1980

Determination of alpha and beta factors for domestic wastewaters under different operating conditions.

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Recommended Citation

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DETERMINATION OF ALPHA AND BETA FACTORS FOR DOMESTIC WASTEWATERS UNDER DIFFERENT OPERATING CONDITIONS

by

© Prem Krishan Tewari

A Thesis
submitted to the Faculty of Graduate Studies
through the Department of
Civil Engineering in Partial Fulfillment
of the requirements for the Degree
of Master of Applied Science at
The University of Windsor

Windsor, Ontario, Canada

1980

To My Family

ABSTRACT

DETERMINATION OF ALPHA AND BETA FACTOR FOR DOMESTIC WASTEWATERS UNDER DIFFERENT OPERATING CONDITIONS

by

Prem Krishan Tewari

The growing cost of energy has placed a great burden on the wastewater treatment plants. Other factors contributing to this great burden are: increase in industrial effluents, both in quality and diversity, and the tremendous increase in population. The unit worst hit by this is the biological reactor in the activated sludge treatment process. This study was conducted, under different operating conditions, to determine alpha - the ratio of oxygen uptake rates in wastewater and tap water, respectively; and beta - the ratio of D.O. saturation concentrations in wastewater and tap water, respectively. Three different laboratory scale tank geometries were employed to analyze four different types of wastewaters, collected from two sources.

The volume of samples in the three tanks was 9.0 L, 12.0 L and 20.0 L. The range of air flow rates was 40 to 182 cc/min/L. Since an interference was observed with the chemicals while chemically deoxygenating one of the samples, the nitrogen stripping method was adopted for that sample. The rates of oxygen uptake, K_La, in water and wastewater were measured with a D.O. measuring probe. A computer programme comprising of SAS package NLINDF, was used to analyze the data for calculating K_La by the nonlinear least-square regression technique.

The results showed that K_La values were affected by air flow rate, water depth, tank geometry, temperature and wastewater characteristics.

Also, it increased with the successive addition of sodium sulfite. However, the α factor was not affected by air flow rate, tank geometry and water depth; but, wastewater characteristics had influenced the alpha values. The results were analyzed statistically and average values of α for the four samples ranged between 0.67 and 0.925.

This study also showed that the dissolved oxygen saturation value increased with an increase in depth. It was observed that the D.O. saturation value, obtained after applying correction for the dissolved solids concentration to the values read from the Table in Standard Methods, was very close to the D.O. value obtained by the Winkler method. On the other hand, the D.O. saturation values obtained with the probe and the calculated values showed discrepancies in the results.

The β factor was calculated using saturation values obtained by a different method.

It is concluded that, even though no significant difference was observed among the values obtained by different methods, it is convenient to calculate β factor from the D.O. saturation values obtained from the Standard Methods after applying correction for the dissolved solids. The β values ranged between 0.89 and 1.00 with an average of 0.97.

ACKNOWLEDGEMENTS

My heartfelt thanks to Dr. J. K. Bewtra, whose continuous and patient guidance, along with healthy criticism has helped in the preparation of this thesis.

I also express my sincere gratitude to Mr. Frank Kiss and Mr. Peter Feimer, laboratory technicians, for rendering valuable technical assistance.

Many thanks go to my brother, Dr. K. K. Tewari and others, who persevered with me throughout the completion of my studies. Their assistance became invaluable at times.

Lastly, the author wishes to express his sincere gratitude to the Natural Sciences and Engineering Research Council Canada, who made this work possible.

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INTRODUCTION

In this space age, human beings are trying harder and harder to achieve higher and higher. This has resulted in the discovery of many new chemicals everyday. Such technological advancements have increased industrial effluents both in quantity and diversity. Also, the steadily increasing population has resulted in increased quantity of domestic wastewater. The increase in pollutants has placed a great burden on the wastewater treatment plants to produce effluents of suitable quality before discharging them into local bodies of water.

This tremendous burden could be released either by redesigning the entire plants or modifying certain unit operations. The unit operation most affected due to increase in organic pollutants is the biological reactor in the activated sludge process. In this process, air is supplied to the contents in the reactor, known as mixed-liquor, containing organic matter and bacterial mass. This supply of air directly oxidizes certain types of wastes to more stabilized form, acts as a source of oxygen for the bacteria which can stabilize different types of organic pollutants and keeps the flocs in suspension.

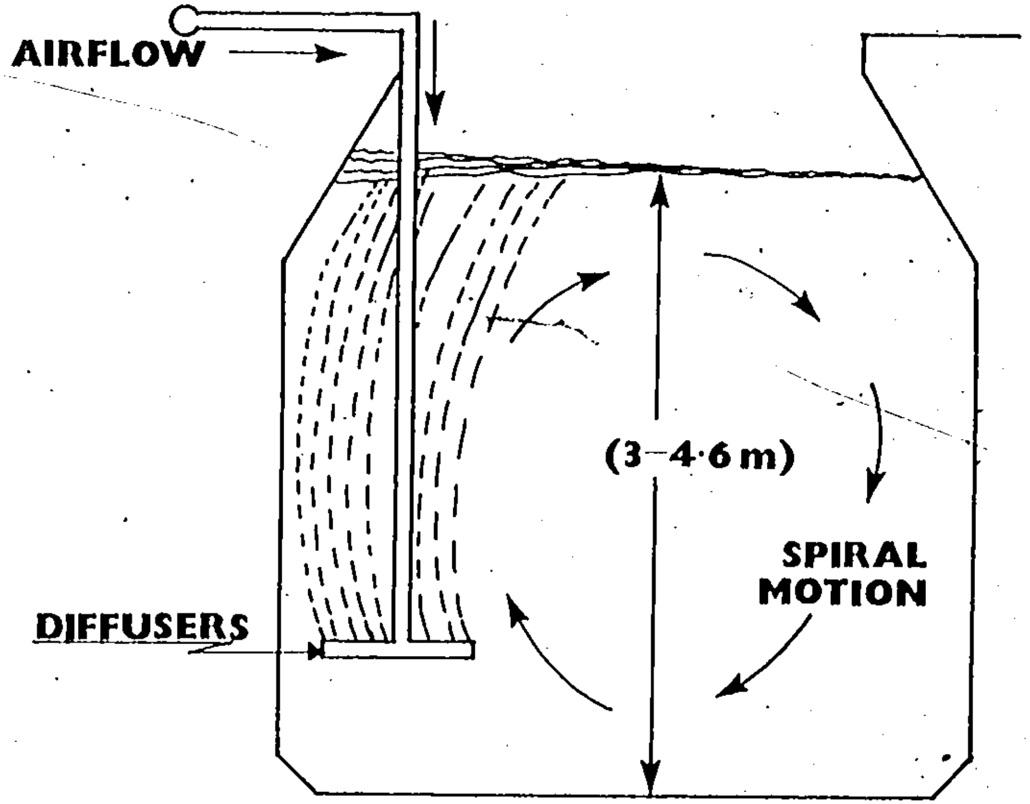
There are different techniques used for supplying air to the mixed-liquor. Surface aeration, also known as mechanical aeration, and subsurface aeration are the two most common methods. Subsurface aeration can be fine bubble aeration or coarse bubble aeration. In fine bubble devices, air bubbles form at the surface of the diffusers, whereas in coarse bubble devices, air breaks into bubbles after coming out of the diffusers (1). Due to the climatic conditions, use of mechanical aerators is discouraged in cold countries.

Higher oxygen transfer efficiencies are achieved with fine air bubble systems, but the clogging of diffusers is a big standing problem. These problems of general occurrence have resulted in the use of coarse bubble diffusion system in activated sludge treatment plants. Fig. 1 shows the placement of diffusers near the aeration tank bottom in a conventional aeration tank (2).

Due to the resulting low density of air-water mixture above the air outlets, as well as the direction of fluid flow, a rising, circulating spiral motion of the mixture results throughout the entire tank (1). In this arrangement, flocs remain in suspension due to circulating velocity. However, the main disadvantage is the increase in the overall rising velocity which decreases the contact time between the bubbles and the liquid (1).

The presence of surface active materials in wastewater changes the surface tension which cause the oxygen uptake rate in wastewater to differ from that in pure water. The necessity for developing a common base has been fulfilled by taking a ratio between rates of oxygen uptake in wastewater and tap water respectively, and this ratio has been designated as alpha factor, α. The α value changes with wastewater characteristics and may therefore change from time to time (3). The dissolved salts in wastewater can be organic or inorganic, biodegradable or nonbiodegradable in nature and these substances reduce the solubility of the dissolved oxygen in water. Beta factor, β, is used to correct for the effect of salt concentration in the wastewater on the solubility of dissolved oxygen (4).

In the design and operation of aeration tanks, it is imperative to have reliable values for α and β factors. It is a common practice



NOTE: The moving spiral velocity is in the order of 0·15 m per min.

FIG. I — A TYPICAL DIFFUSED AIR, CONVENTIONAL ACTIVATED SLUDGE AERATION TANK to conduct parallel oxygen uptake experiments on effluent from treatment plant and tap water and determine α and β values. These experiments have been conducted in field or laboratory without giving consideration to the size of aeration units. In this investigation, two different types of wastewaters were studied in three different laboratory units and the results are compared to determine the effects of tank geometry and airflow rates on α and β values.

CHAPTER II

LITERATURE REVIEW

A. "Two Film" Theory of Gas Transfer

The biochemical purification of wastewater involves mass transfer process, which is based on "Two Film" theory developed by Lewis and Whitman (5) in 1924. Ippen (6) revised it in 1952, and it has been employed extensively in the computation of oxygen absorption rates in water. This theory is explained with reference to sketches in Fig. 2, which represents oxygen concentration profiles that are present across air-water interface. The mass transfer occurs by slow rate of molecular diffusion between the two phases by a driving force, which is a partial pressure gradient in the gas phase and a concentration gradient in the liquid phase. For gases with low solubility, like oxygen in water, the gas film offers very little resistance as compared to the liquid film, and $P_i = P_g$. Therefore, it can be assumed that the entire resistance to the transfer of oxygen into the water is caused by the liquid film and the concentration of oxygen in the solution at the interface is that of saturation, i.e., $C_i = C_s$ = saturation concentration of dissolved oxygen at the partial pressure, P_g (7, 8).

The use of this theory is justified with two assumptions:

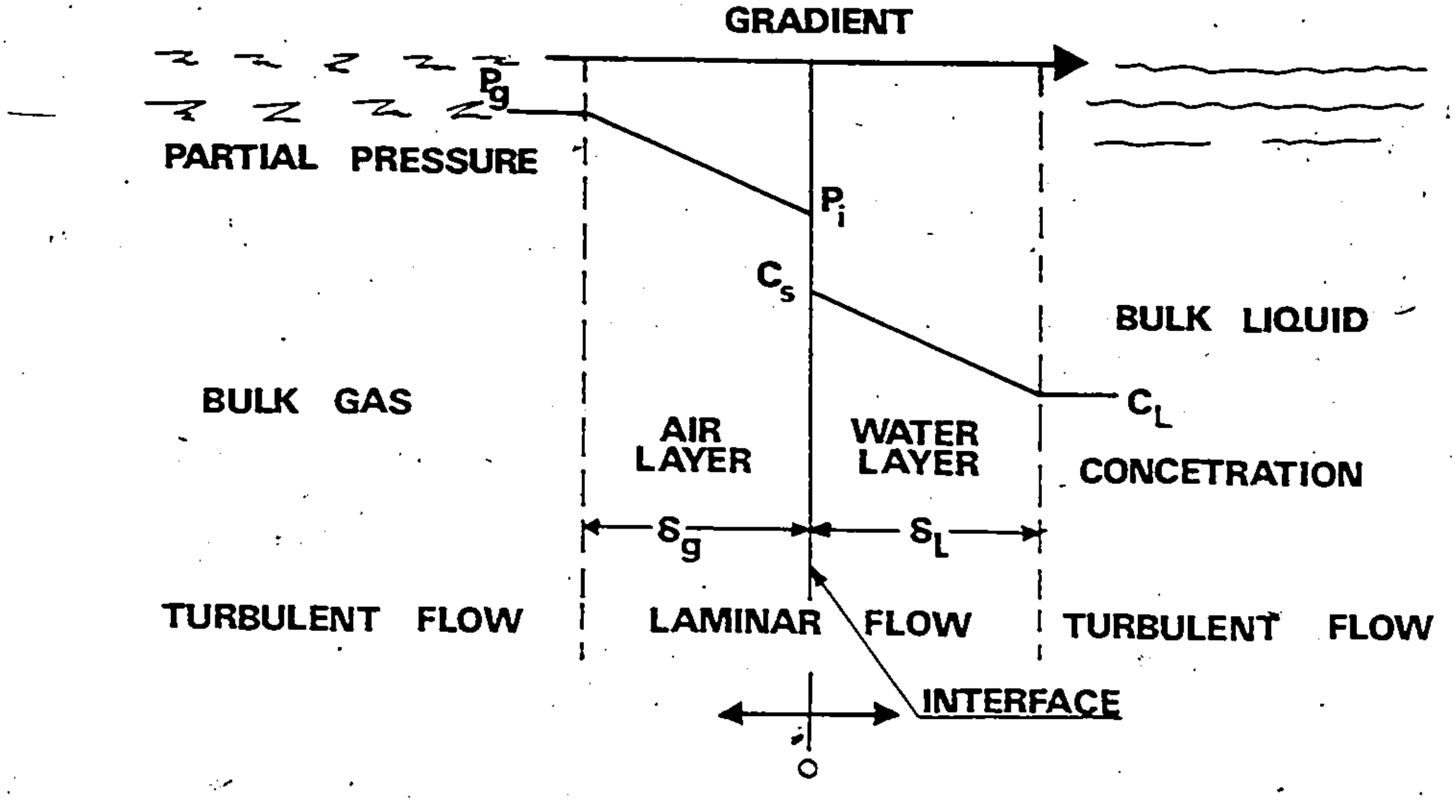
(i) oxygen is completely mixed in the gas phase, i.e., P_g is same in the entire bulk volume of air, and

(ii) dissolved oxygen concentration, C_L, is same in the bulk water (9).

B. Basic Mathematical Model for Oxygen Transfer

The diffusional process is defined by Fick's Law (10):

$$\frac{dm}{dt} = - D_L A \frac{dC}{dy} \qquad \ldots\ldots \quad 1$$



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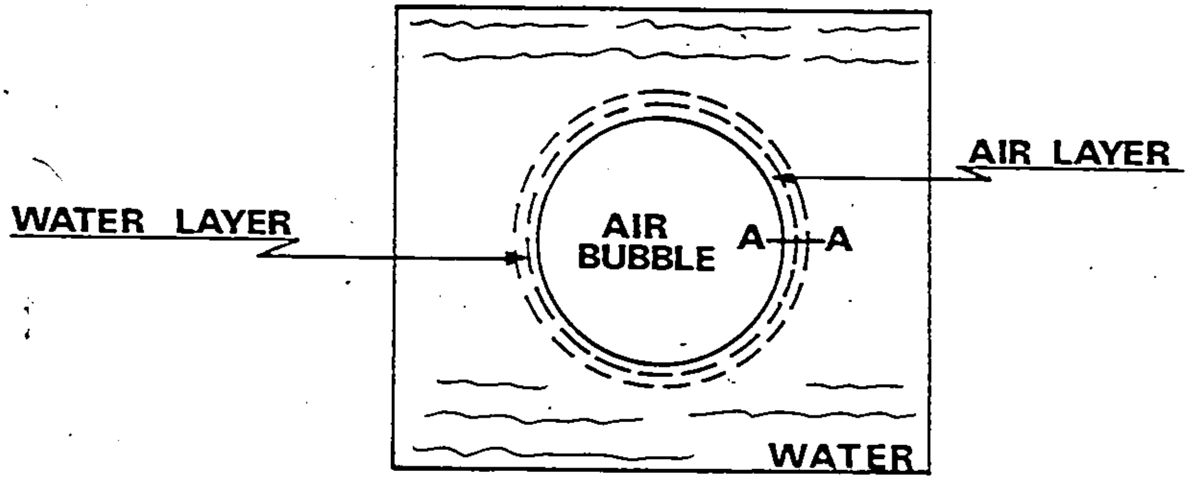


FIG. 2 - MASS TRANSFER OF OXYGEN INTO WATER "TWO FILM THEORY"

where,

$\frac{dm}{dt}$ = time rate of mass transfer by diffusion, MT^{-1}

D_L = diffusion coefficient for oxygen in water, L^2T^{-1}

A = cross-sectional area through which diffusion occurs or absorbing area, L^2

and $\frac{dC}{dy}$ = concentration gradient in the direction parallel to the cross-sectional area, ML^{-4}

Mass transfer takes place through laminar films at the gas and liquid interfaces and through the turbulent body of fluid until a dynamic equilibrium is reached. Since the concentration of dissolved oxygen is considered uniform throughout the depth, the rate of mass transfer may be expressed as (7):

$$\frac{dm}{dt} = \frac{D_L}{Y_L} A(C_s - C_L) = \frac{D_g}{Y_g} A(P_i - P_g) \qquad \ldots\ldots \quad 2$$

$$= K_L A(C_s - C_L) \qquad \ldots\ldots \quad 3$$

(because the resistance in the gas phase is negligible as compared to that in the liquid phase)

where,

D_g = molecular diffusivity of the gas through the gas film, L^2T^{-1}

Y_g = hypothetical gas film thickness, L

Y_L = hypothetical liquid film thickness, L

K_L = liquid film coefficient, LT^{-1}

This mass equation may equally be represented in concentration units by introducing the volume of the liquid, $\forall$.

Thus,

$$\frac{1}{\forall}\frac{dm}{dt} = \frac{dC}{dt} = K_L \frac{A}{\forall}(C_s - C_L)$$

or

$$\frac{dC}{dt} = K_L a(C_s - C_L) \qquad \ldots\ldots \; 4$$

where K_La = overall transfer coefficient, T^{-1}.

This form of equation is widely accepted and used for determining oxygen uptake rates in modern aeration systems. In practice, the ratio between K_La values obtained with wastewater effluent and tap water respectively, has been defined as alpha factor, α. Similarly, the ratio of dissolved oxygen saturation concentration values for wastewater effluent and tap water respectively is defined as beta factor, β.

C. Previous Investigations Associated with Measurements of Oxygen Transfer Efficiency and Alpha and Beta

Both the Water Pollution Control Federation, WPCF, and American Water Works Association, AWWA, recommend a standard procedure for measuring oxygen uptake rates in wastewater and clean water. The ratio in these oxygen uptake rate values is called alpha factor; whereas the ratio in dissolved oxygen saturation values for wastewater and clean water is called beta factor. Only a limited amount of literature exists on alpha and beta measurements as compared to the publications on oxygenation in water.

The type of aeration device, mixing intensity and wastewater constituents are reported to affect alpha and beta measurements. A number of researchers like Bass and Shell (11), Stuckenberg, Wahbeh and McKinney (4) and many more (12), (13), (14) have described the apparatus used to conduct alpha measurements. Otoski (14) tried different aeration devices and observed variations in alpha values. Bass and Shell (11) conducted tests for alpha measurement on a complex industrial wastewater. From their studies, it appeared that the results could vary up to 40% by using different aeration devices. Kalinske (15) and others (12) recommended that same type of aeration device should be used for the test as would be used in the field. WPCF Manual No. 5 (16) recommends that great care should be exercised in the interpretation of the bench scale alpha data for the field conditions. The reason being that the pattern of turbulence has an influence on alpha. Otoski (14) found a direct relationship between turbulence and alpha value for different types of aeration devices studied. The turbulence affects the rate of oxygen uptake and hence alpha. To minimize the effect, Bass and Shell (11), Stuckenberg et al. (4) and Weis and Lad (17) have recommended that the K_La value for bench scale test for alpha measurement should be approximately equal to the field value. A study conducted by Otoski (14) to compare bench scale with full scale alpha measurements showed results contradictory to the above mentioned recommendation for submerged aeration devices.

Contradictory observations have been reported by various investigators on the effect of suspended solids on alpha values. Stuckenberg et al. (4) have suggested two ways in which mixed-liquor suspended solids (MLSS) can affect oxygen transfer; by changing viscosity and by releasing soluble organics. But for the most part, they believe that the MLSS concentration in the aeration tank is not high enough to adversely affect viscosity. Living microbial mass would release soluble organics only in oxygen deficit environment which could reduce alpha. So as long as the cells remained aerobic, there was no problem. They further suggested the remedy to employ final effluent or supernatant from the settled mixed-liquor. But Damhaug and Balmer (18) using supernatant had concluded that the determination of alpha on activated sludge supernatant or secondary effluent might give misleading results. They also recommended that it was important to include the effects of suspended solids. They obtained a negative effect on the K_La value, whereas Matson and Bennett (19) presented their finding by reporting that microorganisms could increase oxygen transfer rates by disrupting the liquid surface film surrounding the gas bubbles and hence, produce a higher alpha value. These two findings contradict each other.

The presence of materials such as proteins, detergents, oil and other surface active agents affect film characteristics and surface tension which tends to decrease oxygen transfer. Aiba and Toda (20) suggested that quiescent conditions were created at the interface due to these surface active agents and hence decreased the surface renewal rate. A research on fine bubble dome diffusers by British Research Laboratory (21) showed that alpha value for water with 5 mg/L of detergent concentration produced an alpha value of less than 0.5; whereas, for the mixed-liquor it was 0.6; however, it varied from 0.3 to 0.8 depending upon aeration time. Pfeffer, Hart and Schmid (22), while experimenting on wastewater from Topeka plant, found very low values of alpha. They suspected that alpha values of 0.45 for the contact tank and 0.60 for the reaeration tank were unique only to the Topeka plant. However, they did emphasize the necessity of considering lower design values of alpha than presently used. Eckenfelder and O'Connor (7) have reported a wide variation in alpha values. Even 100% fluctuations in alpha values for similar raw wastes are possible. As bio-oxidation proceeds and contaminants are destroyed, the rate of oxygen uptake approaches that in clean water. King (23) discovered that the oxygen transfer rate decreased sharply when domestic wastewater was added to the activated sludge and then rose as the organic materials were stabilized. Thus, the complexity of wastewater makes alpha to vary over a wide range. Gilbert (3) had observed a change in alpha value from 0.8 to 0.5 over a period of 4 hours in a brewry waste. The factors influencing were production schedule and rain water dilution. At the same time, the magnitude of error in the selection of alpha and beta values can be substantial. Gilbert (3) had observed that a reduction in alpha factor from 0.7 to 0.5 would result in an oxygen deficit of 40% between requirements at field versus standard conditions, keeping other factors the same. Similarly, an increase in alpha factor to 0.9 would result in an excess standard oxygen value of 22%. When both the alpha and beta values vary from the design values, the total effect is compounded.

The beta has been generally referred to as the salinity correction factor. It involves the measurement of saturation concentration of dissolved oxygen in wastewater and tap water. There are several methods for measuring dissolved oxygen, but membrane electrode method is mostly applied for the measurement in wastewater. Bass and Shell (11) have reported that the probes yield false saturation readings because they measure percent saturation and not actual dissolved oxygen and therefore should not be used for beta measurements. Gilbert (3) on the other hand does not agree to it. Kayser (24) had concluded that the values of oxygen uptake rate were independent of wrong calibration. It was only necessary that the electrode reading should be proportional to the oxygen concentration. Kalinske et al. (25) have reported that all probes have some delay in measuring dissolved oxygen and they measure a concentration that existed a short time previously. Thus, it can significantly influence the values in the initial part of the test. They have further stated that it could be proved mathematically that this delay would result in K_La values lower than the correct values..

There are mainly two techniques to deoxygenate the basin-by sulfite addition and by nitrogen stripping. The former technique involves the addition of chemical sodium sulfite, in addition to cobalt chloride, which acts as a catalyst. Recently, there have been some arguments over the cobalt chloride concentration. Kalinske et al. (25) had observed cobalt interference in the dissolved oxygen test. They have stated that when sodium sulfite was used to deoxygenate the water, more than 0.05 mg/L cobalt ion concentration caused a chemical interference in the dissolved oxygen concentration by Winkler method. This chemical interference varied with the cobalt ion concentration, the number of sulfite additions and the aeration period between tests and saturation. They recommended that no additional cobalt was required after the initial addition and only technical grade chemicals should be used. Their experience showed that as many as twenty tests could be made in a single batch of water without significant error in oxygen measurements. They further recommended that if higher concentrations were to be used, a fast response probe should be employed for oxygen measurement, so the effect of cobalt concentration does not remain critical. Based on the results of their study, Naimie and Burns (26) concluded that a cobaltous ion concentration of 2 mg/L and less caused 80% to 90% of the error in the dissolved oxygen measurements by Winkler's method. This was attributed to the formation of hydrogen peroxide in the test. At relatively higher concentrations, hydrogen peroxide gets catalytically decomposed to trivalent and tetravalent cobalt oxides which cause interference. This interference could probably be eliminated at pH 6.9 or less, whereas maximum interference would occur at pH 10 or 11. Stanton and Bradley (27) had proposed that, in order to rectify this interference, the magnitude of the interference in a blank should be determined and that value should be subtracted from the one obtained by Winkler's method.

The stoichiometric relationship for the oxidation of sodium sulfite in Appendix A shows that 7.89 mg/L of sodium sulfite is required to remove 1.0 mg/L of dissolved oxygen. Since the aeration device itself is recommended to be used to mix the sodium sulfite within the basin (4), a little more should be added depending upon the geometry of the tank and the mixing characteristics. Gaden (28) had observed that use of large quantities of sodium sulfite produced high transfer values. Kalinske (25) had reported that interference in Winkler's method increased with higher sulfite addition. On the other hand, the nitrogen stripping process is purely a physical method. The bubbling of nitrogen through the water or wastewater takes out the dissolved oxygen from it.

The analysis for the measurement of rate of oxygen uptake in submerged aeration system is made by two approaches. These two approaches involve modelling of oxygen transfer process. Baillod (29) criticized the conventional approach for neglecting the effect of exit gas depletion and called it the "apparent k_La". His approach was more realistic as it considered the influence of gas side oxygen depletion and can be concluded as "true K_La". He further concluded that the field predictions based on the conventional method provided "apparent alpha values", whereas modified model gave "true alpha values". Brown (30) had reviewed some of the fundamental statistical concepts in regression analysis and the methods of computing K_La were evaluated on the basis of data truncation, saturation concentration and error structure. His findings were that the exponential method, using a weighted nonlinear regression technique, appeared most attractive for the analysis of non-steady state oxygen transfer data.

The study of factor alpha involves the measurement of oxygen uptake rates in wastewater and clean water. The prime motive of the various studies related to oxygen transfer in water was to increase the oxygen transfer efficiency, thereby reducing the high costs associated with the unit operation. The phenomenon of oxygen transfer is occuring in nature, since the inception of life on Earth. One of the earliest attempts to investigate the factors associated with the efficiency of aeration was made by Eckenfelder (31). He observed that the depth of diffuser submergence had an enormous increasing effect on the overall efficiency of the aeration system. But, the power required also increased linearly with increasing depth.

Carver (32), while employing a venturi diffuser for discharging bubbles into a six inch lucite column filled with water, noticed that for a given bubble size, the percentage absorption increased linearly with column height. He concluded that the higher the retention time, the greater was the transfer of oxygen. In 1955, King (23) studied the oxygen transfer mechanism in a conventional spiral flow aeration tank. He reported that if the velocity of the overturning current was more than what was necessary to produce adequate mixing, then this velocity should be reduced in order to increase the bubble retention time in the liquid to obtain higher absorption efficiency. A similar investigation was made by Lamb (33). He reported that the velocity of the air bubble was the vectorial sum of its terminal velocity of rise and the velocity of the air-water mixture. This high velocity in the conventional treatment plants reduced the bubble detention time. Consequently, he suggested that an improvement could be achieved by spreading the diffuser uniformly over the entire tank bottom, which in turn would reduce the velocity of air-water mixture. Bewtra (34), too, had reported similar observations. While working with Nicholas (35), on a full scale tank, they had demonstrated mathematically that increasing the velocity of the air-water mixture had two-fold effect in the aeration tank. It decreased the usable energy induced in the liquid along with decreasing transfer of oxygen. They concluded that the circulating velocity should be just enough to keep biological flocs in suspension. Alani's work on a two-column aeration tank, as quoted by Bewtra (35), demonstrated that percent oxygen absorption was inversely proportional to the circulating velocity throughout the tank which was later on verified by Mavinic (36, 37).

Morgan and Bewtra (38), while conducting tests on a conventional spiral air flow aeration tank concluded that the rate of oxygen transfer for a given airflow rate was proportional to the diffuser submergence. Bewtra and Nicholas (35) found out that the rate of oxygen absorption per unit of power input increased with a decrease in submergence depth. These observations support the observations made by Eckenfelder (31). Lister and Boon (39), while experimenting on a tank 1.5 m x 1.5 m x 8.5 m and using fine bubble diffused-air system had shown that in a flat bottomed tank, the rate of transfer of oxygen into water and mixed-liquor was little affected by the depth of liquid within the range 1.2 to 8.2 m. They also concluded that higher overall oxygenation efficiencies would be achieved in completely mixed aeration tanks, than in plug flow tanks. Pasveer (40) also had noted that the air bubbles entered the conventional systems with water velocity 2 to 3 times as great as that of the air bubble resulting in contact time as low as 1/3 to 1/4 of the expected value.

While working on the same problem, Pasveer and Sweeris (40, 41) came out with a totally different approach, i.e., horizontal flow diffused air system. They reasoned that the time of contact would be determined by the self velocity of ascent of the air bubble, which is very much the same as if the air bubble ascends in a quiescent water column. While working on a ring shaped aeration tank with variable horizontal velocity of flow, they demonstrated that efficiency of aeration in the horizontal flow system rose to 2 to 2.5 times as compared to spiral flow or vertical flow systems with the same water depth. Not only was there higher efficiency, but there was a reduction of 60% in the length of the porous tubes and 60% of the volume of air and energy required for spiral flow system.

In 1958, a new concept was developed keeping in mind that the diffuser submergence and bubble retention time had individual influence on the aeration efficiency. This new concept is called U-tube concept and was first studied by Bruijn and Tuinzaad (42) from the Netherlands, while striving to achieve higher aeration efficiency with least possible energy input. This U-tube concept struck to them while experimenting on a U-shaped tube, 3.2 inch in diameter, vertically mounted with one stem being a 44 foot long downdraft tube, while the other was 9.5 feet shorter. The diffuser was located at the top of the tube. Oxygen transfer efficiencies obtained were much higher due to pressure increase and the longer contact time of the downward travelling bubbles. This two-fold effect lead them to modify their original experimental set up, thus resulting in a U-tube with downward travelling air-water mixture in the inlet stem and rising in the outlet stem. Thus, distance travelled by air-water mixture was longer and, hence, higher transfer efficiency. Also, it exhibited the least energy requirement out of the present existing systems of aeration. In addition, it required less space, low construction cost and very low maintenance and supervision.

The U-tube concept was further developed by Speece et. al. (43), using various improvement techniques. They separated the downflow and upflow chambers by baffles and employed various size bubble diffusers. They observed that in a gas transfer process, gas-liquid mixture was temporarily pressurized by means of a temporary hydrostatic head resulting in a higher rate of oxygen transfer. They further proposed that, depending on the availability of sufficient hydraulic head, the free fall of the water into the inlet of the U-tube would entrain air bubbles and negate the use of any external power required.
Speece (44) has recommended the application of U-tube in various situations.

Recently, Speece (44, 45), had investigated another technique for obtaining higher aeration efficiency by increasing the bubble detention time. He studied an aeration system with water flowing downwards in aeration chamber with expanding cross-section like an inverted cone. He named this system as the Downflow Bubble Contact Aeration, DBCA, system. The dual advantage claimed for this system is the ability to efficiently dissolve oxygen while simultaneously stripping dissolved nitrogen from the water. The emphasis in this system is that the entering velocity of water should be higher than the buoyant velocity of the air bubbles to prevent them from escaping at the top, while the exit velocity of water should be lower than the buoyant velocity of the bubbles in order to keep them within the system. Thus, air bubbles are entrapped within the system, which results in higher transfer efficiency. Speece has concluded that this increase in oxygen transfer efficiency is mainly due to a very long period of contact bubbles within the hood. Filling of the cone chamber with bubbles also provides higher ratio of bubble interfacial area to water volume. In addition, higher turbulence within the hood adds for the higher gas transfer rates. He observed that about 1.0 mg/L of dissolved nitrogen is stripped for every 3.5 mg/L of oxygen dissolved.

Eckenfelder (46), had mentioned that by dividing the larger bubbles into smaller sizes by tank turbulence alone, the surface area to bubble volume ratio could be increased. Morgan and Bewtra (47), observed that better transfer efficiencies were obtained when bubble shearing devices were used along the coarse bubble spargers to create smaller air bubbles to increase both the bubble-liquid interfacial area, as well as liquid turbulence. Pasveer (48) had stated that for smaller gas bubbles, higher ratios of interfacial surface area to bubble volume were obtained. Carver (32) had reported that bubbles in the range of 0.1-0.6 mm radius and greater than 4.0 mm radius exhibited higher terminal velocities. Thus, the larger the bubble size, the greater is the terminal velocity, i.e., lesser retention time, as well as a reduction in bubble surface area. Pasveer (40) and Dobbins (49), had pointed out the problem of clogging in fine bubble diffused aeration systems. USEPA (50) has stated that the fine bubble diffuser system is more efficient and cheaper to operate, but involves greater capital investment and higher maintenance than a coarse bubble system.

The rate of air supply has considerable effect on oxygen transfer efficiency. Carver (32), found out that increasing the gas flow rate decreased oxygen absorption rate. This result was attributed to the more frequent generation of the larger gas bubbles. He further stated that wakes were formed as the bubbles rose, which set an upward motion in the liquid called "chimney effect". This effect intensified with the higher air flow rate, thus reducing oxygen absorption efficiency. Looking into the same problem, Eckenfelder (46) stated that the mean diameter of the air bubbles produced at any air flow rate was a direct exponential function of that flow rate. During the same study, he emphasized the need for relating absorption efficiency to actual tank conditions. Bewtra _et_. _al_. (35, 38, 47), while experimenting on a full scale aeration tank, reported that for Saran porous diffusers, improved efficiency was obtained by reducing the unit rate of air flow, whereas with spargars, an insignificant difference existed.

King (23, 51) had investigated the effects of size and spacing of the diffusers with respect to the tank. He, using a spiral flow aeration tank, reported that for the normal working depths, the different plate area should be as large as practical and economical. He further concluded that for 5 to 10% increase in the plate area, oxygen transfer increased about 8%, keeping all other conditions identical. He pointed out that by setting porous plate diffusers in a row farther from the wall and also spaced apart, the oxygen transfer efficiency would face an improvement. The reason for the increased efficiency was the decrease in the velocity of the rising liquid just above the diffusers.

Bewtra (34, 35, 52) also had looked into the effects of diffuser size and spacing for a full scale aeration tank and arrived at the conclusion that, with same air flow rates, a wide band of diffusers gave a greater oxygen transfer than a narrow band. The movement of diffusers away from the walls resulted in appreciably higher increase in oxygen transfer. The effect of tank geometry was studied by Morgan and Bewtra (47), by comparing oxygen transfer in a two column aeration tank representing conditions in a conventional spiral flow system, with that in a single column tank. The efficiencies in the two column unit were only 0.6 times those in the single column unit, while keeping all other conditions the same. Rapid surface renewal, bubble breakage and high turbulence in the confined column were found as the reasons for the higher transfer efficiency. They (38) further pursued the effects of the geometry in a full scale tank 24 foot wide by dividing it into two 12 foot wide units. To maintain the same ratio of air flow to water volume, one diffuser in the 12 foot tank was compared to two diffusers in the 24 foot tank. Only higher air flows showed remarkably higher transfer efficiencies due to the greater bubble entrainment in the smaller tank. Later on, Bewtra (34), concluded that as the ratio of the width of the air water mixture stream of the effective tank width was increased, the number of air bubbles entrapped in the downward moving water in the spiral flow tank also increased, which resulted in the increased contact time and hence, higher efficiency. His explanation for the higher efficiency was that the entrapped air bubble was carried downward by the liquid stream whenever the natural buoyant force acting on the air bubble was overpowered by the drag force due to the circulating velocity of the liquid. This circulating velocity, in turn, was greatly affected by the tank geometry (52). Bewtra and Nicholas (35) also investigated the effect of tank width on oxygen transfer efficiency, while using a wide band diffuser system. By decreasing the width, higher values were obtained for fine bubble Saran tubes than for the coarse bubble spargars. They associated this achievement to the entrainment of a large percent of air bubbles in the downward moving water zone and thus carried to the bottom of the tank.

The intensity of agitation and turbulence have a marked effect on the oxygen transfer. Eckenfelder (31) had studied these effects. The sludge cells tend to join together, which increases resistance to oxygen transfer. Higher agitation breaks them. While studying the effects of the boundary layer, Pasveer (40) had suggested that, for the higher dissolution of the oxygen, not only should there be a boundary layer at the water air interface as large as possible, but also a rapid renewal of that boundary layer by maintaining a continuous replacement of new water layers from the bulk volume of the water. Eckenfelder (46) had suggested that higher oxygen transfer rates were also achieved by a high oxygen deficit or driving force. He recommended that the level of the dissolved oxygen be maintained at about 2.0 mg/L in the waste treatment aeration tank to maintain aerobic conditions in the system.

Improved transfer efficiencies could be achieved by employing improved aerating devices like turbine aerators, jet aerators, disc type units and impingement aerators. These devices have been discussed in detail by Eckenfelder (46). Improved efficiencies were observed by Morgan and Bewtra (47), while using hydraulic shear box and venturi diffusers in a full scale aeration tank. "Pressure Injection", another improved technique of aeration has been mentioned by Thackston and Speece (53). In this, a small amount of the total volume is compressed and air is mixed with it until the water is supersaturated. When this supersaturated water joins the main stream, excess air comes out of the solution as tiny air bubbles, which rise through and aerate the water. The use of pure oxygen in a U-tube system was tried by Speece et al. (43) and they reported 500% higher dissolved oxygen levels as compared to a system in which air was used.

In late 1979, Lakin and Salzman (54) examined subsurface aeration systems to develop an appropriate model for evaluating submerged aeration process equipment on a standard basis and a unified semiflow reactor approach was presented. The results indicated that the method of evaluation presented was superior to other techniques for several reasons listed in the paper.

There are some other factors which affect the transfer of oxygen into water. Boon, while presenting the discussion on Eckenfelder's paper (55) stated that the studies at the Water Research Centre in the United Kingdom had shown that the coefficient of oxygen uptake rate decreased by about 20% when the concentration of suspended solids was increased from 1400 to 6600 mg/L. Kalbskopf (56) and others had identified significant effects of the presence of surface active agents on mixing patterns. This in turn, no doubt, influences the oxygen transfer rates.

Naimie, Nelson and McCarthy (57), while studying the effects of pH, iron and manganese on the rate of oxygen uptake had reported that the results were consistent, but different for phosphate and non-phosphate buffered systems when the systems were deoxygenated by sulfite addition or nitrogen stripping, within the pH range studied. In their experiments, probes were used to measure the dissolved oxygen and iron and manganese concentrations were at low background levels. They further concluded that iron and manganese and probably other transitional elements substantially enhanced, up to 100% in those evaluations, the oxygen mass transfer from the gas phase to the liquid phase. A contrary statement was made by Boon while presenting discussion of this paper. He reported that changes in the hardness of the water and small changes in the concentrations of inorganic salts, including sodium sulfate contents, had little effect on the results. An addition of 5 mg/L of detergent affected the results by 5% only.

D. Factors Affecting Alpha and Beta Values

Important factors affecting alpha values are (3, 4, 58):

(i) Wastewater characteristics
    (a) Biochemical Oxygen Demand, BOD
    (b) Chemical Oxygen Demand, COD
    (c) Suspended Solids, SS
    (d) Surface tension of the wastewater
(ii) Temperature
(iii) Aeration Device
(iv) Power level
(v) Basin Configuration

Similarly, the important factors affecting beta values are (3, 58):

(i) Wastewater Constituents such as
  (a) Salt Concentration
  (b) Organic Matter
  (c) Dissolved Gases
(ii) Barometric Pressure
(iii) Temperature

E. Suggestions from the Workshop Toward an Oxygen Transfer Standard

This workshop was organized by USEPA and was held in April 1979 in Asilomar, California, U. S. A.

The experts in the field of oxygen transfer were brought together to identify:

(a) research needs in the development of an effective consensus standard for oxygen transfer devices, and
(b) the areas of agreement and disagreement in the evaluation of oxygen transfer devices.

Consequently, the group came up with the following suggestions (59):

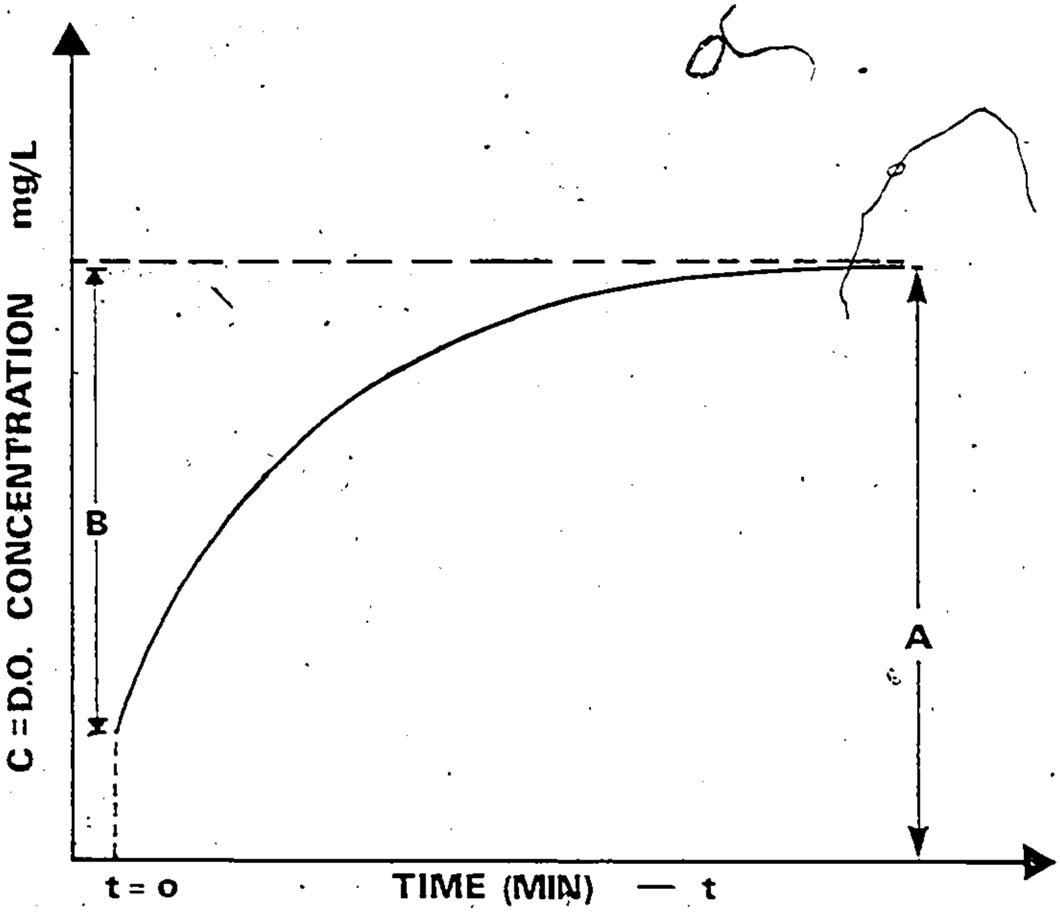
1. The recommended model for the analysis of unsteady state clean water oxygen transfer is

$$C = A-Be^{-Dt} \quad ..... \quad 5$$

where A, B, C and t are explained in Fig. 3.

2. The parameters A, B and D should be estimated by fitting the model to concentration-time data by means of a nonlinear least squares regression technique. Also, the standard deviation at the parameter estimates should be examined.

3. Values of C less than 10% to 20% of the saturation value A may be truncated to avoid lingering effects of deoxygenation techniques,



MODEL USED ; $X = B_1 + B_2 e^{(B_3 t)}$

WHERE,

$B_1 = A$; $B_2 = -B$; $B_3 = -D = -K_L a$; $X = C$

FIG. 3 — MODEL EQUATION FOR VARIATION IN D.O. CONCENTRATION WITH TIME

and because these data contribute little to the ability to estimate A and D.

4. Truncation of the data near saturation should be avoided as these data have significant effect on the parameter estimates for A and D.
5. A test should be continued at least for a period equal to 6/D.
6. Temperature should be measured at the beginning and at the end of the experiment with a desirable variation of $2^{\circ}C$ or less. The average and extreme values of temperature should be reported.
7. The analysis should be made with minimum of 10 to 15 data points. Approximately two-thirds of these final points should be evenly distributed over the period of time covered by 0.5/D to 2/D. The remaining one-third points should be evenly distributed over 2/D to 6/D period. In cases of rapid transfer, the minimum time between data points should be 0.5 minutes. For multiple sample points, the value of A and D should be obtained separately for each point and then average should be taken.

Further, the group had recommended that the testing procedural document should include:

1. Recording specified conditions for reporting air flow and observed data relating to the existing conditions of measurement.
2. A statement recommending the use of appropriate codes or manuals for air flow measurement.
3. Appropriate procedure for system pressure measurement exclusive of air flow requirements.
4. The requirement of reporting the detailed description of the test geometry for any test conducted.
5. A statement regarding the preferred water temperature range for testing.

6. A statement that nitrogen stripping is an acceptable procedure.
7. A statement that the use of analytical grade sodium sulfite for deoxygenation is an acceptable procedure.
8. The recognition that technical grade Na_2SO_3 can be used as a deoxygenating chemical with the provision that adequate quality control to avoid testing interference be followed.
9. A statement recommending the use of $CoCl_2 \cdot 6H_2O$ in solution form as the source of the cobalt catalyst for deoxygentation.
10. The testing procedural document should address the proper cobalt concentration for testing with due consideration given to adequate catalyst (say > Co as Co) for deoxygenation and provisions for elimination of dissolved oxygen testing interferences with higher concentrations. A portable maximum concentration of 2.0 mg/L as Co was suggested.
11. The standard procedure should require a sulfite addition adequate to reach zero D.O. and to remain zero for a reasonable period (say 2 minutes).
12. The addition of sulfite in slurry form should be the recommended procedure with an alternate procedure for dry chemical addition delineated and consideration for multiple point addition addressed.
13. The use of D.O. probes for in-place and external measurements should be included as an acceptable D.O. measurement procedure. It should be duly noted that appropriate detailed analytical care must be exercised to assure accurate results with probe measurements.
14. The testing document should address the question of allowable number of sulfite additions per tank of water with consideration given to setting testing limits of sulfite or total dissolved solids concentration.

15. The testing document should provide the option of deleting the initial run on a fresh tank of water to account for uncertain interactions with sulfite addition.
16. The testing document should address the question of chemical interferences and iodine vapourization in Winkler D.O. analysis.
17. The testing document should address the question of termination of runs in the case of repetitive testing with consideration of length of run necessary to reach C_s in every case and obtaining appropriate data for the recommended method of calculation of K_La.
18. The testing document should define a common procedure for attaining measured oxygen saturation value.
19. The testing document should address the number of repetitive tests required and the reproductability limits of multiple testing.
20. The testing document should focus on clean water testing only and surfactants should not be used to modify the clean water test liquid basis.

The recommendations of the discussion on alpha and beta factors are presented below (59):

1. Since alpha was not a constant, a single evaluation was not adequate. A number of analyses should be made on the process waters during testing and full scale operation to develop a range of values.
2. A sample of the MLSS at the influent and effluent ends of the aeration basin should be analyzed for alpha in the bench, pilot or full scale operation. If no process system was operating, alpha should be completed on the raw wastewater.
3. At least two samples should be analyzed for alpha, which should be based upon the variability of the wastewater.

4. Only one analysis per sample was recommended for both clean and dirty (process) waters. Multiple sampling was strongly recommended.
5. Four types of samples were recommended with preference to the mixed liquor at the influent and the effluent end of the basin, with the solids remaining. Upon the nonavailability of it, the raw wastewater, settled aerator basin effluent and aerated effluent (solids with a constant oxygen uptake) could be used, as an alternative for alpha analysis.
6. If liquid samples were available, the alpha analysis should be made as follows:
   (a) Raw Wastewater
   (b) Bench Scale Mixed Liquor
   (c) Pilot Scale Mixed Liquor
   (d) Full Scale Mixed Liquor
7. In all cases, except the raw wastewater, the clean water portion of the alpha test would be completed in the actual aeration basin (i.e., Bench, Pilot and Full Scale).
8. Any aeration device could be used in the laboratory scale tests. The pilot plant aeration device should be identical to the full scale device.
9. The K_La value for the alpha test should be the same as the expected full scale aeration basin K_La value.
10. A correlation should be made to relate the Bench, Pilot and Full Scale alpha as per Table I.
11. All dissolved oxygen measurements be completed using a properly calibrated dissolved oxygen probe.
12. Aeration basin influent and effluent samples should be analyzed

for beta. The saturation value for dirty water be corrected for total dissolved solids.

13. The research be initiated to establish a better understanding of the temperature correction factor.

TABLE I - BENCH, PILOT AND FULL SCALE ALPHA CORRELATION

Aeration Type	Alpha Bench	Alpha Pilot	Alpha Full Scale
1	c'	ac'	a'c'
2	c'	bc'	b'c'
3	c'	cc'	c'c'
4	c'	dc'	d'c'

CHAPTER III

APPARATUS AND INSTRUMENTS

A. Apparatus

Three different bench scale geometrical shapes of aeration tanks, as shown in Figures 4, 5 and 6 were used in this study. All of these tanks were made from 3/8" thick plexiglass. The location of the diffusers was fixed arbitrarily with a common choice to place them near the bottom. In Fig. 4, the diffuser was porous, spherical stone, commercially available from Fisher Scientific Company. It was located in the centre of the tank. In Fig. 5, the coarse bubble diffuser employed was a 3/8" diameter copper tube, ring shaped with twelve evenly spaced 1/16" diameter holes along the inside edge of the ring. This arrangement gave a fairly even distribution of air bubbles throughout the cross-section of the plexiglass column. The diffuser ring was fastened on the inside of the column and the air was supplied through four, 1/8" diameter, copper tubes which were connected to the main air line. The third tank had a diffuser made from a plexiglass tube, 4 inches long with six drilled holes, evenly spaced. It was located at one end of the tank and it resembled a conventional aeration unit.

B. Air Flow Meter

The compressed air supply line was under constant pressure and connected to the feeder tube of the diffuser through an air flow meter, Lab Crest Mark III, supplied by Fisher Scientific Company. It operates as a rotameter with a ball floating inside a variable area metering tube. Use of the various tube and float combinations under standard conditions in the flow meter frame permitted gas flow rate measurements from 0.4 mL to 23400 mL per minute (60). The air flow rates were

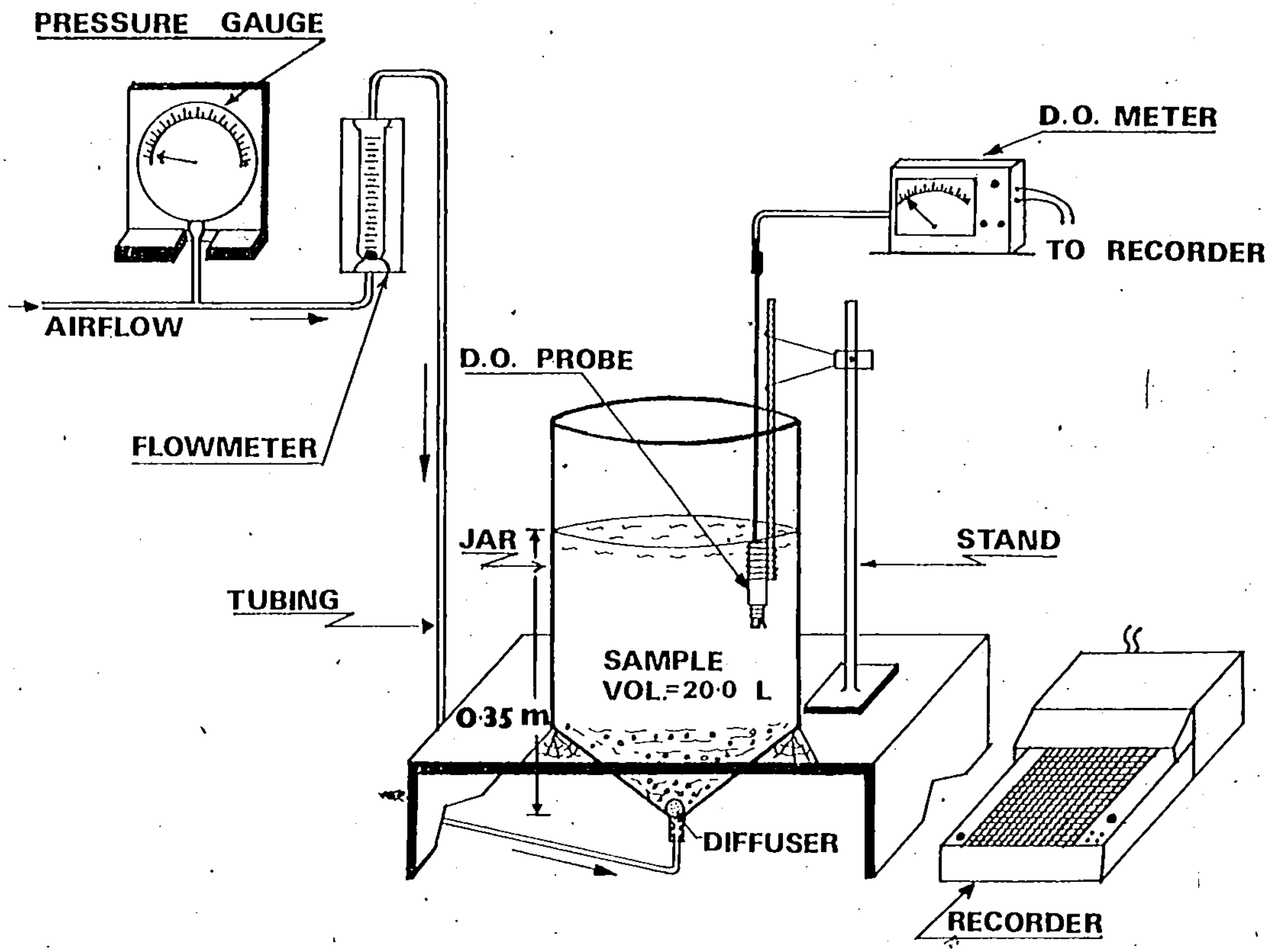


FIG. 4 - SCHEMATIC DIAGRAM FOR JAR BASIN APPARATUS

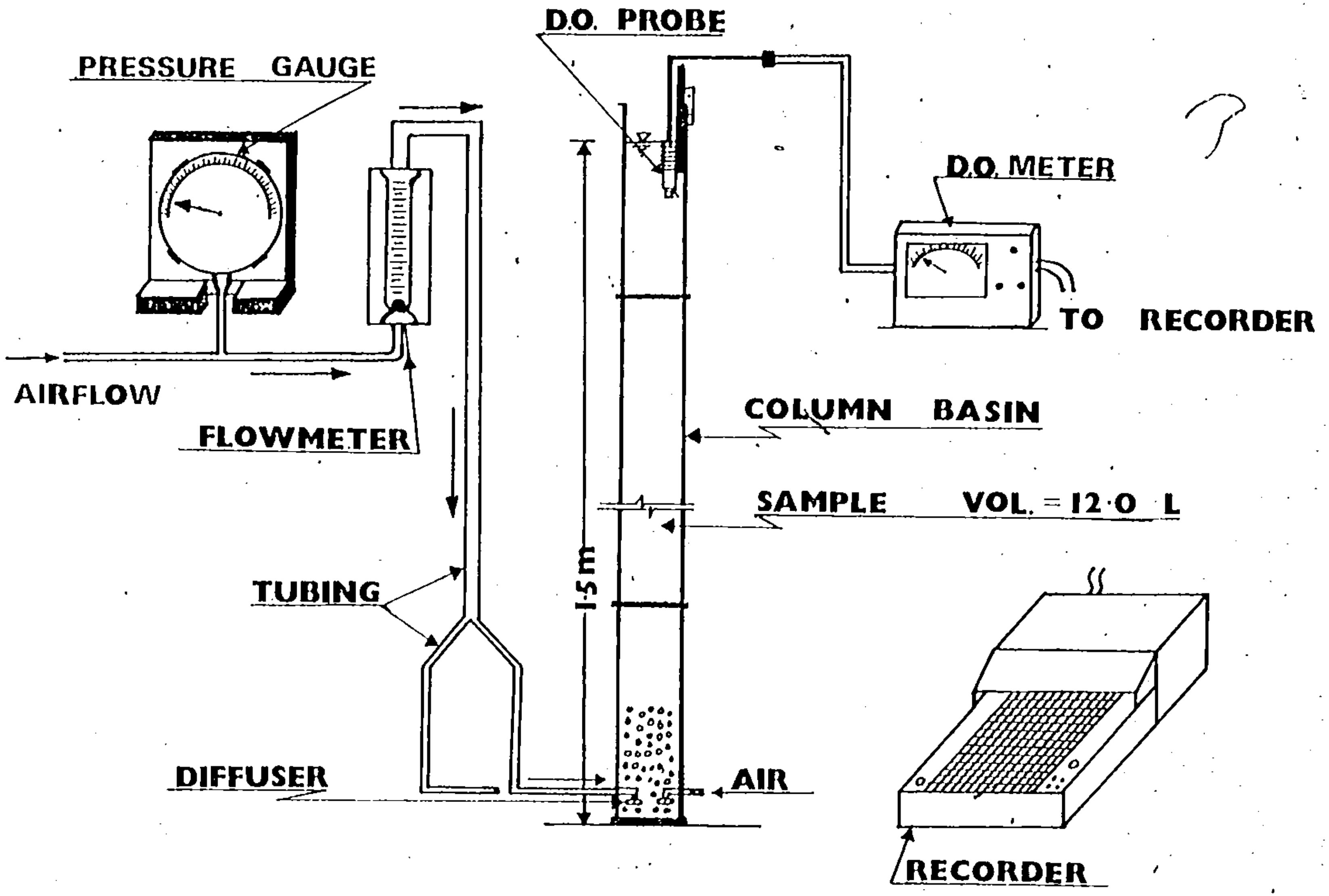


FIG. 5 — SCHEMATIC DIAGRAM FOR COLUMN BASIN APPARATUS

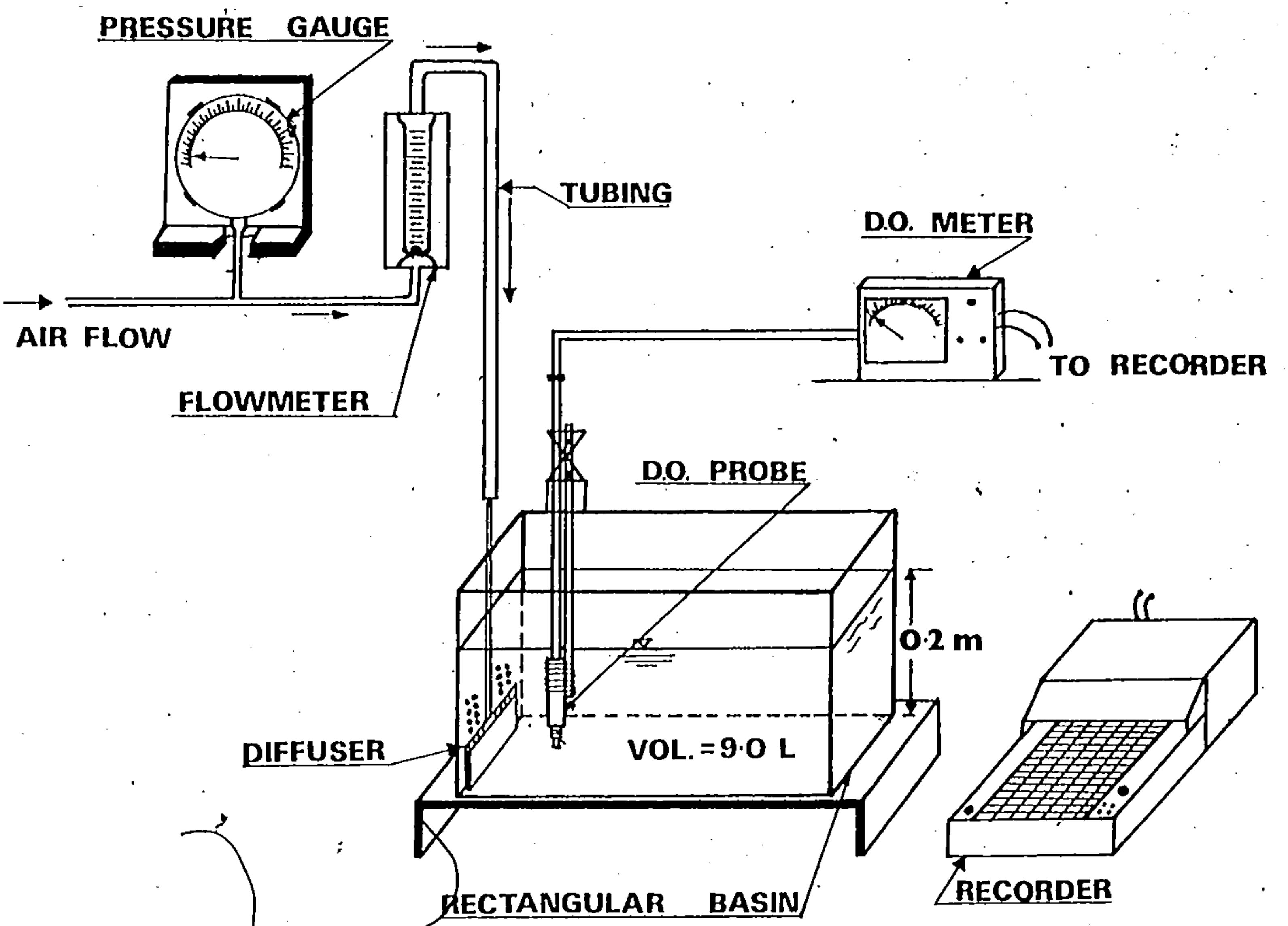


FIG. 6 – SCHEMATIC DIAGRAM FOR RECTANGULAR BASIN APPARATUS

obtained from calibration curves supplied by the manufacturer. A correction was applied for actual temperature and pressure of air supply (60).

C. Dissolved Oxygen Analyzer and Recorder

The YSI Model 54 Oxygen Meter was used for measuring dissolved oxygen concentration in water and wastewater from the Wastewater Treatment Plant. The sensing element was a Clark type membrane-covered polarographic probe (61). This instrument was calibrated to read directly in parts per million or mg/L from 0-20 mg/L with an accuracy of ± 1% of full scale reading at the temperature of calibration. The range for temperature measurement was -5 to 45°C with an accuracy of ± 0.7°C, including probe. The dissolved oxygen measuring probe was a gold cathode and silver anode polarographic system (61).

The strip chart recorder used in this study was a Hitachi-Perkin Elmer Model No. 165 with a maximum graph width of 10 inches and with a chart speed in the range of 5-240 mm/min..

CHAPTER IV

EXPERIMENTAL PROCEDURE AND COMPUTATIONS

A. Experimental Procedure

The schematic diagrams of diffused aeration systems for alpha and beta determinations are shown previously in Figures 4, 5 and 6, employing a jar basin, a column basin and a rectangular basin, respectively. In all, two different types of effluent samples, collected at four different times as described in Table II, were tested for alpha and beta determinations. Two of these four samples, Samples I and IV, were the supernatants from the activated sludge treatment plant, while the other two, Samples II and III, were the supernatants from primary sedimentation tank, using chemical coagulation. All the samples were aerated vigorously for three to four days and then at a slow rate for the next couple of days. This extended aeration assured that the biomass had completely stabilized and exerted no oxygen demand. Then the samples were analyzed for alpha and beta. The standard procedure recommended by WPCF and AWWA for the measurement of oxygen uptake rate under unsteady state conditions in clean water and wastewater was adopted in this study and is described as follows:

The first step was to fix the range of air flow rate for the jar basin as the experiments were started on that geometry. Stuckenberg et al. (4), Weis and Lad (17) and Bass and Shell (11) have recommended that alpha tests should be conducted so that the alpha test vessel K_La values approximately the field values to minimize the turbulence factor. Initial experiments with jar basin showed that standard air flow rate of 3277 cc/min. resulted in $(K_La)_T$ of 0.548 min.$^{-1}$, which is very close to the values reported by Gilbert (3) for full scale aeration.

TABLE II - DETAILS OF SAMPLES TESTED

Sample Number	Source	Date and Time of Collection	Method of Deoxygenation
I	Little River Treatment Plant (East End)	May 27, 1980 2:00 PM	Chemical
II	West Windsor Pollution Control Plant	June 11, 1980 3:00 PM	Nitrogen Stripping
III	West Windsor Pollution Control Plant	July 8, 1980 4:00 PM	Chemical
IV	Little River Treatment Plant (East End)	July 11, 1980 3:00 PM	Chemical

Consequently, it was decided to use several air flow rates in a range of 1414-3670 scc/min.. Air flow rates in other test basins were adjusted so that air flow rates per unit volume of the test liquid were the same, with the exception of sample I.

The next step involved the calibration of dissolved oxygen, D.O., measuring probe. Fresh tap water was aerated in the test basin for about one hour and was left without aeration for about half an hour in order to allow the water to reach equilibrium in case it was supersaturated. The dissolved oxygen in this water was determined by chemical analysis using Winkler's method with Azide modification as recommended in Standard Methods (62). The probe reading was adjusted to this D.O. value while aerating the water because calibration should be done under conditions similar to those for experiments. The calibration air flow rate was approximately the mean value of the air flow range used during actual testing. The probe membrane was replaced after about three weeks and recalibrated. The error in calibration may not be significant because Kayser (24) has reported that the rate of oxygen absorption is independent of the probe calibration.

The next step involved the deoxygenation of basin sample. Chemical deoxygenation technique was used for samples I, III and IV. Technical grade Na_2SO_3, about 1.5 to 2 times the theoretical quantity required to entirely deaerate the basin, and, about 0.05 mg/L of Co^{++} as $CoCl_2$ were used. Slightly more Na_2SO_3 was added in column basin, since it involved greater depth and higher oxygen uptake rates. Sufficient quantity of Na_2SO_3 was added so that dissolved oxygen concentration remained zero for about at least two minutes (59). A sample calculation for the amount of $CoCl_2$ and Na_2SO_3 required for a typical run is given in Appendix A. Normally, six runs were made on one batch of sample. Sodium sulfite was added for each of these runs, whereas $CoCl_2$ was added only once during the first run (25). The chemicals were dissolved in about 200 mL volume of sample taken from the basin. The air flow was started to ensure proper mixing and this solution was added into the basin at least, at three different points on the water surface.

While deoxygenating sample II with Na_2SO_3 and $CoCl_2$, certain interferences were noticed since about fifty times the calculated amount of Na_2SO_3 was required. Also, the sample became cloudy in appearance and this cloudiness kept on increasing for about three hours while dissolved oxygen remained at zero.

The observed rate of reaeration was extremely slow. A white precipitate settled down when aeration was stopped. Consequently, nitrogen stripping was employed for deoxygenation of this sample. The nitrogen gas was bubbled through sample II at a high rate until the dissolved oxygen reading dropped to about 0.8 mg/L. After that the rate of deoxygenation became very, very slow and nitrogen stripping was stopped and aeration was started. The other steps in the procedure for measuring oxygen uptake rate were the same. The dissolved oxygen concentrations were read with the D.O. probe and recorded directly on a strip chart recorder. It is desirable that the fluid in front of the membrane should be agitated (61). Preliminary investigations showed that agitation due to aeration alone gave satisfactory calibration and no additional agitator was necessary. The D.O. monitoring probe indicated higher reading whenever air bubbles were stuck to the membrane of the probe. This problem was overcome by shaking off the bubbles from the probe and smoothening the resultant undulations in the curve by hand.

The test was continued until a fairly constant reading for D.O. was obtained for about five minutes. At the end of each set of experiments, the aeration was continued for at least twelve hours in order to determine the changes, if any, in the saturation value. A chemical analysis for dissolved oxygen by Winkler method was also carried out at that time for tap water. The chemical analysis for wastewater was not possible due to certain interferences.

Some loss in sample volume in aeration basin due to evaporation was observed. The water level in the aeration basin was checked after each experiment and losses were made up by adding an equal volume of sample. The probe position was kept fixed in each basin, both for clean water and wastewater, thus avoiding the possible change in K_La with changing the probe position.

The maximum change in liquid temperature during these experiments was ± 0.5°C, which is less than the recommended limit of ± 2°C (59). The temperature was recorded both at the start and at the end of each test run.

B. Method for Computing Alpha and Beta

"Two Film" theory of gas transfer by Lewis and Whitman (5) is employed for the computation of alpha, α, and beta, β, factors. Since

$$\alpha = \frac{K_La \text{ Wastewater}}{K_La \text{ Tap Water}} \quad \ldots\ldots \quad 6$$

and

$$\beta = \frac{C_s \text{ Wastewater}}{C_s \text{ Tap Water}} \quad \ldots\ldots \quad 7$$

it becomes necessary to measure the overall transfer coefficients, K_La, and D.O. saturation values, C_s, in both the tap water and wastewater samples under identical conditions. For measuring oxygen transfer rates, first a known volume of the sample was deoxygenated and then it was reaerated. The rate of oxygen uptake was determined, using the following relationships:

$$\frac{dC}{dt} = K_L a(C_s - C) \qquad \ldots\ldots \quad 8$$

or

$$\frac{dC}{(C_s - C)} = K_L a \; dt \qquad \ldots\ldots \quad 9$$

where,

$\frac{dC}{dt}$ = rate of change of dissolved oxygen in the liquid, mg L^{-1} hr^{-1}

$K_L a$ = overall transfer coefficient, hr^{-1}

C_s = equilibrium concentration of oxygen at the interface, mg L^{-1}; also, assumed to be the saturation value

C = concentration of oxygen in the liquid at time t, mg L^{-1}

$(C_s - C)$ = oxygen saturation deficit in the liquid at time t, mg L^{-1}

Upon integration, Equation 9 becomes,

$$\ell_n (C_s - C)_{C_o}^{C} = K_L a \; t \qquad \ldots\ldots \quad 10$$

where C_o = initial concentration of oxygen in the liquid at time t = 0, mg L^{-1}

or $$\ell_n \left(\frac{C_s - C}{C_s - C_o}\right) = K_L a \; t$$

or $$\frac{C_s - C}{C_s - C_o} = e^{-K_L a \; t}$$

or $$C = C_s - (C_s - C_o) e^{-K_L a \; t} \qquad \ldots\ldots \quad 11$$

which corresponds to the model:

$$C = A - Be^{-Dt} \qquad \ldots\ldots \quad 12$$

Equation 11, being nonlinear, can be used to analyze K_La by nonlinear least-square regression technique. Values of C_s, C and t, as obtained from the recorder plot, were substituted in the model given by Eq. 12 to obtain a best fit curve. Values of C less than 10% of the saturation value were truncated to avoid lingering effects of deoxygenation techniques (59). As the dissolved oxygen concentration approached saturation, truncation was discouraged (59) as these values significantly influence the estimation of C_s and K_La. However, as shown in Table III, even after truncating D.O. data values above 80% of the observed C_s value, there was no effect on K_La values. Workshop Toward an Oxygen Transfer Standard (59) recommends that the values of C_s as observed should be used in computations.

SAS Package NLINDF was used on the computer to obtain a best fit curve through data by nonlinear least-square regression technique (63). The computer programme used the values of C_s, C and t, obtained from the above best fit curve to plot $\log(C_s - C)$ vs t and statistically computed the slope of best fit line. K_La values were obtained by multiplying this slope with 2.303. At the same time, computed values of C_s were also recorded. It is shown by computations in Table IV, that a variation in C_s values has insignificant effect on K_La values.

The measurement of alpha involves the ratio of K_La value for wastewater to the K_La value for the tap water. Since K_La is temperature dependent, all values were converted to a common base of 20°C before taking ratios. Bewtra _et al_. (64) have reported the following relationship for temperature correction:

$$(K_La)_T = (K_La)_{20} \times 1.02^{(T-20)} \quad \ldots\ldots \quad 13$$

where T = water temperature in °C at which K_La was measured. Similarly, the value of D.O. saturation is temperature dependent and all C_s values were converted to 20°C, using table given in <u>Standard Methods</u> (62), before taking ratios.

A typical set of data and example of computations for alpha and beta factors is given in Appendix B.

TABLE III - EFFECT OF TRUNCATION OF DATA ABOVE 80% OF SATURATION VALUE ON K_La

No.	Air Flow Rate cc/min.	Cumulative Na_2SO_3 added g	Cumulative $CoCl_2$ added mg	Temp. ^oC	Air Pressure kPa	Saturation Value Used mgL^{-1}	K_La hr^{-1}
1	1414	6.2	1.0	18.5	184.9	8.90	19.20
1*	1414	6.2	1.0	18.5	184.9	7.12	19.20
2	2516	12.6	1.0	18.3	181.5	9.05	32.97
2*	2516	12.6	1.0	18.3	181.5	7.24	32.97

* D.O. Values above 0.80 C_s were truncaced in data analysis

TABLE IV - EFFECT OF CHANGING THE SATURATION VALUE ON K_La AND Y-INTERCEPT

No.	Air Flow Rate cc/min.	Temp. ^oC	Cumulative Na_2SO_3 added g	Cumulative $CoCl_2$ added mg	Air Pressure kPa	Saturation Value Used mgL^{-1}	$(K_La)_{20}$ hr^{-1}	Y-Intercept mgL^{-1}
1	2862	19.8	11.7	4.2	186.3	8.50	36.11	8.54
2	2862	19.8	11.7	4.2	186.3	8.70	39.69	8.56

No. 1 is the actual run with observed saturation value of 8.5 mg/L, whereas for No. 2, the saturation value is assumed to be 8.7 mg/L. Y-intercept gives the calculated value for C_s.

CHAPTER V

RESULTS

As mentioned earlier, this study was performed on three different geometries and two different methods for deoxygenation of wastewater were employed, as described in Chapter IV. The raw data and a sample calculation for a typical run are attached in Appendix E and B, respectively. The range of the temperature was maintained between 18°C to 25°C during this study. For comparison purposes, K_La values obtained at different temperatures were corrected to 20°C, using Equation 13.

Several readings for oxygen uptake rates were taken at a fixed standard air flow rate of 3293 cc/min. and in a given geometry of jar basin to determine the reproducibility of the results. The 95% confidence interval for $(K_La)_{20}$ was calculated to be ± 8.7% of the mean value as shown in Table V. Various factors contributed to this variation in K_La values. These include variation in air flow rates, concentration of cobalt ions, amount of sodium sulfite added and errors in taking observations and calculations.

On an average, five runs at different air flow rates were made with each sample in each type of test tank. The $(K_La)_{20}$ values and the corresponding α-values at each air flow rate for each of these test conditions are shown in Table VI to XII.

The measurement of factor β involved taking ratios of D.O. saturation in wastewater to that in tap water. In this study, D.O. saturation values, C_s, were obtained in one or more of the following manners:

(i) D.O. probe reading in each run after these readings had stabilized as shown for a typical plot in Appendix B.

TABLE V - CALCULATIONS TO DETERMINE 95% CONFIDENCE INTERVAL FOR $K_L a$ VALUES

No.	Air Flow Rate cc/min.	Water Temp. °C	Air Pressure kPa	Cumulative Na_2SO_3 added g	Cumulative $CoCl_2$ added mg	$(K_L a)_T$ hr^{-1}	$(K_L a)_{20}$ hr^{-1}
1	3246	20.00	182.2	2.9	1	35.76	35.76
2	3306	19.50	172.5	9.0	3	39.70	40.10
3	3284	20.00	172.5	12.0	4	41.22	41.22
4	3303	19.00	172.5	3.0	1	36.25	36.96
5	3284	20.00	172.5	6.0	2	40.14	40.14
6	3303	19.00	172.5	9.0	3	40.25	41.06
7	3303	19.00	172.5	12.0	4	35.85	36.57
8	3277	20.00	178.7	16.0	5	40.53	40.53
9	3302	19.90	178.7	3.0	1	37.54	37.60
10	3301	19.85	178.7	6.1	1	38.80	38.92
11	3301	19.85	178.7	9.2	1	39.31	39.43
12	3300	19.65	178.7	12.4	1	39.04	39.31
13	3299	19.50	178.7	15.6	1	39.61	40.00

Mean $(K_L a)_{20}$ = 39.10 hr^{-1}

Standard Deviation = ± 1.70 hr^{-1}

95% Confidence Interval = ± 3.41 hr^{-1}

TABLE VI – α-VALUES FOR JAR BASIN WITH WASTEWATER SAMPLE I

No.	Air Flow Rate cc/min.		Average Air Flow Rate cc/min/L of the sample vol.	$(K_La)_{20}$ hr^{-1}		$\alpha = \frac{(K_La)_{20} \text{ Wastewater}}{(K_La)_{20} \text{ Tap Water}}$
	Tap Water	Wastewater		Tap Water	Wastewater	
1	1414	1402	70.40	24.04	17.66	0.74
2	2133	2107	106.00	31.44	22.75	0.72
3	2516	2482	124.95	34.10	24.64	0.72
4	3277	3235	162.80	40.55	29.32	0.72
5	3668	3614	182.05	44.15	30.51	0.69

Mean = 0.72

TABLE VII - α-VALUES FOR COLUMN BASIN WITH WASTEWATER SAMPLE I

No.	Air Flow Rate cc/min.		Average Air Flow Rate cc/min/L of the sample vol.	$(K_La)_{20}$ hr^{-1}		$\alpha = \frac{(K_La)_{20}\text{ Wastewater}}{(K_La)_{20}\text{ Tap Water}}$
	Tap Water	Wastewater		Tap Water	Wastewater	
1	635	637	53.00	37.08	26.71	0.72
2	1013	1016	84.54	50.62	38.94	0.77
3	1236	1237	103.04	55.85	44.84	0.80
4	1616	1618	134.75	61.19	52.48	0.86
5	1855	1856	154.62	65.52	54.81	0.84

Mean = 0.80

TABLE VIII - α-VALUES FOR RECTANGULAR BASIN WITH WASTEWATER SAMPLE I

No.	Air Flow Rate cc/min.		Average Air Flow Rate cc/min/L of the sample vol.	$(K_L a)_{20}$ hr^{-1}		$\alpha = \frac{(K_L a)_{20} \text{ Wastewater}}{(K_L a)_{20} \text{ Tap Water}}$
	Tap Water	Wastewater		Tap Water	Wastewater	
1	358	359	39.83	2.30	2.51	1.09
2	622	625	69.27	4.93	4.40	0.89
3	734	735	81.61	6.49	5.06	0.78
4	1059	1059	117.66	8.63	6.45	0.75
5	1208	1209	134.27	9.58	7.25	0.76

Mean = 0.85

TABLE IX - α-VALUES FOR RECTANGULAR BASIN WITH WASTEWATER SAMPLE II

No.	Air Flow Rate cc/min.		Average Air Flow Rate cc/min/L of the sample vol.	$(K_La)_{20}$ hr^{-1}		$\alpha = \frac{(K_La)_{20}\ \text{Wastewater}}{(K_La)_{20}\ \text{Tap Water}}$
	Tap Water	Wastewater		Tap Water	Wastewater	
1	628	620	69.33	5.62	5.00	0.89
2	944	933	104.27	7.64	7.19	0.94
3	1112	1099	122.83	8.33	7.99	0.96
4	1445	1433	159.88	10.41	9.44	0.91
5	1615	1600	178.61	11.28	10.78	0.96

Mean = 0.93

TABLE X - α-VALUES FOR JAR BASIN WITH WASTEWATER SAMPLE II

No.	Air Flow Rate cc/min.		Average Air Flow Rate cc/min/L of the sample vol.	$(K_La)_{20}$ hr^{-1}		$\alpha = \frac{(K_La)_{20} \text{ Wastewater}}{(K_La)_{20} \text{ Tap Water}}$
	Tap Water	Wastewater		Tap Water	Wastewater	
1	1414	1392	70.15	24.04	23.54	0.98
2	2133	2092	105.62	31.44	26.99	0.86
3	2516	2463	124.48	34.10	32.2	0.94
4	3277	3210	162.17	40.53	36.83	0.91
5	3668	3585	181.32	44.15	39.80	0.90

Mean = 0.92

TABLE XI - α-VALUE FOR JAR BASIN FOR WASTEWATER SAMPLE III

No.	Air Flow Rate cc/min.		Average Air Flow Rate cc/min/L of the sample vol.	$(K_La)_{20}$ hr^{-1}		$\alpha = \frac{(K_La)_{20}\ \text{Wastewater}}{(K_La)_{20}\ \text{Tap Water}}$
	Tap Water	Wastewater		Tap Water	Wastewater	
1	1414	1391	70.12	24.04	15.47	0.64
2	2133	2091	105.60	31.44	22.80	0.72
3	2516	2463	124.50	34.10	23.20	0.68
4	3277	3209	162.15	40.53	25.45	0.63
5	3668	3585	181.32	44.15	28.95	0.66

Mean = 0.67

TABLE XII – α-VALUES FOR JAR BASIN FOR WASTEWATER SAMPLE IV

No.	Air Flow Rate cc/min.		Average Air Flow Rate cc/min/L of the sample vol.	$(K_La)_{20}$ hr^{-1}		$\alpha = \frac{(K_La)_{20} \text{ Wastewater}}{(K_La)_{20} \text{ Tap Water}}$
	Tap Water	Wastewater		Tap Water	Wastewater	
1	1414	1396	70.25	24.04	20.61	0.86
2	2133	2098	105.77	31.44	27.56	0.87
3	2516	2462	124.45	34.10	28.67	0.84
4	3277	3209	162.15	40.53	35.58	0.88
5	3668	3584	18[illegible].30	44.15	39.73	0.90

Mean = 0.87

(ii) D.O. concentration in tap water samples by Winkler method at the end of each experiment after aerating for at least 12 hours.

(iii) Calculated value of $B_1 = C_s$ for each run by statistical analysis of data as shown in Appendix B.

(iv) From D.O. saturation values reported in <u>Standard Method</u> (62) after making correction for dissolved solid concentrations.

All these saturation values were converted to the corresponding values at 20°C after applying appropriate conversion factors obtained from <u>Standard Method</u> (62). The C_s values obtained for all these experiments are given in Tables XIII to XV.

In order to study the effect of water depth in aeration basin on the D.O. saturation value, experiments were conducted in the column basin by varying the water depth. The range of depth covered in this study was 0.30 to 1.80m. At each depth, the tap water was aerated at a fixed air flow rate for at least 12 hours. The water sample was withdrawn near the bottom of the column and analyzed for D.O. using the Winkler method. The D.O. saturation values, obtained in this study, for different depths were corrected to 20°C and are presented in Table XVI.

TABLE XIII - D.O. SATURATION VALUES - JAR BASIN

Tap Water

No.	Observed Saturation Value C_s mg/L	Calculated Saturation Value C_s mg/L	C_s Corrected for Dissolved Solids from Table in Standard Method mg/L	C_s by Winkler Method mg/L
1	8.69	8.65	9.16	
2	8.80	8.80	9.14	
3	8.80	8.80	9.13	
4	8.90	8.85	9.11	
5	8.90	8.87	9.10	9.10
AVE.	8.82	8.79	9.13	
Wastewater; Sample I				
1	8.42	8.62	9.03	
2	8.43	8.58	9.02	
3	8.43	8.56	9.01	
4	8.44	8.54	8.99	
5	8.41	8.54	8.98	
AVE.	8.43	8.57	9.01	
Wastewater; Sample II				
1	8.43	8.39	9.10	
2	8.53	8.65	9.10	
3	8.59	8.62	9.10	
4	8.59	8.68	9.10	
5	8.59	8.60	9.10	
AVE.	8.55	8.59	9.10	
Wastewater; Sample III				
1	8.46	8.61	9.13	
2	8.55	8.74	9.12	
3	8.59	8.81	9.10	
4	8.43	8.71	9.09	

TABLE XIII - D.O. SATURATION VALUES - JAR BASIN

Wastewater; Sample III (continued)

No.	Observed Saturation Value C_s mg/L	Calculated Saturation Value C_s mg/L	C_s Corrected for Dissolved Solids from Table in Standard Method mg/L	C_s by Winkler Method mg/L
5	8.59	8.75	9.07	
AVE.	8.52	8.72	9.10	
	Wastewater; Sample IV			
1	8.51	8.61	9.15	
2	8.62	8.66	9.14	
3	8.64	8.91	9.12	
4	8.76	8.86	9.11	
5	8.69	8.73	9.09	
AVE.	8.64	8.75	9.12	

TABLE XIV - D.O. SATURATION VALUES - COLUMN BASIN

Tap Water

No.	Observed Saturation Value C_s mg/L	Calculated Saturation Value C_s mg/L	C_s Corrected for Dissolved Solids from Table in <u>Standard Method</u> mg/L	C_s for Winkler Method mg/L
1	9.05	8.75	9.17	
2	9.02	9.06	9.16	
3	9.01	9.02	9.16	
4	9.05	9.08	9.14	
5	9.10	9.26	9.13	9.2
AVE.	9.04	9.02	9.15	
	Wastewater; Sample I			
1	8.83	8.70	9.04	
2	8.99	9.11	9.03	
3	8.96	9.16	9.03	
4	8.98	9.07	9.01	
5	9.01	9.22	9.00	
AVE.	8.95	9.05	9.02	

TABLE XV - D.O. SATURATION VALUES - RECTANGULAR BASIN

Tap Water

No.	Observed Saturation Value C_s mg/L	Calculated Saturation Value C_s mg/L	C_s Corrected for Dissolved Solids from Table in Standard Method mg/L	C_s for Winkler Method mg/L
1	9.21	10.00	9.18	
2	9.24	8.96	9.18	
3	9.26	9.54	9.17	
4	9.24	9.63	9.17	
5	9.26	9.49	9.16	9.09
AVE.	9.24	9.52	9.17	
	Wastewater; Sample I			
1	8.48	9.37	9.05	
2	8.38	9.18	9.05	
3	8.53	9.18	9.05	
4	8.50	8.62	9.04	
5	8.54	8.78	9.04	
AVE.	8.49	9.03	9.05	
	Wastewater; Sample II			
1	7.87	8.09	9.10	
2	8.26	8.40	9.10	
3	8.68	8.70	9.10	
4	8.40	8.53	9.10	
5	8.40	8.52	9.10	
AVE.	8.32	8.45	9.10	

TABLE XVI - D.O. SATURATION VALUES IN WATER AT DIFFERENT DEPTHS

No.	Water Depth m	Water Temperature °C	Saturated Dissolved Oxygen mg/L
1	0.30	20	8.80
2	0.60	20	8.80
3	0.90	20	9.00
4	1.20	20	9.10
5	1.50	20	9.20
6	1.80	20	9.25

CHAPTER VI

DISCUSSION

The determination of alpha was carried out in the laboratory under different operating conditions. Three different types of test basins, jar basins, column basins and rectangular basins were used. Four different samples of wastewater, collected from two different sources, were analyzed. The air flow rates ranged between 40 to 182 cc/min/L and five different air flow rates were used for each sample. The water depth varied between different test basins and ranged from 0.19 to 1.5 m and the volume in the three test basins were 20.0 L, 12.0 L and 9.0 L, respectively.

While adding sodium sulfite in sample II, it was observed that even a large quantity of sodium sulfite was unable to deplete the D.O. and also the reaeration rate was very low. When the cobalt-ion concentration was increased, the reaction rate had increased. Obviously, certain substances in this sample were reacting with cobalt-ions added in normal concentration and prevented the D.O. depletion with sodium sulfite. Therefore, it is important to conduct small laboratory investigations with wastewater samples to determine the amount of catalyst required, before carrying out full scale investigations. Alternatively, the nitrogen stripping method will have to be employed.

The results, reported in the previous Chapter, were statistically analyzed to determine the effect of different operating conditions on the alpha and beta factors. It was observed that the K_La values were influenced significantly by the air flow rate, water depth, tank geometry and characteristics of wastewater. It is also observed from Table V, that with every successive addition of sodium sulfite, there was an increase in $K_L a$ value under otherwise identical conditions.

The analysis of variance test (65) on alpha values was carried out on the results obtained for sample I, Tables VI to VIII, for all three test basins and at all air flow rates. The analysis results are shown in Table XVII. It reveals that, at 95% confidence level, the alpha factor is independent of air flow rate, water depth and geometrical configuration. Thus, the mean value of alpha factor for sample I is obtained as 0.79. Similar statistical analysis of alpha values for sample II, Table IX and X, is shown in Table XVIII. It is again observed that operating conditions have no effect on alpha factor at 95% confidence level. The mean value of alpha factor for sample II is obtained as 0.925. Similarly, the mean alpha values for samples III and IV are 0.67 and 0.87, respectively. Therefore, it is obvious that alpha factor varies with the characteristics of wastewater sample.

It can be seen from Tables XIII to XV that the observed D.O. saturation concentration is less than the calculated D.O. saturation concentration for all the basins. Also, the D.O. saturation values, obtained after correcting for the dissolved solids according to the Table in the Standard Methods (62), are mostly higher than the calculated D.O. saturation values. The observed D.O. saturation values were the probe readings taken from the plot, Fig. 7. A correction may have to be applied to the probe reading if the operating conditions are not the same as the calibrating conditions. Moreover, it is possible that the sample may not have reached saturation level at the end of the plot. It is also observed from Table XVI that the D.O. saturation value increases with increase in depth. All these factors had contributed to the discrepancies in results. The Winkler method is most accurate to

TABLE XVII - ANALYSIS OF VARIANCE IN ALPHA VALUES FOR SAMPLE I

No.	Jar Basin α-Values	Column Basin α-Values	Rectangular Basin α-Values	All Systems α-Values
1	0.73	0.72	1.09	2.54
2	0.72	0.77	0.89	2.38
3	0.72	0.80	0.78	2.30
4	0.72	0.86	0.75	2.33
5	0.69	0.84	0.76	2.29
$\Sigma\alpha$	3.58	3.99	4.27	11.84
$\bar{\alpha}$	0.716	0.798	0.854	$\boxed{0.789}$
$\Sigma\alpha^2$	2.564	3.197	3.729	9.490
$\frac{(\Sigma\alpha)^2}{n}$	2.563	3.184	3.647	9.345
$\Sigma\alpha^2-\frac{(\Sigma\alpha)^2}{n}$	0.00072	0.013	0.08242	0.1443

Source of Variance	Sum of Squares	Degree of Freedom	Mean Square
Between Samples	0.04858	2	0.0243
Within Samples	0.09572	12	0.00797
Total	0.1443	14	

$F = \frac{0.0243}{0.00797} = 3.0489$; $F_{.05}$ from Table (65) $= 3.89$

TABLE XVIII - ANALYSIS OF VARIANCE IN ALPHA VALUES FOR SAMPLE II

No.	Jar Basin α-Values	Rectangular Basin α-Values	All Systems
1	0.98	0.89	1.87
2	0.86	0.94	1.80
3	0.94	0.96	1.90
4	0.91	0.91	1.82
5	0.90	0.96	1.86

$\Sigma\alpha$	4.59	4.66	9.25
$\bar{\alpha}$	0.932	0.918	$\boxed{0.925}$
$\Sigma\alpha^2$	4.347	4.2217	8.5687
$\frac{(\Sigma\alpha)^2}{N}$	4.34312	4.21362	8.55623
$\Sigma\alpha^2 - \frac{(\Sigma\alpha)^2}{n}$	0.00388	0.00808	0.01245

Source of Variance	Sum of Squares	Degree of Freedom	Mean Square
Between Samples	0.00049	1	0.00049
Within Samples	0.01196	8	0.001495
Total	0.01245	9	0.001383

$$F = \frac{0.00049}{0.001495} = 0.328 \; ; \quad F_{.05} = 5.32$$

measure oxygen saturation value in tap waters, but this method is inaccurate with wastewaters. The results confirm that D.O. saturation values for water, obtained by Winkler method after extended aeration for at least 12 hours, are very close to the values obtained from Table (62).

The above discussion shows that there are many chances of error in calculating β factor. The Workshop Toward An Oxygen Transfer Standard (59) discourages the use of probe reading for calculating β values. It recommends to calculate β by applying a correction to D.O. saturation values for dissolved solids concentration in wastewater and water.

Table XIX lists the β values calculated for different samples by taking ratios between average saturation values obtained for wastewater and tap water, respectively, with similar methods. It is observed that β values ranged between 0.89 and 1.00, depending on the tank geometry and the method used for obtaining saturation value. The characteristics of wastewater showed no significant effect on average β values. The average β for all samples was observed to be 0.97. Therefore, it is concluded that any of the methods used for calculating β will provide reasonably accurate results; however, it would be more convenient to use saturation values from Table in <u>Standard Methods</u> (62) after correcting for dissolved solids concentration.

TABLE XIX - β-VALUES FOR DIFFERENT D.O. SATURATION CONCENTRATION

Sample No.	Jar Basin, β for			Column Basin, β for			Rectangular Basin, β for			Average β
	Observed Saturation Values	Calculated Saturation Values	Correction for Dissolved Solids Saturation	Observed Saturation Values	Calculated Saturation Values	Correction for Dissolved Solids Saturation	Observed Saturation Values	Calculated Saturation Values	Correction for Dissolved Solids Saturation	
I	0.96	0.97	0.98	0.99	1.00	0.98	0.92	0.95	0.99	0.97
II	0.97	0.98	0.99	-	-	-	0.90	0.89	0.99	0.95
III	0.97	0.99	0.99	-	-	-	-	-	-	0.98
IV	0.98	0.99	0.99	-	-	-	-	-	-	0.99

CHAPTER VII

CONCLUSIONS

This study was performed in the laboratory to determine alpha and beta factors for different wastewater samples under different operating conditions and the following conclusions can be drawn:

1. Certain wastewater samples may interfere with cobalt ions. Therefore, it is important to conduct small laboratory investigations with wastewater samples to determine the amount of chemicals required, before performing full scale investigations. Alternatively, nitrogen stripping will have to be employed.
2. K_La values were influenced significantly by the air flow rate, water depth, tank geometry and characteristics of wastewater. Also, with every successive sodium sulfite addition, K_La value increased under otherwise identical conditions.
3. At 95% confidence interval, alpha factor is independent of air flow rate, water depth and geometrical configurations. However, it does vary with the wastewater characteristics. In this study α values ranged between 0.67 and 0.925.
4. The D.O. saturation concentration increases with an increase in water depth.
5. The D.O. saturation values obtained by different methods showed discrepancies; however, each of these methods provided reasonably accurate results for β. It is more convenient to calculate β factor after applying corrections to D.O. saturation values for dissolved solids concentration in wastewater and water.
6. The β values are not significantly affected by the air flow rates, water depth, tank geometry and wastewater characteristics. The average β for all samples was observed to be 0.97.

APPENDICES

APPENDIX A

Calculations for the Amount of Na_2SO_3 and $CoCl_2 \cdot 6H_2O$ Required

a) The stoichiometric relationship between Na_2SO_3 and O_2 is as follows:

$$2\ NaSO_3 + O_2 = 2\ Na_2SO_4 \qquad \text{.....}\ 14$$

$$2(23x2+32+3x16) + 2x16 = 2(23x2+32+4x16)$$

$$\text{or}\quad 252\ mg + 32\ mg \rightarrow 284\ mg$$

Therefore, theoretically, 252/32 = 7.88 mg/L of Na_2SO_3 per mg/L of dissolved oxygen is required to deoxygenate the sample.

b) Cobalt ion concentration required = 0.05 mg/L ..... (25)

$$\therefore \text{ amount of } CoCl_2 \cdot 6H_2O \text{ required} = \frac{237}{59} \times 0.05$$

$$= 0.20\ mg/L$$

For 20 litres of sample, $CoCl_2$ required

$$= 0.20 \times 20 = 4\ mg$$

APPENDIX B

Typical Data and Computations for Alpha and Beta Factors

The dissolved oxygen concentration values vs time for sample IV were read from the plot in Fig. 7. The data are listed below with Y as time in minutes and X as D.O. concentration in mg L^{-1}:

TABLE XX - TYPICAL DATA

OBS	Y	X
1	0.0	0.45
2	0.5	1.20
3	1.0	2.00
4	1.5	2.80
5	2.0	3.55
6	2.5	4.20
7	3.0	4.70
8	3.5	5.15
9	4.0	5.55
10	4.5	5.95
11	5.0	6.28
12	5.5	6.50
13	6.0	6.75
14	6.5	6.95
15	7.0	7.10
16	7.5	7.28
17	8.0	7.40
18	9.0	7.58
19	10.0	7.73
20	11.0	7.85
21	12.0	7.90
22	13.0	7.95
23	15.0	8.00
24	18.0	8.05
25	22.0	8.10

Other data relevant to this experiment were:

Standard Air Flow Rate = 3209 cc/min.

Temperature = 24°C = 535.2°R

The above data were analyzed by using a computer programme, Appendix C, to obtain a best fit curve which is plotted in Fig. 8. The print out for computations are attached as Tables XXI to XXIII.

The values from Fig. 8 were plotted as $\log(C_s - C)$ versus t in Fig. 9 and a best fit line was drawn statistically through these data. The computer print out for computations is attached as Table XXIV. The values of intercept and slope are given below:

TABLE XXIV - LOG PLOT OF VARIATION OF OXYGEN WITH TIME

Model: Model 01 Dep Var: LX	SSE DFE MSE	0 20 0	F Ratio Prob>F R-Square	999999.99 0.0001 1.0000
Variable	DF Parameter Estimate	Standard Error	T Ratio	Prob>|T|
Intercept Y	2.077607 - 0.278820	0 0		

From the above Table, slope = 0.27882 min^{-1}

$$(K_L a)_T = 0.27882 \times 2.303 = 0.6421\ \text{min}^{-1}$$

$$= 38.53\ \text{hr}^{-1}$$

From Equation 13,

$$(K_L a)_T = (K_L a)_{20} \times (1.02)^{T-20}$$

or

$$(K_L a)_{20} = 38.53 \times \frac{1}{(1.02)^{24-20}}$$

$$= 35.59\ \text{hr}^{-1}$$

```
TABLE XXI  -  S T A T I S T I C A L   A N A L Y S I S   S Y S T E M

                         NON-LINEAR LEAST SQUARES ITERATIVE PHASE

                    DEPENDENT VARIABLE: X          METHOD: STRICT DESCENT

     ITERATION          B1              B2              B3                 RESIDUAL SS

          0         8.10000000     -7.65000000      0.00000000           863.91060000
          1         9.65215728     -6.09784272     -0.04239120            73.51465904
          2         9.59354318     -6.15645682     -0.06038272            47.82947153
          3         9.09754223     -6.65245703     -0.17080140            13.98484983
          4         8.82444549     -6.92554402     -0.21855943            10.69082123
          5         8.08809099     -7.86212998     -0.28473388             0.22697838
          6         8.18275392     -7.99603898     -0.28233920             0.16766591
          7         8.18193408     -7.99523285     -0.28136300             0.16057276
          8         8.19258829     -7.98500000     -0.27867942             0.15827036
          9         8.19242329     -7.98610209     -0.27875416             0.15826709
         10         8.19241072     -7.98602614     -0.27875319             0.15826687
         11         8.19220989     -7.98532517     -0.27875139             0.15826581
         12         8.19185639     -7.98534321     -0.27882403             0.15826406
         13         8.19187901     -7.98535310     -0.27882165             0.15826406
         14         8.19187893     -7.98533848     -0.27882034             0.15826406

NOTE: CONVERGENCE CRITERION MET.
      |SS-LASTSS|<=.000010

                         SUMMARY TABLE FOR FINAL ITERATION

              NUMBER OF ITERATION=  14
              NUMBER OF FUNCTION EVALUATIONS IN THIS ITERATION=  6
              NORM OF THE GRADIENT= 0.000039509
              ESTIMATED NUMBER OF SIGNIFICANT DIGITS= 5.3
              FINAL VALUE OF THE MARQUARDT PARAMETER= 0.000001863
```

TABLE XXII - STATISTICAL ANALYSIS SYSTEM

```
        NON-LINEAR LEAST SQUARES SUMMARY STATISTICS     DEPENDENT VARIABLE X

         SOURCE                DF      SUM OF SQUARES         MEAN SQUARE
         REGRESSION             3        990.96283594        330.32094531
         RESIDUAL              22          0.15826406          0.00719382
         UNCORRECTED TOTAL     25        991.12110000

         (CORRECTED TOTAL)     24        127.11386400

PARAMETER          ESTIMATE          ASYMPTOTIC                       ASYMPTOTIC 95 %
                                     STD. ERROR                   CONFIDENCE INTERVAL
                                                               LOWER              UPPER
B1               8.19187893          0.03896416          8.11107284         8.27268502
B2              -7.98533348          0.06046868         -8.11074184        -7.85993512
B3              -0.27882034          0.00501433         -0.28921933        -0.26842135

                    ASYMPTOTIC CORRELATION MATRIX OF THE PARAMETERS

                                   B1          B2          B3

                      B1     1.000000   -0.359230    0.781521
                      B2    -0.359230    1.000000    0.108747
                      B3     0.781521    0.108747    1.000000
```

```
TABLE XXIII - S T A T I S T I C A L   A N A L Y S I S   S Y S T E M
                                                                          0:55 FRIDAY, JULY 18

                          LOG PLOT OF VARIATION  OF  OXYGEN  WITH  TIME

OBS     Y       X        B1         B2          B3          XNEW        RNEW         LX

  1    0.5    1.20    8.19188    -7.9853    -0.27882    1.24566    -0.04566     1.9382
  2    1.0    2.00    8.19188    -7.9853    -0.27882    2.14957    -0.14957     1.7988
  3    1.5    2.80    8.19188    -7.9853    -0.27882    2.93585    -0.13585     1.6594
  4    2.0    3.55    8.19188    -7.9853    -0.27882    3.61981    -0.06981     1.5200
  5    2.5    4.20    8.19188    -7.9853    -0.27882    4.21477    -0.01477     1.3806
  6    3.0    4.70    8.19188    -7.9853    -0.27882    4.73230    -0.03230     1.2411
  7    3.5    5.15    8.19188    -7.9853    -0.27882    5.18249    -0.03249     1.1017
  8    4.0    5.55    8.19188    -7.9853    -0.27882    5.57410    -0.02410     0.9623
  9    4.5    5.95    8.19188    -7.9853    -0.27882    5.91475     0.03525     0.8229
 10    5.0    6.28    8.19188    -7.9853    -0.27882    6.21107     0.06893     0.6835
 11    5.5    6.50    8.19188    -7.9853    -0.27882    6.46883     0.03117     0.5441
 12    6.0    6.75    8.19188    -7.9853    -0.27882    6.69305     0.05695     0.4047
 13    6.5    6.95    8.19188    -7.9853    -0.27882    6.88809     0.06191     0.2653
 14    7.0    7.10    8.19188    -7.9853    -0.27882    7.05775     0.04225     0.1259
 15    7.5    7.28    8.19188    -7.9853    -0.27882    7.20533     0.07467    -0.0135
 16    8.0    7.40    8.19188    -7.9853    -0.27882    7.33371     0.06629    -0.1530
 17    9.0    7.58    8.19188    -7.9853    -0.27882    7.54252     0.03748    -0.4318
 18   10.0    7.73    8.19188    -7.9853    -0.27882    7.70053     0.02947    -0.7106
 19   11.0    7.85    8.19188    -7.9853    -0.27882    7.82009     0.02991    -0.9894
 20   12.0    7.90    8.19188    -7.9853    -0.27882    7.91055    -0.01055    -1.2682
 21   13.0    7.95    8.19188    -7.9853    -0.27882    7.97901    -0.02901    -1.5471
 22   15.0    8.00    8.19188    -7.9853    -0.27882    8.07000    -0.07000    -2.1047
```

Similarly, for tap water at standard air flow rate of 3277 cc/min.,

$$(K_L a)_{20} = 40.53 \text{ hr}^{-1}$$

$$\therefore \qquad \alpha = \frac{(K_L a)_{20} \text{ wastewater}}{(K_L a)_{20} \text{ tap water}} = \frac{35.59}{40.53} = 0.88$$

NOTE: The symbols used in the attached computer programme and print outs correspond to the notations in the oxygen uptake model, Eq. 12, as given below:

$B_1 = A$

$B_2 = -B$

$B_3 = -D$

$X = C$

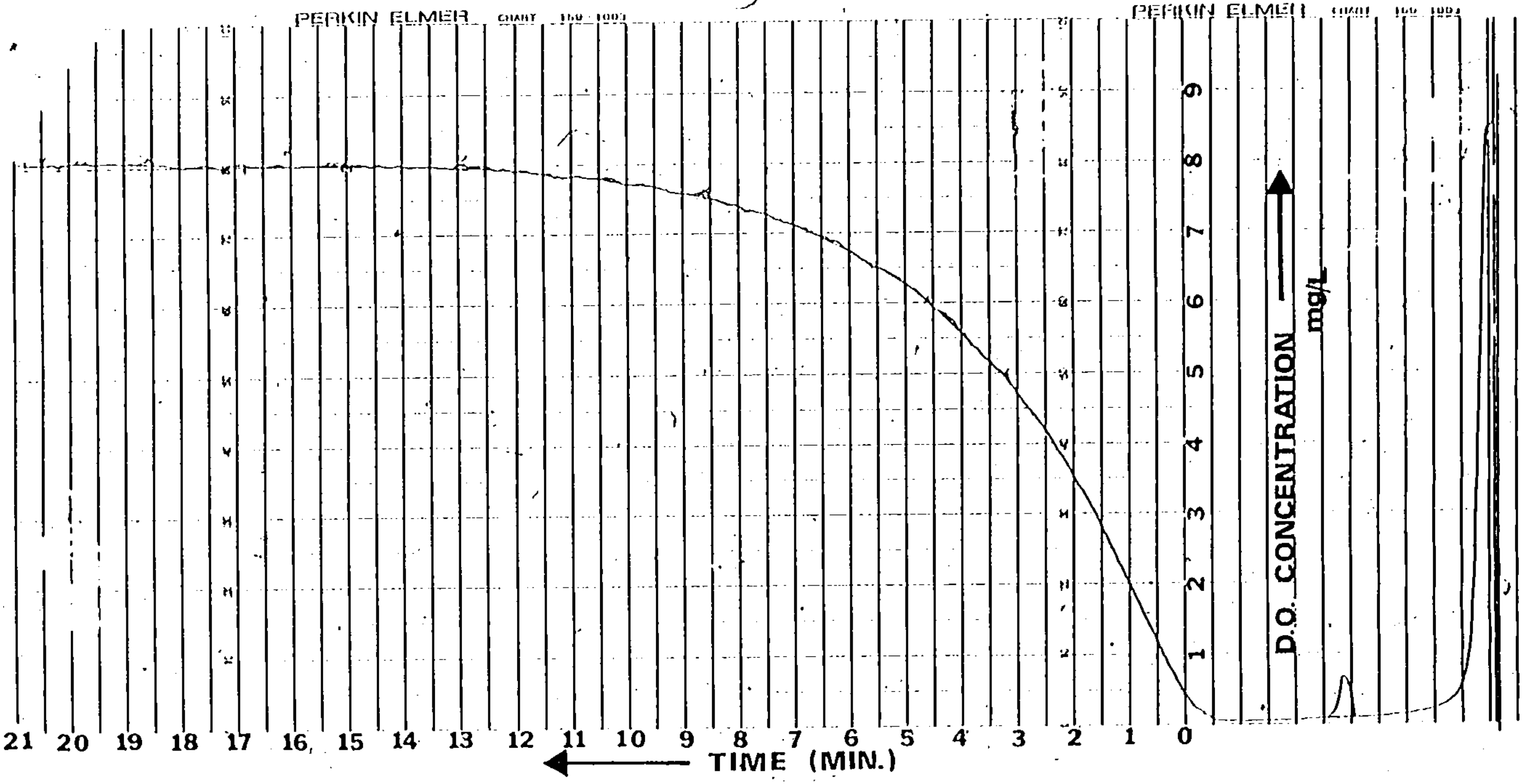
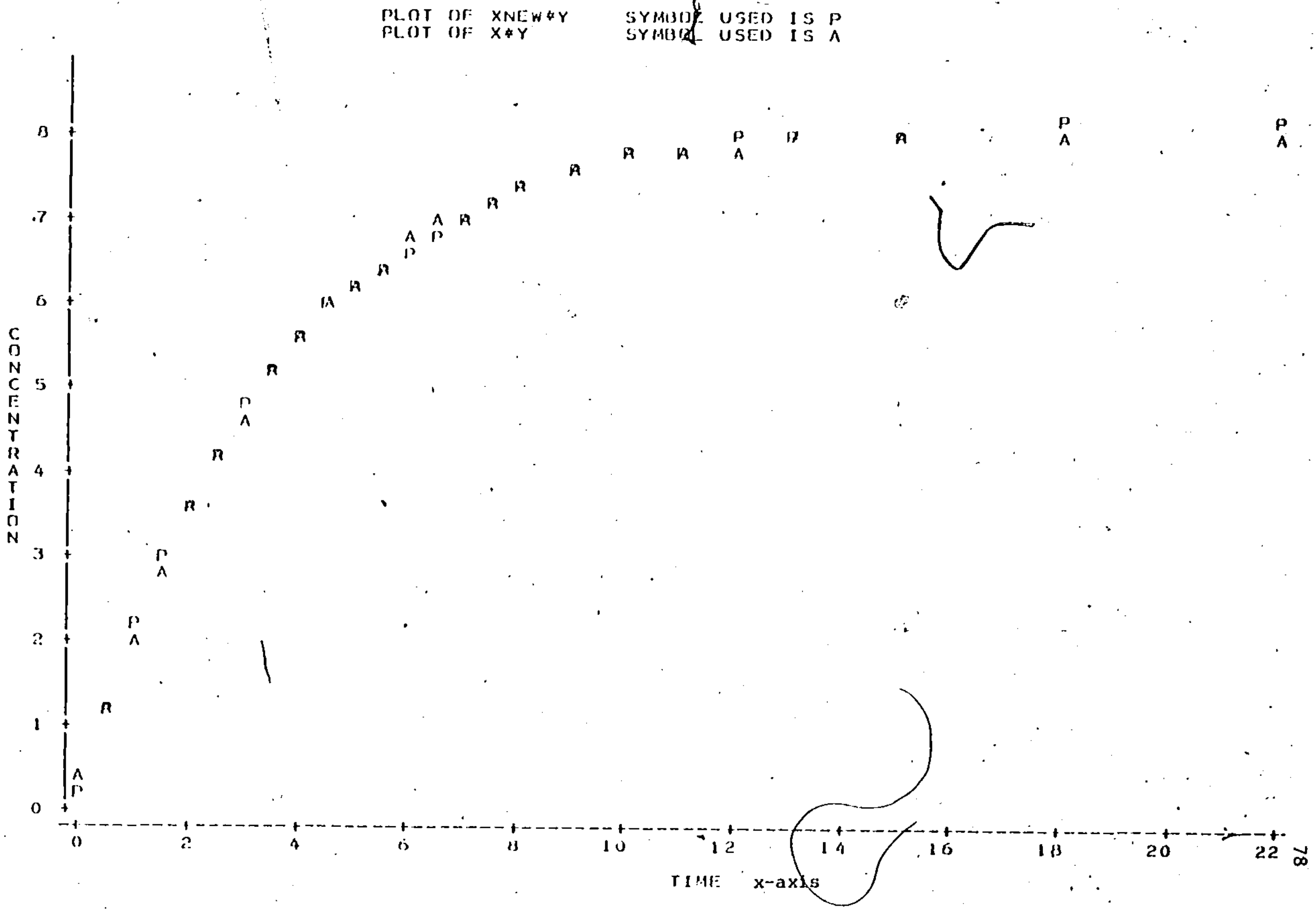


FIG. 7 - A TYPICAL PLOT OF THE RECORDED DATA

FIG. 8 - CONCENTRATION OF DISSOLVED OXYGEN VS TIME



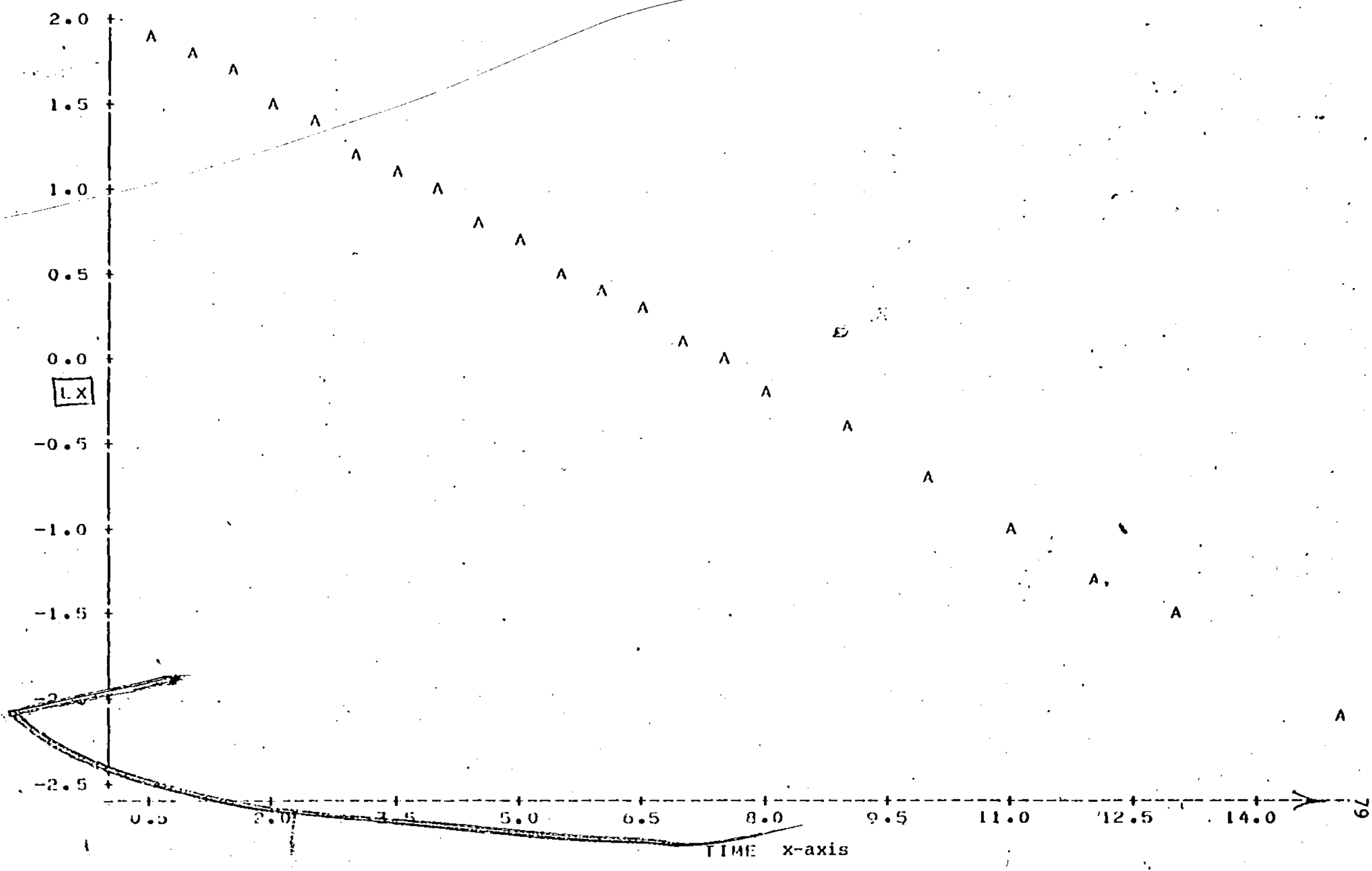


FIG. 9 - LOG PLOT OF VARIATION OF OXYGEN WITH TIME

PLOT OF LX*Y LEGEND: A = 1 OBS, B = 2 OBS, ETC.

APPENDIX C

Computer Programme for Calculating $(K_La)_T$

```
//TEST JOB  (XXXXXXXXXX.2.5..2257),'PREM',CLASS=B
//   EXEC  SAS,OPTIONS='LS=100,PS=60'                                      JOB 710
//SYSIN DD *
IEF142I - STEP WAS EXECUTED - COND CODE 0000
IEF373I STEP /SAS      / START 80200.0054
IEF374I STEP /SAS      / STOP  80200.0056 CPU   0MIN 04.98SEC MAIN 200K LCS   0K
IEF375I  JOB /TEST     / START 80200.0054
IEF376I  JOB /TEST     / STOP  80200.0056 CPU   0MIN 04.98SEC

1                         S T A T I S T I C A L   A N A L Y S I S   S Y S T E M
                                                                          0:55 FR
NOTE: THE JOB TEST HAS BEEN RUN UNDER RELEASE 79.3B OF SAS
      AT THE UNIVERSITY OF WINDSOR.

1            DATA OXYGEN;
2            INPUT  Y X @@;
3            LABEL  X=CONCENTRATION  Y=TIME;
4            CARDS;

NOTE: SAS WENT TO A NEW LINE WHEN INPUT STATEMENT
      REACHED PAST THE END OF A LINE.
NOTE: DATA SET WORK.OXYGEN HAS 25 OBSERVATIONS AND 2 VARIABLES. 651 OBS/TRK.
NOTE: THE DATA STATEMENT USED 0.28 SECONDS AND 128K.

8             PROC PRINT;

NOTE: THE PROCEDURE PRINT USED 0.29 SECONDS AND 128K AND PRINTED PAGE 1.

9           PROC  NLINDF;
10                PARMS  B1=8.10  B2=-7.65  B3=0.00;    BOUNDS  B3<6.20;
11            MODEL  X=B1+B2*EXP(B3*Y);
12            OUTPUT  OUT=NEW
13            PARMS= B1    B2    B3
14          PREDICTED=XNEW
15          RESIDUAL=RNEW;
16

NOTE: DATA SET WORK.NEW HAS 25 OBSERVATIONS AND 7 VARIABLES. 217 OBS/TRK.
NOTE: THE PROCEDURE NLINDF USED 2.21 SECONDS AND 160K AND PRINTED PAGES 2 TO 3.

16            PROC  PLOT  DATA=NEW;
17            PLOT  XNEW*Y='P'      X*Y='A'/O;
18          TITLES CONCENTRATION OF DISSOLVED OXYGEN 'VS' TIME;
19

NOTE: THE PROCEDURE PLOT USED 0.45 SECONDS AND 130K AND PRINTED PAGE 4.

19           PROC PRINT  DATA=NEW;
20

NOTE: THE PROCEDURE PRINT USED 0.35 SECONDS AND 128K AND PRINTED PAGE 5.

20            DATA  NEW2;
21            SET  NEW;
22                 IF .31<XNEW<8.10;
23            LX=LOG(B1-XNEW);
24          LABEL  XNEW=CONCENTRATION;
25

NOTE: DATA SET WORK.NEW2 HAS 22 OBSERVATIONS AND 8 VARIABLES. 191 OBS/TRK.
NOTE: THE DATA STATEMENT USED 0.17 SECONDS AND 128K.

25          PROC  PLOT  DATA=NEW2;
26          PLOT  LX*Y;
27          TITLES LOG PLOT OF VARIATION  OF  OXYGEN  WITH  TIME;
NOTE: THE PROCEDURE PLOT USED 0.40 SECONDS AND 130K AND PRINTED PAGE 6.

28            PROC  PRINT  DATA=NEW2;
29

NOTE: THE PROCEDURE PRINT USED 0.39 SECONDS AND 128K AND PRINTED PAGE 7.

29          PROC  SYSREG;   MODEL   LX=Y;

NOTE: THE PROCEDURE SYSREG USED 0.31 SECONDS AND 132K AND PRINTED PAGE 8.

NOTE: SAS USED 160K MEMORY.

NOTE: SAS INSTITUTE INC.
      SAS CIRCLE
      BOX 8000
      CARY, N.C. 27511
```

For Line 10,

Parameter B_1 = Saturation Value from the plot

$B_2 = (B_1 - X_0)$, where X_0 is the value of dissolved oxygen at time t = 0.

For Line 22,

Lower limit for XNEW = 0.1 x B_1 (58)

Upper limit for XNEW = B_1 (58)

APPENDIX D

Calculations for Obtaining Standard Air Flow Rates

The curves provided by the manufacturer of rotameter read air flow rates corresponding to the actual temperature and pressure. These values should be corrected to obtain standard air flow rates at the following conditions:

Pressure = 14.7 psia = 101.4 kPa

Temperature = $60^{o}F = 15.5^{o}C$

The correlation for obtaining air flow rate under standard condition is:

$$Q = Q_r \sqrt{\frac{P_r \times T}{T_r \times P}} \qquad \ldots\ldots \quad 15$$

where,

Q = flow rate in cc/min.

Q_r = flow rate from the calibration curve corresponding to the scale reading, cc/min.

P = operating pressure, kPa

P_r = reference pressure, 101.4 kPa

T = operating temperature, ^{o}R

T_r = reference temperature, $60^{o}F = 520^{o}R$

$\therefore$ For a scale reading of air flow = 4350 cc/min., at $T = 24^{o}C = 535.2^{o}R$ and $P = 191.8$ kPa

$$\text{Standard } Q = 4350 \sqrt{\frac{101.4 \times 535.2}{191.8 \times 520}} = 3209 \text{ cc/min.}$$

APPENDIX E

TABLE XXV - RAW EXPERIMENTAL DATA

Jar Basin; Tap Water

No.	Air Flow Rate cc/min.	Mean Temp. °C	Cumulative Na_2SO_3 added g	Cumulative $CoCl_2$ added mg	Sequence of Run	Air Pressure kPa	K_La hr^{-1}
1	3850	19.8	11.70	4.2	4	186.30	35.98
2	3350	19.5	3.00	1.2	1	179.40	31.38
3	3350	19.5	6.00	2.2	2	179.40	33.09
4	4350	20.00	2.90	1.0	1	182.20	35.77
5	4350	19	9.00	3.0	3	178.00	39.69
6	4350	20	12.00	4.0	4	178.00	41.22
7	4350	19	3.00	1.0	1	178.00	36.25
8	4350	20	6.00	2.0	2	178.00	40.07
9	4350	19	9.00	3.0	3	178.00	40.25
10	4350	19	12.00	4.0	4	178.00	35.86
11	4350	19.9	3.00	1.0	1	178.70	37.53
12	4350	19.85	6.10	1.0	2	178.70	38.80
13	4350	19.85	9.20	1.0	3	178.70	39.33
14	4350	19.65	12.40	1.0	4	178.70	39.03
15	4350	19.50	15.60	1.0	5	178.70	39.60
16	1900	18.5	6.20	1.0	2	184.92	23.34
17	2850	18.3	9.30	1.0	3	182.85	30.39
18	3350	18.3	12.60	1.0	4	181.47	32.97
19	4350	20	16.0	1.0	5	178.70	40.54
20	4850	20	19.50	1.0	6	177.33	44.21
Jar Basin; Wastewater Sample I							
21	1900	21.05	6.10	2.2	2	190.44	18.04
22	2850	21.1	9.20	2.2	3	189.75	23.26
23	3350	21.15	12.35	2.2	4	189.06	25.50
24	4350	21.2	15.60	2.2	5	186.99	30.01
25	4850	21.3	18.95	2.2	6	186.30	31.32

Column Basin; Tap Water

No.	Air Flow Rate cc/min.	Mean Temp. °C	Cumulative Na_2SO_3 added g	Cumulative $CoCl_2$ added mg	Sequence of Run	Air Pressure kPa	K_La hr^{-1}
26	850	21.75	4.20	1.3	2	185.61	38.40
27	1350	22.15	6.40	1.3	3	184.23	52.83
28	1640	22.4	8.70	1.3	4	182.85	58.57
29	2140	22.65	11.05	1.3	5	182.16	64.48
30	2450	22.90	13.50	1.3	6	181.47	69.38
31	850	21.25	2.10	1.3	1	185.61	37.92
Column Basin; Wastewater Sample I							
32	850	22.25	4.20	1.3	2	184.23	27.92
33	1350	22.9	6.40	1.3	3	183.54	41.25
34	1640	23.0	8.70	1.3	4	182.85	47.58
35	2140	23.1	11.05	1.3	5	182.16	55.93
36	2450	23.3	13.52	1.3	6	181.47	58.50
37	850	22	2.10	1.3	1	184.23	24.66
Rectangular Basin; Tap Water							
38	490	20.65	1.80	1.0	2	193.20	2.31
39	850	20.50	2.70	1.0	3	192.51	4.97
40	1000	20.65	3.60	1.0	4	191.82	6.58
41	1440	20.80	4.60	1.0	5	191.13	8.77
42	1640	20.65	5.65	1.0	6	190.44	9.95
Rectangular Basin; Wastewater Sample I							
43	490	21.75	1.90	1.0	2	192.51	2.6
44	850	21.75	2.80	1.0	3	191.82	4.54
45	1000	21.40	3.70	1.0	4	191.82	4.93
46	1440	21.25	4.70	1.0	5	191.13	6.60
47	1640	21.50	5.75	1.0	6	190.44	7.47

Rectangular Basin; Tap Water

<table>
<tr><th>No.</th><th>Air Flow Rate cc/min.</th><th>Mean Temp. °C</th><th>Cumulative Na_2SO_3 added g</th><th>Cumulative $CoCl_2$ added mg</th><th>Sequence of Run</th><th>Air Pressure kPa</th><th>K_La hr^{-1}</th></tr>
<tr><td>48</td><td>855</td><td>22.25</td><td>1.60</td><td>1.0</td><td>2</td><td>192.51</td><td>5.86</td></tr>
<tr><td>49</td><td>1282.5</td><td>22.65</td><td>2.45</td><td>1.0</td><td>3</td><td>191.82</td><td>8.05</td></tr>
<tr><td>50</td><td>1507.5</td><td>23.0</td><td>3.35</td><td>1.0</td><td>4</td><td>191.13</td><td>8.83</td></tr>
<tr><td>51</td><td>1957.5</td><td>23.35</td><td>4.30</td><td>1.0</td><td>5</td><td>190.44</td><td>11.12</td></tr>
<tr><td>52.</td><td>2182.5</td><td>21.65</td><td>5.30</td><td>1.0</td><td>6</td><td>189.75</td><td>11.66</td></tr>
<tr><td colspan="8">Rectangular Basin; Wastewater Sample II</td></tr>
<tr><td>53</td><td>855.0</td><td>20.5</td><td colspan="2" rowspan="5">Nitrogen Stripping</td><td>1</td><td>195.96</td><td>5.04</td></tr>
<tr><td>54</td><td>1282.5</td><td>21.0</td><td>2</td><td>195.27</td><td>7.33</td></tr>
<tr><td>55</td><td>1507.5</td><td>20.5</td><td>3</td><td>194.58</td><td>8.08</td></tr>
<tr><td>56</td><td>1957.5</td><td>22.5</td><td>4</td><td>193.89</td><td>9.93</td></tr>
<tr><td>57</td><td>2182.5</td><td>22.5</td><td>5</td><td>193.20</td><td>11.32</td></tr>
<tr><td colspan="8">Jar Basin; Wastewater Sample II</td></tr>
<tr><td>58</td><td>1900</td><td>23</td><td colspan="2" rowspan="5">Nitrogen Stripping</td><td>1</td><td>193.89</td><td>24.99</td></tr>
<tr><td>59</td><td>2850</td><td>23</td><td>2</td><td>193.20</td><td>28.65</td></tr>
<tr><td>60</td><td>3350</td><td>23</td><td>3</td><td>192.51</td><td>33.67</td></tr>
<tr><td>61</td><td>4350</td><td>23</td><td>4</td><td>191.13</td><td>39.07</td></tr>
<tr><td>62</td><td>4850</td><td>23</td><td>5</td><td>190.44</td><td>42.28</td></tr>
<tr><td colspan="8">Jar Basin; Wastewater Sample III</td></tr>
<tr><td>63</td><td>1900</td><td>22.25</td><td>6.1</td><td>2.2</td><td>2</td><td>193.89</td><td>16.18</td></tr>
<tr><td>64</td><td>2850</td><td>22.75</td><td>9.7</td><td>2.2</td><td>3</td><td>193.20</td><td>24.08</td></tr>
<tr><td>65</td><td>3350</td><td>23.0</td><td>12.85</td><td>2.2</td><td>4</td><td>192.51</td><td>24.62</td></tr>
<tr><td>66</td><td>4350</td><td>23.0</td><td>16.10</td><td>2.2</td><td>5</td><td>191.13</td><td>27.02</td></tr>
<tr><td>67</td><td>4850</td><td>23.0</td><td>19.45</td><td>2.2</td><td>6</td><td>190.44</td><td>30.72</td></tr>
</table>

Jar Basin; Wastewater Sample IV

No.	Air Flow Rate cc/min.	Mean Temp. °C	Cumulative Na_2SO_3 added g	Cumulative $CoCl_2$ added mg	Sequence of Run	Air Pressure kPa	K_La hr^{-1}
68	1900	23.8	6.1	2.2	2	194.58	22.21
69	2850	23.8	9.2	2.2	3	193.89	29.72
70	3350	23.9	12.35	2.2	4	193.20	3.99
71	4350	24.0	15.55	2.2	5	191.82	38.53
72	4850	23.9	18.8	2.2	6	191.13	42.91

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