64	7.49	5.162	CCl ₄ -N ₂ rotameter unstable
2-18*	9.4414	32.5	1.460	9.22	15.00	21.70	22.00	42.90	61.95	4.48	2.049	
2-19	10.1539	32.5	0.495	10.55	29.00	14.94	32.50	68.07	34.99	3.32	0.741	

* used in statistical analysis of Chapter 5

Table A-5 Three Layer Runs, Second Bolt of Foam Material

Run No.	W _t (grams)	T (°C)	Q (/min)	C (mg/)	t _b (min)	M _b [*] (mg/gr)	t _b ⁺	M _o (min)	M _t (mg/gr)	K _A (i/gr)	UA	Comments
2-22*	13.7052	26	0.99	7.87	90	51.16	102.0	142.87	81.22	10.32	3.230	box temp. varied +1°C
2-49*	14.4605	28	0.70	5.19	161	40.19	103.0	228.43	57.45	11.07	3.500	
2-59	13.9337	28	0.69	12.57	90	56.27	113.5	155.28	97.03	7.72	1.773	box temp. varied 1°C
2-60*	13.4803	28	1.28	5.19	87	42.87	90.5	135.97	67.01	12.92	3.892	box temp. varied 1°C
2-57	12.9797	28	1.28	12.62	38	47.29	49.5	74.37	92.55	7.73	3.957	
2-37*	13.2172	32.5	0.50	7.86	160	47.57	175.5	255.64	76.01	9.67	1.160	
2-25	12.98531	32.5	0.99	3.15	71	17.09	86.0	131.64	31.68	10.06	3.129	starting time incorrect
2-27*	12.9780	32.5	0.99	7.87	74	44.43	88.5	118.74	71.28	9.05	6.215	
2-66	13.4411	32.5	0.99	12.37	60	47.73	72.0	97.13	88.57	7.16	4.481	
2-35*	13.7545	32.5	1.50	7.75	51	43.11	55.5	85.17	71.99	9.28	2.325	
2-40*	12.7279	37	0.70	5.19	118	33.68	130.0	180.87	51.63	9.95	3.195	
2-58*	13.6272	37	1.30	5.19	66	32.66	72.0	103.05	51.02	9.83	5.807	
2-62*	13.7751	37	1.26	5.28	78	38.27	85.0	122.02	59.86	11.34	3.513	
2-32*	13.5977	40	1.00	7.91	65	37.76	73.5	105.18	61.1	7.74	2.813	
2-9	14.7596	32.5	0.99	9.59	78.00	50.13	87.50	113.97	73.29	7.644	3.723	
2-13	14.8346	32.5	0.99	10.10	67.00	45.20	77.60		75.59			
2-22*	14.4331	32.5	1.470	10.07	45.00	46.19	52.30	73.41	75.35	7.477	3.561	
2-23	15.0409	32.5	0.495	10.37	149.00	50.87	165.50	202.51	69.78	6.665	5.391	

* used in statistical analysis of Chapter 5

Table A-6. Third Bolt of Carbon Impregnated Foam Material

Conditioned

Run No.	Layers	W _t	T	Q	C _c	t _b	M _b [*]	t _b ⁺	M _o [*]	M _t [*]	K _A	UA
3-1-WT	3	15.3932	37.0	1.3	10.450	120	105.90	122.0	9.33	126.75	12.13	20.741
3-2-WT	1	5.1193	37.0	0.7	5.24	79	56.60	95.5	27.44	100.65	19.21	6.285
3-3-WT	1	4.7749	37.0	1.3	10.30	28	79.47	29.0	9.65	129.21	12.54	8.603
3-4-WT	1	4.9470	40.0	1.0	10.45	40	84.54	41.0	12.58	131.46	12.58	7.430
3-23-WT	1	5.0451	37.0	1.3	10.45	27	72.68	33.5	9.92	134.76	12.80	9.279
3-5-WT	3	16.0761	32.0	1.0	3.15	394	77.21	399.0	29.39	92.58	29.39	15.320
3-13-WT	1	5.0624	32.5	0.99	7.87	41	63.11	54.0	15.69	122.25	15.53	7.980
3-17-WT	3	14.7066	32.5	0.99	7.86	174	92.17	185.0	15.57	121.31	15.41	8.060
3-24-WT	1	4.8988	32.5	0.99	7.86	44	69.87	58.04	16.35	127.39		

Table A-7 Comparison Runs to Determine Effect of Foam Material Treatment, Third Bolt of Foam Material

Run No.	Sweat Treated											
	L	W _t	T	Q	C _O	t _b	M _O [*]	M _O [*]	M _t [*]	K _A	K _A	U _A
3-6-ST	1	5.071	32.5	1.0	7.87	43	62.08	14.19	111.68	14.19	8.177	8.177
3-7-ST	3	15.1282	32.5	1.0	7.75	164	84.02	13.69	106.09	13.69	8.951	8.951
3-8-ST	1	4.8895	37	1.3	10.43	20	55.46	9.41	114.03	10.93	5.606	5.606
3-9-ST	3	14.8746	37	1.3	10.47	93	85.10	.51	115.83	11.06	5.642	5.642
3-12-ST	1	4.6564	28	1.29	10.47	20	58.01	8.49	113.47	10.84	8.958	8.958
As Received												
3-21-AR	1	5.1273	32.5	.99	7.94	44	67.46	15.36	120.76	15.21	7.172	7.172
3-22-AR	3	15.1469	32.5	1.0	7.87	157	79.98	14.53	114.33	14.53	6.629	6.629
3-10-AR	1	5.1598	37	1.3	10.47	26	68.67	8.82	120.05	11.46	14.055	14.055
3-20-AR	3	15.3595	37	1.3	10.60	92	82.54	9.02	124.27	11.72	8.663	8.663
Conditioned												
3-13-WT	1	5.0624	32.5	0.99	7.87	41	63.10	15.69	122.22	15.53	7.980	7.980
3-17-WT	3	14.7056	32.5	0.99	7.87	174	92.18	15.57	121.31	15.41	8.060	8.060
3-3-WT	1	4.7749	37	1.3	10.30	26	72.91	9.65	129.21	12.55	8.803	8.803
3-1-WT	3	15.3932	37	1.3	10.45	116	102.37	9.33	126.75	12.13	20.741	20.741
Dried in Desiccator												
3-15-D	1	5.1941	32.5	0.99	7.87	48	72.00	15.33	119.40	15.17	6.713	6.713
3-14-D	3	15.3120	32.5	0.99	7.86	178	90.46	15.34	119.38	15.19	10.749	10.749
3-19-D	1	4.9722	37	1.3	10.47	29	79.39	10.11	137.61	13.14	8.318	8.318
3-18-D	3	14.6848	37	1.3	10.47	102	94.54	9.36	127.40	12.17	4.943	4.943

Table A-8. Effect of Poisoning by Sweat and Sweat Components on Carbon Impregnated Foam Material
Lactic Acid Treated (1 g/l)

Run No.	L	W _t	T	Q	C _O	t _b	M _b [*]	M _O [*]	M _t [*]	K _A	U _A
Lactic Acid Treated (1 g/l)											
3-27-LA	1	4.5865	32.5	0.99	7.86	34	57.68	14.29	111.20	14.15	8.669
3-30-LA	3	14.7712	32.5	0.99	7.86	154	81.13	14.12	109.87	13.93	5.954
3-35-LA	1	4.7815	37	1.30	10.43	18	51.04	7.96	107.92	10.35	4.688
3-29-LA	3	13.7735	37	1.30	10.43	89	87.61	8.46	114.71	11.00	7.316
Urea treated (.5g/l)											
3-33-U	1	4.8542	32.5	0.99	7.86	46	73.74	15.76	122.63	15.60	9.614
3-32-U	3	14.2229	32.5	0.99	7.86	160	87.54	14.49	112.75	14.35	7.973
3-31-U	1	4.8503	37	1.3	10.43	29	81.07	9.20	124.74	11.96	7.034
3-34-U	3	14.1418	37	1.3	10.43	92	88.21	8.66	117.42	11.26	9.038
Charcoal impregnated foam material - treated with solution of 5g/l lactic acid											
3-37-LA	1	4.6030	32.5	0.99	7.81	31	52.07	12.40	95.88	12.28	5.727
3-36-LA	1	5.0117	37.5	1.3	10.39	20	53.90	8.08	109.14	10.50	7.679
3-41-LA-JD**	1	4.9988	37.0	1.3	10.39	20	54.04	8.61	116.30	11.19	4.601
Charcoal impregnated foam material - treated with solution of 2.5 g/l urea											
3-38-U	1	4.9346	32.5	0.99	7.86	40	63.08	13.06	101.63	12.92	10.127
3-39-U	1	4.8564	37	1.3	10.43	21	58.63	8.21	111.32	10.67	9.958
3-40-JD**	1	4.9314	37	1.3	10.39	22	60.26	8.55	115.48	11.12	7.068
Charcoal impregnated foam material - treated with real sweat											
3-42-RST	1	5.0100	32.5	0.99	7.76	34	52.66	13.41	103.02	13.28	4.905
3-43-RST	1	5.0441	37	1.3	10.39	18	48.20	9.30	125.62	12.09	3.225

**Sample placed in desiccator for two days after treating and before being run.

Table A-9. Comparison Runs at Three Conditions

Run No.	L	W_t	T	Q	C_o	M_o	M_l	K_A	UA	Treatment
3-6-ST	1	5.0710	32.5	1.0	7.87	71.93	2712	14.19	8.4768	Sweat treated
3-13-WT	1	5.0624	32.5	1.0	7.87	79.41	3308	15.53	7.9785	Conditioned
3-15-D	1	5.1941	32.5	1.0	7.87	79.60	3298	15.17	12.4770	Conditioned, dried
3-7-ST	3	15.1282	32.5	1.0	7.75	207.17	21776	13.69	8.9505	Sweat treated
3-17-WT	3	14.7066	32.5	1.0	7.87	228.96	26649	15.41	8.0595	Conditioned
3-14-D	3	15.3120	32.5	1.0	7.86	234.91	28208	15.19	7.9665	Conditioned, dried
3-8-ST	1	4.3895	37	1.3	10.47	41.11	935	10.93	5.6055	Sweat treated
3-3-WT	1	4.7749	37	1.3	10.30	46.06	1128	12.55	8.6025	Conditioned
3-19-D	1	4.9722	37	1.3	10.47	50.27	1394	13.14	9.4830	Conditioned, dried

Table A-10. Comparison Runs on the Fourth Bolt of Cloth

Run No.	W _t	T	Q	C	N _o [*]	M _O	M _L	M _t [*]	K _A	U _A	Comments
12-2-ST	3.5169	32.5	1	7.76	12.14	16.59	168.26	36.61	4.716	7.6455	excess sweat wrung out
12-3-S	3.7910	32.5	1	7.76	6.76	14.93	139.73	30.56	3.938	6.2370	sweat treated
12-4-ST	3.6562	32.5	1	7.76	8.49	15.06	138.96	31.96	4.118	6.2045	excess sweat wrung out
12-5-ST	3.7741	32.5	1	7.76	4.11	16.56	222.65	34.05	4.388	2.5470	excess sweat wrung out
12-6-ST	3.7217	32.5	1	7.76	11.47	18.07	189.27	37.67	4.855	10.1115	sweat treated
12-7-ST	3.6539	32.5	1	7.76	10.62	16.51	171.22	35.06	4.518	6.3990	sweat treated
12-8-CD	3.2939	32.5	1	7.76	21.20	19.44	212.93	45.80	5.902	14.3550	conditioned, dried
12-9-WI	3.6570	32.5	1	7.76	19.10	21.36	270.24	45.32	5.6570	8.8650	conditioned
12-12-AR	3.4400	32.5	1	7.76	12.41	17.16	180.12	38.71	4.988	7.8075	as received

Table A-11. Fourth Bolt of Carbon Impregnated Foam Material

Fourth bolt of cloth, as received

Run No.	L	W _t	T	Q	C	t _b	M _t *	M _o *	M _t *	K _A	UA
11-3-AR	1	3.8463	32.5	0.99	7.82	4	8.05	4.22	32.67	4.18	0.767
11-8-AR	3	11.4988	32.5	0.99	7.82	20	13.53	3.14	24.43	3.11	2.000
11-1-AR	1	4.1937	37	1.3	10.39	1	12.88	2.50	33.77	3.25	2.960
11-2-AR	1	3.8225	37	1.3	10.39	4	14.13	2.45	33.09	3.19	2.459
11-9-AR	3	11.6264	37	1.3	10.39	13	15.10	2.05	27.69	2.67	5.219

Fourth bolt of cloth, conditioned

11-4-WT	1	3.7481	32.5	0.99	7.81	4	8.25	5.00	38.66	4.95	3.441
11-7-WT	3	11.4435	32.5	0.99	7.86	29	19.72	4.14	32.21	4.10	3.317
11-5-WT	1	3.8522	37	1.3	10.39	4	14.03	3.55	47.95	4.62	1.719
11-6-WT	3	11.4106	37	1.3	10.39	20	23.67	2.87	38.77	3.73	1.106

Fourth bolt of cloth conditioned and dried

12-8-CD	1	3.2939	32.5	1.0	7.76	10	23.590	5.902	45.784	5.902	4.785
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Fourth bolt of cloth sweat treated on the applicator with air blowing over it for 3 1/2 hours

12-10-ST	1	4.1980	32.5	1.0	7.76	4	7.372	3.795	29.410	3.794	1.109
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Fourth bolt of cloth sweat treated on the applicator with air blowing over it for 7 hours

12-11-ST	1	3.8035	32.5	1.0	7.76	4	8.148	3.139	24.367	3.138	1.551
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(Both 11 and 12 designations refer to Bolt-4.)

Table A-12. Comparison Between New And Old Sample Holders

Run No.	L	W _t	T	Q	C _c	t _b	M _b [*]	M _o [*]	M _t [*]	X _A	UA
<u>Old Sample Holder</u>											
12-13-WT	1	3.4610	32.5	1.0	7.76	8.0	18.83	5.825	45.20	5.826	3.907
12-14-WT	1	3.4952				10.0	19.89	5.719	44.38	5.719	4.011
12-16-WT	1	3.4610				10.0	20.18	5.813	45.25	5.815	3.008
<u>New Sample Holder</u>											
12-340-WT	1	3.7623	32.5	1.0	7.76	7.0	14.434	4.790	37.17	4.789	4.266
12-346-WT	1	3.7456				7.0	14.511	4.712	36.57	4.712	4.110
12-347-WT	1	3.6213				7.0	14.977	4.882	37.87	4.881	4.178

Table A-13. Effect of Cobalt-60 Radiation on Carbon Impregnated Foam

Run No.	W_t	t_b	M_b^*	M_t^*	K_A	UA	Irradiation (Hrs.)
12-16-WT	3.4610	9.0	20.18	45.25	5.815	3.6675	
12-37-I	3.4931	8.5	18.88	49.92	5.532	4.4640	12
12-48-I	3.5423	10.7	23.44	45.17	5.820	4.4415	24
12-54-I	3.8504	8.4	16.93	39.64	5.109	2.9760	72

Table A-14. Study of Poisoning Phenomena for 1 Layer Runs

Run No.	W_t	T	Q	C_o	t_b	M_b^*	N_t^*	K_A	UA	Nature of Treatment
12-16-WT	3.4610	32.5	1.0	7.76	9.0	20.18	45.25	5.815	3.668	conditioned
12-23-LA	3.5321				7.0	15.38	40.07	5.163	3.050	no undergarment
12-328-LA	3.6600				7.0	14.84	41.71	5.375	2.852	unmodified undergarment
12-335-LA	3.7345				9.2	19.12	42.35	5.458	4.113	modified undergarment
12-31-ST	3.6000				5.0	10.79	35.42	4.565	2.238	no undergarment
12-336-ST	3.4822				4.0	8.91	35.75	4.607	2.573	unmodified undergarment
12-341-ST	3.9721				7.5	4.65	38.60	4.975	3.269	modified undergarment

Table A-15. Study of Poisoning Phenomena for 2 Layer Runs

Run No.	W_t	T	Q	C_o	t_b	M_o^*	M_t^*	K_A	UA	Nature of Treatment
12-63-WT	7.9600	32.5	1.0	7.76	31.5	30.71	46.00	5.928	6.002	conditioned
12-58-LA	7.7071				22.5	22.65	36.52	4.706	4.059	no undergarment
12-333-LA	7.3037				24.2	25.71	41.07	5.292	3.665	unmodified undergarment
12-332-LA	7.6678				27.0	27.33	39.19	5.049	5.933	modified undergarment
12-52-ST	7.2668				15.8	16.87	33.29	4.289	2.042	no undergarment
12-339-ST	7.5417				14.5	14.92	34.82	4.487	1.986	unmodified undergarment
12-343-ST	7.9755				21.0	20.43	39.40	5.076	2.750	modified undergarment

Table A-16. Evaluation of Sweat Poisoning for 2 Layer Runs Each with its Own Independent Reference

Run No.	W_t	T	Q	C_o	t_b	M_o^*	M_o	M_t^*	K_A	UA	Nature of Modification
12-351-WT3	6.9030	32.5	1.0	7.76	13.0	14.61	20.80	23.38	3.013	4.814	
12-351-IA	6.8030				8.0	8.81	16.83	18.92	2.438	2.375	No undergarment
12-353-WT3	6.9853				14.5	16.11	23.87	26.52	3.417	4.367	
12-353-IA	6.9853				12.0	13.33	20.76	23.06	2.971	3.396	unmodified undergarment
12-355-WT3	7.6474				16.0	16.24	25.33	25.70	3.313	4.772	
12-355-IA	7.6474				15.0	15.22	23.28	23.62	3.044	3.636	modified undergarment
12-357-WT3	7.0268				19.0	20.98	28.11	31.04	4.000	5.840	
12-357-ST	7.0268				11.0	12.15	20.67	20.83	2.942	2.310	no undergarment
12-350-WT3	7.7084				18.5	18.62	28.12	29.59	3.648	4.361	
12-350-ST	7.7084				13.0	13.09	20.71	20.85	2.686	3.680	unmodified undergarment
12-359-WT3	6.8855				16.0	18.03	24.57	27.69	3.568	5.571	
12-359-ST	6.8855				14.5	16.34	22.63	25.50	3.287	6.050	modified undergarment

Table A-17. Adsorption of CCl_4 by Various Conditioned Fabrics

Run No.	L	W_t	T	Q	C_o	t_b	M_b^*	t_b^+	M_o^*	M_t^*	K_A	UA
Nomex-Cotton-Carbon Composite VEE 3280												
4-1-WT	1	5.9240	32.5	0.99	7.81	3	3.92	6.0	3.63	28.07	3.59	1.068
4-4-WT	3	17.0421	32.5	0.99	7.81	16	7.26	25.0	2.38	18.40	2.36	1.350
4-2-WT	1	5.5275	37	1.30	10.39	2	4.89	4.3	2.57	34.71	3.34	1.506
4-3-WT	3	16.9686	37	1.30	10.39	9	7.16	15.5	1.87	25.26	2.43	0.864
Carbon-Nomex-Weftamatic VEE 3279												
5-2-WT	1	5.1352	32.5	0.99	7.76	1**	1.50		2.30	17.67	2.28	0.677
5-4-WT	3	15.7943	32.5	0.99	7.87	4	1.97		2.24	17.45	2.22	0.356
5-1-WT	1	5.2652	37	1.30	10.39	1**	2.56		1.53	20.67	1.99	1.061
5-3-WT	3	15.7679	37	1.3	10.43	11	9.46		1.22	16.54	1.59	0.518
Carbon-Nomex Fabric VEE 3219												
6-1-WT	1	4.7278	32.5	0.99	7.81	1**	1.64		3.22	24.90	3.19	0.590
6-4-WT	3	13.6253	32.5	0.99	7.86	7	4.00		2.61	20.31	2.58	0.474
6-2-WT	1	4.6463	37	1.3	10.43	2**	5.84		2.58	34.98	3.35	0.740
6-3-WT	3	15.1309	37	1.3	10.43	5	4.48		1.27	17.22	1.65	0.834
Pluton B-1												
7-3-WT	1	3.2482	32.5	0.99	7.81	1	2.38	7.0	6.36	49.17	6.30	3.353
7-4-WT	3	10.0671	32.5	0.99	7.81	34	26.11	41.0	6.96	53.81	6.89	2.000
7-2-WT	1	3.3583	37	1.3	10.39	2	8.04	5.5	4.34	58.62	5.64	4.403
7-1-WT	3	9.9462	37	1.3	10.39	21	28.63	25.5	4.19	56.59	5.45	2.570
Quilted Fabric VEE 3098												

8-1,2,3,4 immediate breakthrough, very little adsorption of CCl_4

Table A-17 (continued)

British Cloth A46C54												
9-1-WT	1	2.5581	32.5	0.99	7.82	26	78.69	40.0	26.80	207.48	26.53	11.510
9-4-WT	3	7.4954	32.5	0.99	7.86	132	137.04	145.0	26.04	202.63	25.78	7.109
9-2-WT	1	2.5441	37	1.3	10.45	14	74.76	24.0	17.42	236.65	22.65	12.681
9-3-WT	3	7.6294	37	1.3	10.43	84	149.29	95.0	16.49	223.59	21.44	7.559
British Cloth P99												
10-1-WT	1	1.861C	32.5	0.99	7.81	7	29.08	19.0	34.38	265.82	34.04	7.167
10-3-WT	3	6.8461	32.5	0.99	7.86	160	181.86	180.0	34.70	270.01	34.35	16.052
10-2-WT	1	2.2071	37	1.3	10.43	10	61.43	21.0	22.24	301.55	28.91	8.184
10-4-WT	3	5.6492	37	1.3	10.43	67	160.81	24.0	19.67	266.71	25.57	8.681

***CCl₄ peak appeared at first sampling

Table A-18. Reproducibility Data on Two Layer Runs

Run No.	W _t	T	Q	C _o	t _b	M _b [*]	M _o	M _t [*]	K _A	UA
12-351-WT1	6.9030	32.5	1.0	7.76	16	17.99	25.04	28.15	3.628	3.875
12-351-WT2					13	14.61	21.30	23.94	3.086	5.073
12-351-WT3					13	14.61	20.80	23.38	3.013	4.814
12-353-WT1	6.9853				16	17.75	26.12	29.02	3.739	5.555
12-353-WT2					14.5	16.11	23.38	25.97	3.347	4.824
12-353-WT3					14.5	16.11	23.87	26.52	3.417	4.3671
12-355-WT1	7.6474				19	19.28	27.05	27.45		
12-355-WT2					16	16.24	25.74	26.12	3.366	4.148
12-355-WT3					16	16.24	25.33	25.70	3.313	4.772
12-357-WT1	7.0268				20.5	22.64	26.00	28.71	3.700	5.439
12-357-WT2					19	20.98	28.51	31.48	4.057	4.715
12-357-WT3					19	20.98	28.11	31.04	4.000	5.840
12-350-WT1	7.7084				20	20.13	29.63	29.83	3.844	5.745
12-350-WT2					18.5	18.62	27.94	28.13	3.624	4.560
12-350-WT3					18.5	18.62	28.12	29.59	3.648	4.361
12-359-WT1	6.8855				18.0	20.29	25.70	28.96	3.732	5.325
12-359-WT2					16.0	18.03	25.77	29.04	3.742	5.514
12-349-WT3					16.0	18.03	24.57	27.69	3.568	5.571

WT1, WT2 and WT3 refer to first, second and third runs on the same sample.

Table A-19. Index of Various Types of Adsorbents Used

Material	Run Designation	Description	Utility	Data on Sample in Tables Spec. Below
Bolt 1	1	carbon impregnated foam material	initial investigation	A-1, A-2
Bolt 2	2	carbon impregnated foam material	central composite statistical design of experiments used in modeling	1, 4, A-3, A-4, A-5
Bolt 3	3	carbon impregnated foam material	investigation of sweat poisoning	1, 4, A-6
Bolt 4	11 or 12	carbon impregnated foam material	control of sweat poisoning	1, 4, A-7, A-8, A-9, A-10, A-11, A-12, A-13, A-14, A-15, A-16, A-18
VEE 3230	4	Nomex-cotton-carbon composite		A-17
VEE 3279	5	carbon-Nomex-weftamatic		A-17
VEE 3219	6	carbon-Nomex fabric		A-17
Pluton B-1	7	woven carbon fabric		1, 4, A-17
VEE 3098	8	quilted fabric		A-17
A46C54	9 or BC1	British cloth (woven carbon fabric)		1, 4, A-17
P99	10 or BC2	British cloth (woven carbon fabric)		1, 4, A-17

APPENDIX B

Sample Calculation of Degree of Substitution on Cotton Cellulose

Cotton cellulose was modified into triethyl amino ethyl cellulose for the selective removal of lactic acid. A sample calculation for the degree of substitution on cotton cellulose is shown.

dry weight of cotton cellulose fabric = 28.8023 g

dry weight of aminized cellulose = 32.6545 g

dry weight of quaternized cellulose = 34.5049 g

increase in weight due to aminization = $(32.6545 - 28.8023)g = 3.8522 g$

increase in weight due to quaternization = $(34.5049 - 32.6545)g = 1.8504 g$

For aminization the substituent group added to cellulose is $-CH_2-CH_2-N-(C_2H_5)_2$; molecular weight = 100 g/g·mole.

For quaternization the group added to the existing amine is C_2H_5I ; molecular weight = 155.98 g/g·mole.

$$\text{Degree of substitution (D.S.)} = \frac{\text{moles substituent}}{\text{moles cellulose monomer unit}}$$

$$D.S. = \frac{(3.8522/100)g \text{ mole amine}}{(28.8023/162)g \text{ mole cellulose}} = .216$$

$$\text{Degree of quaternization (D.Q.)} = \frac{\text{moles quaternary amine}}{\text{moles of total amine}}$$

$$D.Q. = \frac{(1.8504/155.98)g \text{ mole } C_2H_5I}{(3.8522/100)g \text{ mole amine}} = 0.31$$

The ion exchange capacity of the quaternary amine product, assuming only the quaternized amine removes the acid, is given as follows:

$$\text{Ion exchange capacity} = \frac{(1.8504/155.98)g \text{ mole } C_2H_5I}{34.5049 g \text{ material}} \times \frac{1000 \text{ meq}}{1 g \text{ mole } C_2H_5I} =$$

$$0.34 \text{ meq/g material}$$

$$\text{Concentration of lactic acid} = (0.001g/ml) (1 g\cdot\text{mole}/90 g) (1000 \text{ meq/g mole}) = 0.011 \text{ meq/ml}$$

$$\begin{aligned} \text{Volume of lactic acid solution that can be treated by a 4.5 g sample of material} &= \\ &= (0.34 \text{ meq/g material})(4.5 g \text{ material})/(0.011 \text{ meq/ml}) \\ &= 137.7 \text{ ml} \end{aligned}$$

APPENDIX C

List of Computer Programs

Computer program for calculation of M_0^* , M_0^* and M_t^*

(SWEAT-1)

```
//SWEAT1 JOB NCS.CHE.B2613,ANEJA ,D=NCSSURUP,R=200K
// EXEC PLKRUN
//SYSIN DD *
SWEAT1: PROCEDURE OPTIONS(MAIN);
  DECLARE (I(100),P(100),W(100),G(100)) CONTROLLED;
  DECLARE H(60);
  DECLARE RUN CHARACTER(35);
  ON ENDFILE(SYSIN) GO TO END;
START:
  GET LIST (RUN,RI,RF,RVF,N1,N2,N,DEL1,W1,W2,W3,W4);
  GET LIST (CONC,FL,TEMP);
  ALLOCATE T(N),P(N),W(N),G(N);
  DO I=1 TO N;
    GET LIST ( I(1),P(I),W(I));
    W1=W1+W2+W3+W4;
  END;
  N1=N1+1;
  DO I=1 TO N;
    G(I)=1-P(I)*W(I)/RVF;
  END;
  A1=T(N1-1)-T(1);
  SUM1=0; SUM2=0;
  DO I=N1 TO N2-1 BY 2;
    SUM1=SUM1+G(I);
  END;
  DO I=N1+1 TO N2-1 BY 2;
    SUM2=SUM2+G(I);
  END;
  A2=(G(N1-1)+4*SUM1+2*SUM2+G(N2))*DEL1/3;
```

(SWEAT-1) Cont'd.

```

IF I=N2+1 THEN DO?
  A2=A2-(G(N2-1)+G(N2))*DELT/3;
  A3=0;
  DO I=N2-1 TO N-1;
    A3=A3+(G(I+1)+G(I))*(T(I+1)-T(I))/2;
  END; GO TO HH;
END;

A3=0;
DO I=N2 TO N-1;
  A3=A3+(G(I+1)+G(I))*(T(I+1)-T(I))/2;
END;

HH: AD=A1;
  AT=A1+A2+A3; ABN=AB/WT; ATN=AT/WT;
  PUT EDIT (RUN)(PAGE,LINE(5),COLUMN(25),A);
  PUT EDIT ('CONCENTRATION',CONC,'MG PER LITER')(SKIP(2),
    COLUMN(14),A,COLUMN(26),F(6,3),COLUMN(36),A);
  PUT EDIT ('FLOW RATE',FL,'LITERS PER MINUTE',
    (COLUMN(14),A,COLUMN(26),F(6,3),COLUMN(36),A);
  PUT EDIT ('TEMPERATURE',TEMP,'DEGREES C',
    (COLUMN(14),A,COLUMN(28),F(6,3),COLUMN(36),A);
  PUT EDIT ('TIME',PEAK,'PEAK','G')(SKIP(3),COLUMN(15),A,
    COLUMN(27),A,COLUMN(39),A,COLUMN(52),A);
  PUT EDIT ('MINUTES',HEIGHT,'WIDTH','1-C/CO')(COLUMN(14),A,
    COLUMN(26),A,COLUMN(38),A,COLUMN(50),A);
  PUT EDIT ('')(SKIP(2),A);

DO I=1 TO N;
  PUT EDIT (T(I),P(I),W(I),G(I))(COLUMN(14),F(5,1),
    COLUMN(26),F(5,2),COLUMN(39),F(4,2),COLUMN(50),F(6,4));
END;
  PUT EDIT ('AREA TO BREAK',AB)(SKIP(3),COLUMN(10),A,COLUMN(36),
    F(8,2));
  PUT EDIT ('TOTAL AREA',AT)(COLUMN(10),A,COLUMN(36),F(8,2));

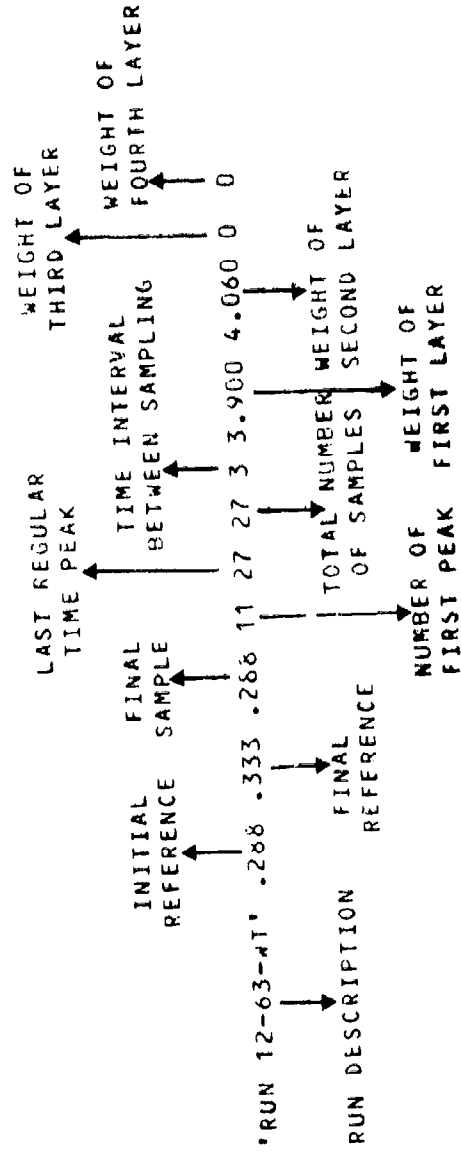
```

(SWEAT-1) Cont'd.

```

PUT EDIT ('NORMALIZED AREA TO BREAK',ABN)(COLUMN(10),A,
COLUMN(36),F(8,2));
PUT EDIT ('NORMALIZED TOTAL AREA',ATN)(COLUMN(10),A,
COLUMN(36),F(8,2));
PUT EDIT ('TOTAL SAMPLE WEIGHT',WT)(COLUMN(10),A,COLUMN(36),
F(8,4));
FREE I,P,W,G;
GO TO START;
END: END SWEAT1;
*DATA;

```



Computer program for the calculation of overall adsorption
coefficient model parameters

```

(SWEAT-2)

//SWEAT2 JOB NCS.CHE.24145,ANEJA ,D=NCSUBUR,R=200K
// EXEC PLKRUN
//SYSIN DD *
SWEAT2: PROCEDURE OPTIONS(MAIN);
  DECLARE (T(100),P(100),W(100),G(100)) CONTROLLED;
  DECLARE RUN CHARACTER(35);
  ON ENDFILE(SYSIN) GO TO END;
START:
  GET LIST (RUN,RI,RF,RVF,N1,N2,N,DELT,N1,W2,W3,W4);
  GET LIST (CGNC,FL,TEMP);
  ALLOCATE T(N),P(N),W(N),G(N);
  DO I=1 TO N;
    GET LIST (T(I),P(I),W(I));
  END;
N1=N1+1;
SIMP: PROCEDURE (G,A2,A3,DELT,N1,N2,N);
  DECLARE (G(100));
  SUM1=0; SUM2=0;
  DO I=N1 TO N2-1 BY 2;
    SUM1=SUM1+G(I);
  END;
  DO I=N1+1 TO N2-1 BY 2;
    SUM2=SUM2+G(I);
  END;
  A2=(G(N1-1)+4*SUM1+2*SUM2+G(N2))*DELT/3;
  IF I=N2+1 THEN DO;
    A2=A2-(G(N2-1)+G(N2))*DELT/3;
    A3=0;
    DO I=N2-1 TO N-1;
      A3=A3+(G(I+1)+G(I))*(T(I+1)-T(I))/2;
    END; GO TO HH;
  END;
  A3=0;
  DO I=N2 TO N-1;
    A3=A3+(G(I+1)+G(I))*(T(I+1)-T(I))/2;

```

(SWEAT-2) Cont'd.

```

END;
HH: RETURN;
END SIMP;
DO I=1 TO N;
  G(I)=1-P(I)*W(I)/RVF;
END;
CALL SIMP (G,A2,A3,DELT,N1,N2,N);
  A1=T(N1-1)-T(1);
  AMO=A1+A2+A3;
  AMO=AMO;
DO I=1 TO N;
  G(I)=(1-P(I)*W(I)/RVF)*T(I);
END;
CALL SIMP (G,A2,A3,DELT,N1,N2,N);
  A1=T(N1-1)**2/2;
  AM1=A1+A2+A3;
  A=(AM1/AMO**2-E.5)/FL;
  DC=1/(A*15);
  DCWT=DC/(W1+W2+W3);
  AWT=W1+W2+W3;
  EKA=AMO/AWT*FL;
L4: PUT EDIT (RUN) (COLUMN(25),A);
L3: PUT EDIT ('CONCENTRATION',CONC,'MG PER LITER')(SKIP(2),
  COLUMN(14),A,COLUMN(26),F(6,3),COLUMN(36),A);
  PUT EDIT ('FLOW RATE',FL,'LITERS PER MINUTE')
  (COLUMN(14),A,COLUMN(26),F(6,3),COLUMN(36),A);
  PUT EDIT ('TEMPERATURE',TEMP,'DEGREES C')
  (COLUMN(14),A,COLUMN(28),F(6,3),COLUMN(36),A);
  PUT EDIT ('MO',AMO)
  (COLUMN(14),A,COLUMN(28),F(6,2));
  PUT EDIT ('M1',AM1)
  (COLUMN(14),A,COLUMN(28),F(10,2));
  PUT EDIT ('A',A)
  (COLUMN(14),A,COLUMN(28),F(6,3));

```

(SWEAT-2) Cont'd.

```

PUT EDIT ('DC',DC)
(COLUMN(14),A,COLUMN(28),F(6,3));
PUT EDIT ('DC4T',DC4T)
(COLUMN(14),A,COLUMN(35),F(8,4));
PUT EDIT ('KA',EKA)
(COLUMN(14),A,COLUMN(28),F(6,3));
PUT EDIT ('WT',ANT)
(COLUMN(14),A,COLUMN(28),F(8,4));

```

```

FREE T,P,W,G;
GO TO START;
END: END SWEAT2;
*DATA;

```

INITIAL REFERENCE	FINAL SAMPLE	LAST REGULAR TIME PEAK	TIME INTERVAL BETWEEN SAMPLING	WEIGHT OF THIRD LAYER	WEIGHT OF FOURTH LAYER
.288	.333	27	3	0	0
.288	.288	11	27	4.060	0
↑ INITIAL REFERENCE ↑ FINAL SAMPLE ↑ LAST REGULAR TIME PEAK ↑ TIME INTERVAL BETWEEN SAMPLING ↑ WEIGHT OF THIRD LAYER ↑ WEIGHT OF FOURTH LAYER ↑ TOTAL NUMBER OF SAMPLES ↑ WEIGHT OF SECOND LAYER ↑ NUMBER OF FIRST PEAK ↑ WEIGHT OF FIRST LAYER					
'RUN 12-63-WT' .288 .333 .288 11 27 27 3 3.900 4.060 0 0					
RUN DESCRIPTION					

(SWEAT-2) Cont'd.

FLOW RATE		INLET TEMPERATURE		INLET CONC.		PEAK HEIGHT		TIME OF MEAN INJECTION		WIDTH	
7.76	1.0	32.5									
0	0	0	0	0	0	0	0	0	0	0	0
1	0	0	0	0	0	0	0	0	0	0	0
2	0	0	0	0	0	0	0	0	0	0	0
3	0	0	0	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0	0	0	0
5	0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0	0
7	0	0	0	0	0	0	0	0	0	0	0
8	0	0	0	0	0	0	0	0	0	0	0
9	0	0	0	0	0	0	0	0	0	0	0
10	0	0	0	0	0	0	0	0	0	0	0
11	0	0	0	0	0	0	0	0	0	0	0
12	0	0	0	0	0	0	0	0	0	0	0
13	0	0	0	0	0	0	0	0	0	0	0
14	0	0	0	0	0	0	0	0	0	0	0
15	0	0	0	0	0	0	0	0	0	0	0
16	0	0	0	0	0	0	0	0	0	0	0
17	0	0	0	0	0	0	0	0	0	0	0
18	0	0	0	0	0	0	0	0	0	0	0
19	0	0	0	0	0	0	0	0	0	0	0
20	0	0	0	0	0	0	0	0	0	0	0
21	0	0	0	0	0	0	0	0	0	0	0
22	0	0	0	0	0	0	0	0	0	0	0
23	0	0	0	0	0	0	0	0	0	0	0
24	0	0	0	0	0	0	0	0	0	0	0
25	0	0	0	0	0	0	0	0	0	0	0
26	0	0	0	0	0	0	0	0	0	0	0
27	0	0	0	0	0	0	0	0	0	0	0
28	0	0	0	0	0	0	0	0	0	0	0
29	0	0	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	0	0	0	0	0	0
31	0	0	0	0	0	0	0	0	0	0	0
32	0	0	0	0	0	0	0	0	0	0	0
33	0	0	0	0	0	0	0	0	0	0	0
34	0	0	0	0	0	0	0	0	0	0	0
35	0	0	0	0	0	0	0	0	0	0	0
36	0	0	0	0	0	0	0	0	0	0	0
37	0	0	0	0	0	0	0	0	0	0	0
38	0	0	0	0	0	0	0	0	0	0	0
39	0	0	0	0	0	0	0	0	0	0	0
40	0	0	0	0	0	0	0	0	0	0	0
41	0	0	0	0	0	0	0	0	0	0	0
42	0	0	0	0	0	0	0	0	0	0	0
43	0	0	0	0	0	0	0	0	0	0	0
44	0	0	0	0	0	0	0	0	0	0	0
45	0	0	0	0	0	0	0	0	0	0	0
46	0	0	0	0	0	0	0	0	0	0	0
47	0	0	0	0	0	0	0	0	0	0	0
48	0	0	0	0	0	0	0	0	0	0	0
49	0	0	0	0	0	0	0	0	0	0	0
50	0	0	0	0	0	0	0	0	0	0	0
51	0	0	0	0	0	0	0	0	0	0	0
52	0	0	0	0	0	0	0	0	0	0	0
53	0	0	0	0	0	0	0	0	0	0	0
54	0	0	0	0	0	0	0	0	0	0	0
55	0	0	0	0	0	0	0	0	0	0	0
56	0	0	0	0	0	0	0	0	0	0	0
57	0	0	0	0	0	0	0	0	0	0	0
58	0	0	0	0	0	0	0	0	0	0	0
59	0	0	0	0	0	0	0	0	0	0	0
60	0	0	0	0	0	0	0	0	0	0	0
61	0	0	0	0	0	0	0	0	0	0	0
62	0	0	0	0	0	0	0	0	0	0	0
63	0	0	0	0	0	0	0	0	0	0	0
64	0	0	0	0	0	0	0	0	0	0	0

(IMPORTANT : THE ADSORPTION RATE CONSTANT,UA,IS 15*DCWT)

Computer program for UA-type model

(SWEAT-3)

```
//SWEAT3 JOB NCS.CHE.B2613,ANEJA ,D=NCSUBUR,R=200K,T=(1,30)
// EXEC PLOCLG
//C-SYSIN DD *
      SWEAT3: PROCEDURE OPTIONS(MAIN);
      DECLARE (CONC(200),T(200),F(200));
      DECLARE (X,R) FLOAT BIN(21);
      DECLARE RUN CHARACTER (35) ;
      GET LIST (NO) ;
      DO LL=1 TO NO ;
      GET LIST (RUN) ;
      T(1)=0; J=150;
      DO M=1 TO J;
      MM=M+1;
      T(MM)=T(M)+2;
      END;
      GET LIST (AM0,AK4,DC) ;
      Q1Z=AM0/AK4*15*DC;
      Q2=15*DC/AK4;
      C=199; N=199;
      DO M=1 TO J;
      DQ1Z=0; DELQ=0;
      DO I=1 TO N;
      DQ1Z=DQ1Z+DELQ;
      DELQ=Q1Z/C;
      X=2*SQR(DQ1Z*Q2*T(M));
      CALL IQ(X,R);
      F(I)=EXP(-DQ1Z)*R;
      END;
      SUM1=0; SUM2=0;
      DO L=2 TO N-1 BY 2;
      SUM1=SUM1+F(L);
      END;
```

(SWEAT-3) Cont'd.

```

DO L=3 TO I-2 BY 2;
  SUM2=SUM2+F(L);
END;
A2=(F(1)+4*SUM1+2*SUM2+F(N))*DELQ/3;
CONC(M)=1-EXP(-Q2*T(M))*A2;
IF CONC(M)>0.99 THEN GO TO L2;
END;

L2: PUT EDIT (RUN) (PAGE,LINE(5),COLUMN(25),A) ;
PUT EDIT ('TIME',C/CO')
      (LINE(8),COLUMN(25),A,COLUMN(38),A);

DO K=1 TO M;
  PUT EDIT (T(K),CONC(K))
      (COLUMN(24),F(7,3),COLUMN(37),F(6,3));
END;

IO: PROC(X,RIO) ;
  DCL (X,RIO,Z) BIN FLOAT (21) ;
  RIO=ABS(X);
  IF RIO <= 3.75E0 THEN DO;
    Z=X*X*7.11111E-2;
    RIO=((((4.5813E-3*Z+3.60768E-2)*Z+2.659732E-1)*Z
      +1.206749E0)*Z+3.089942E0)*Z+3.515623E0)*Z+1.0E0;
  END;
ELSE DO;
  Z=3.75E0/RIO;
  RIO=EXP(RIO)/SQRT(RIO)*((((((3.92377E-3*Z-1.647633E-2)*Z
    +2.635537E-2)*Z-2.057706E-2)*Z+9.16261E-3)*Z-1.57565E-5)*Z
    +2.25319E-3)*Z+1.328592E-2)*Z+3.989423E-1);
END;

```

(SWEAT-3) Cont'd.

```
END IQ;  
END ;  
END:END SWEAT3;  
/*  
//G.SYSIN DD *  
*DATA
```

1 ← NUMBER OF RUNS TO BE ANALYZED

'RUN-1' ← RUN NUMBER

15.08,4.291,0.1944
↓ ↓ ↓
MO KA DCWT

/*
//

Computer program for pcre diffusion model

(SWEAT-4)

```
//SWEAT4 JOB NCS.CHE.B2613,ANEJA, D=NCSUBUR,R=200X,T=(1,30)
// EXEC PLOCLC
//C.SYSIN DD *
    SWEAT4: PROCEDURE OPTIONS(MAIN);
    DECLARE (CONC(200),T(200),F(1000));
    DECLARE RUN CHARACTER (35) ;
    GET LIST (NO) ;
    T(1)=0; J=150;
    DO M=1 TO J;
        MM=M+1;
        T(MM)=T(M)+2;
    END;

    DO KK=1 TO NO ;
    GET LIST (RUN) ;
    GET LIST (AMO,AKA,DC);
    TEST=0;
    L=1.0;
    A=AMO/AKA*3*DC;
    B=2/AKA*DC;
    DO M=1 TO J;
        N=1000; DELY=0.01; Y=0; I=0;
        L1: I=I+1;
        IF I>N THEN GO TO L3;
        Y=Y+DELY;
        W1=(Y*(SINH(2*Y)+SIN(2*Y))/(COSH(2*Y)-COS(2*Y)))-1;
        W2=Y*(SINH(2*Y)-SIN(2*Y))/(COSH(2*Y)-COS(2*Y));
        XF=EXP(-A*W1)/Y;
        F(I)=XF*(SIN(B*T(M)*Y**2-A*W2));
        L=-I*L;
        IF L>0 THEN GO TO L1;
        IF XF-.000005<0 THEN GO TO L2;
        GO TO L1;
    L3: PUT EDIT ('I>N') (PAGE,LINE(5),COLUMN(25),A);
```

(SWEAT-4) Cont'd.

```

L2: SUM1=0; SUM2=0;
DO L=2 TO I-1 BY 2;
  SUM1=SUM1+F(L);
END;
DO L=3 TO I-2 BY 2;
  SUM2=SUM2+F(L);
END;
  A2=(4*SUM1+2*SUM2+F(I))*DELY/3;
  CONC(M)=0.5+2/3.14*A2;
  IF (CONC(M)-TEST)/CONC(M)-.0005<0 THEN GO TO L4;
  TEST=CONC(M);
  GO TO L1;

L4: IF CONC(M)-0.9900>0 THEN GO TO L6;
L7: END;
L6: PUT EDIT (RUN) (PAGE,LINE(6),COLUMN(25),A) ;
  PUT EDIT ('TIME','C/CO')
    (LINE(8),COLUMN(25),A,COLUMN(38),A);
DO K=1 TO M;
  PUT EDIT (T(K),CONC(K))
    (COLUMN(24),F(7,3),COLUMN(37),F(6,3));
END;
END;
END:END SWEAT4;

/*
//G.SYSIN DD *
```

(SWEAT-4) Cont'd.

*DATA

1 ← NUMBER OF RUNS TO BE ANALYZED

'RUN-1' ← RUN NUMBER

15.08, 4.291, 0.1944

↓
MO

↓
KA

↓
DCWT

/*
//