KINETICS OF TRIHALOMETHANES FORMATION DURING CHLORINATION OF DRINKING WATER

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ABSTRACT

A kinetic study was undertaken of the formation of trihalomethanes (THMs) during chlorination of water. Raw water from a local river was chlorinated in a constant temperature bath at 5°C, 25°C and 45°C. Reaction progress was followed by periodically taking samples from the reacting mixture and analyzing them for total and individual THMs. Precursors (humic and fulvic acids) were monitored using UV absorbance at 254 nm as a surrogate parameter. Bromide concentration was measured with a recently developed electrode. Chlorine concentration was monitored using an iodometric method. Experiments were also performed using a "synthetic water" prepared in the laboratory using known concentrations of a commercial humic acid reagent as THMs precursor.

Different kinetic models were postulated and tested using a nonlinear regression program. The model chosen, based on total trihalomethanes (TTHMs) formation, was found appropriate to describe the behavior of TTHMs formation in natural and synthetic water. The model was divided in two portions: short-term (less than 8 hours) and long-term (up to 96 hours). Best parameter estimates were obtained for the

synthetic and natural waters. An Arrhenius functionality with temperature was developed, and activation energies and frequency factors calculated.

The kinetic behavior of TTHMs formation in synthetic water was found to be significantly different from that in natural water, pointing out again to the site-specific nature of THMs formation.

RESUMEN

En este trabajo se llevó a cabo un estudio cinético de las reacciones de formación de trihalometanos (THMs) durante la cloración de agua. Agua cruda de un río de la localidad fue clorada en un baño de temperatura constante a 5°C, 25°C y 45°C. El progreso de la reacción se seguía tomando muestras periódicas de la mezcla reactiva y analizándolas para THMs totales e individuales. La concentración de precursores (ácidos húmicos y fúlvicos) era determinada indirectamente por absorbancia en la región ultra-violeta a 254 nm. La concentración del ión bromuro era determinada utilizando un electrodo introducido en el mercado recientemente. La concentración de cloro se media utilizando métodos iodométricos. Algunas corridas experimentales se hicieron usando un "agua sintética" preparada en el laboratorio usando un reactivo comercial de ácido húmico como precursor de THMs.

Se postularon y probaron diferentes modelos cinéticos usando un programa de regresión no-lineal. El modelo escogido, basado en la formación de trihalometanos totales (TTHMs), describía apropiadamente el comportamiento de las reacciones de formación de TTHMs tanto en el agua sintética como en la natural. El modelo desarrollado consiste en dos

natural.

Se estableció una relación del tipo de Arrhenius entre los parámetros individuales y la temperatura evaluando los correspondientes factores de frecuencia y energías de activación.

Se encontró que la cinética de formación en TTHMs en agua sintética es significativamente distinta de lo observado en el agua natural, lo que subraya de nuevo que la formación de THMs durante la cloración de agua es un fenómeno que depende mucho de las condiciones locales.

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CHAPTER 1

INTRODUCTION

Since the 1974 discovery of trihalomethanes (THMs) formation in drinking water as a result of chlorination (Rook,1974; Bellar, et. al., 1974) much research has been conducted to determine whether THMs affect the health of consumers, how THMs should be measured, and how water quality conditions influence THMs formation. Research has also centered on treatment techniques that a drinking water utility could use to reduce THMs concentration in distributed water, what effect altering treatment procedures to control THMs will have on the bacteriological quality of distributed water, and the cost of the various treatment possibilities (Jolley,1981).

The results of these studies were the basis for the U.S. Environmental Protection Agency (USEPA) amendment to the National Interim Primary Drinking Water Regulation issued November 29, 1979 - an amendment establishing a maximum contamination level (MCL) of 0.10 mg/L total trihalomethanes (TTHM) in drinking water (Federal Register,1979).

Unfortunately the rates of these reactions are generally unknown. The selection of physicochemical conditions to minimize undesirable reaction products cannot be determined analytically (Trussell and Umphres,1978).

Although numerous THMs formation curves are found in the literature, very little work of a practical nature has been done on kinetics of the THMs reaction. More work must be done. Kinetic models will allow a more adequate formulation of treatment plant designs that minimize THMs formation, and better prediction of the influence of environmental parameters on plant performance. In view of the lack of knowledge on the rates of the multiple reaction pathways, a possible alternative approach is the development of an empirical reaction rate model based on the overall reaction stoichiometry. Some of the major needs for further research include studies to develop an overall quantitative picture of the kinetics of the THMs reaction.

In this work we obtained data on the formation of total and individual THMs during the chlorination of water at different temperatures. Reaction progress was followed by taking samples of the reacting mixture, periodically, and analyzing for THMs, precursors (humic and fulvic acids and

bromide ion) and chlorine. A kinetic model was postulated and fitted to the experimental data. Modelling and statistical testing were done using a non linear regression program. The experiments were done using raw water from a local river, and also with a "synthetic water" prepared in the laboratory using a commercial source of humic acid as THM precursor.

The formation of THMs during free chlorination of drinking water results from a complex mechanism of attack by aqueous halogen species on natural aquatic humic substances, i.e.; humic and fulvic acids, rather than organic compounds whose source is industrial water pollution. Thus, THMs result from the generalized reaction (Jolley,1981):

Free Chlorine	+	Precursors (Humic Substances) and Bromide	---->	THMs	+ other by-products

Several factors influence this reaction (Stevens,1976; Stevens and Symons,1978; Stevens,1979). The precise effect on kinetics (rate) of THMs formation of various parameters influencing it, or the yield at "completion" of the reaction is difficult to predict because of the complexity of the reactions between aqueous free chlorine and the mixture of precursors of largely unknown structure.

In the last few years, numerous researchers have studied the formation of these products (Dore, et.al,1982), and a great number of organic compounds that are possible

precursors of importance to this process, have been identified. Two classes of compounds which have been considered as possible haloform precursors are humic materials (Rook,1976) and low molecular weight methyl ketones (Stevens, 1976).

Humic acids according to Dragunov (1961) and Kleinhempel (in Rook,1977) consist of polymers of benzene polycarboxylic acids, polyhydroxybenzenes, polyhydroxybenzoic acids, sugars and small amounts of N-bases. Humic acids and fulvic acids both give identical monomeric by-products in various degradation methods surveyed by Schnitzer and Khan (1972). Examples of degradation products generally found are resorcinol, phloroglucinol, pyrogallol, catechol, orcinol, 2,6-dihydroxy-toluene, o- and m-phtalic acids, and 3,5-dihydroxybenzoic acids.

To establish a reaction pathway for chloroform from its precursor, knowledge of the structure is necessary. It is still not known exactly in which way the monomers are linked together. Dubach and Metha (in Rook,1977) stated that no two molecules of humic acids are exactly identical. Figure 1 shows two tentative structures for fulvic acids: the upper model is that of Dragunov (1961), the second structure is a more recent proposal of Kleinhempel (in Rook,1977).

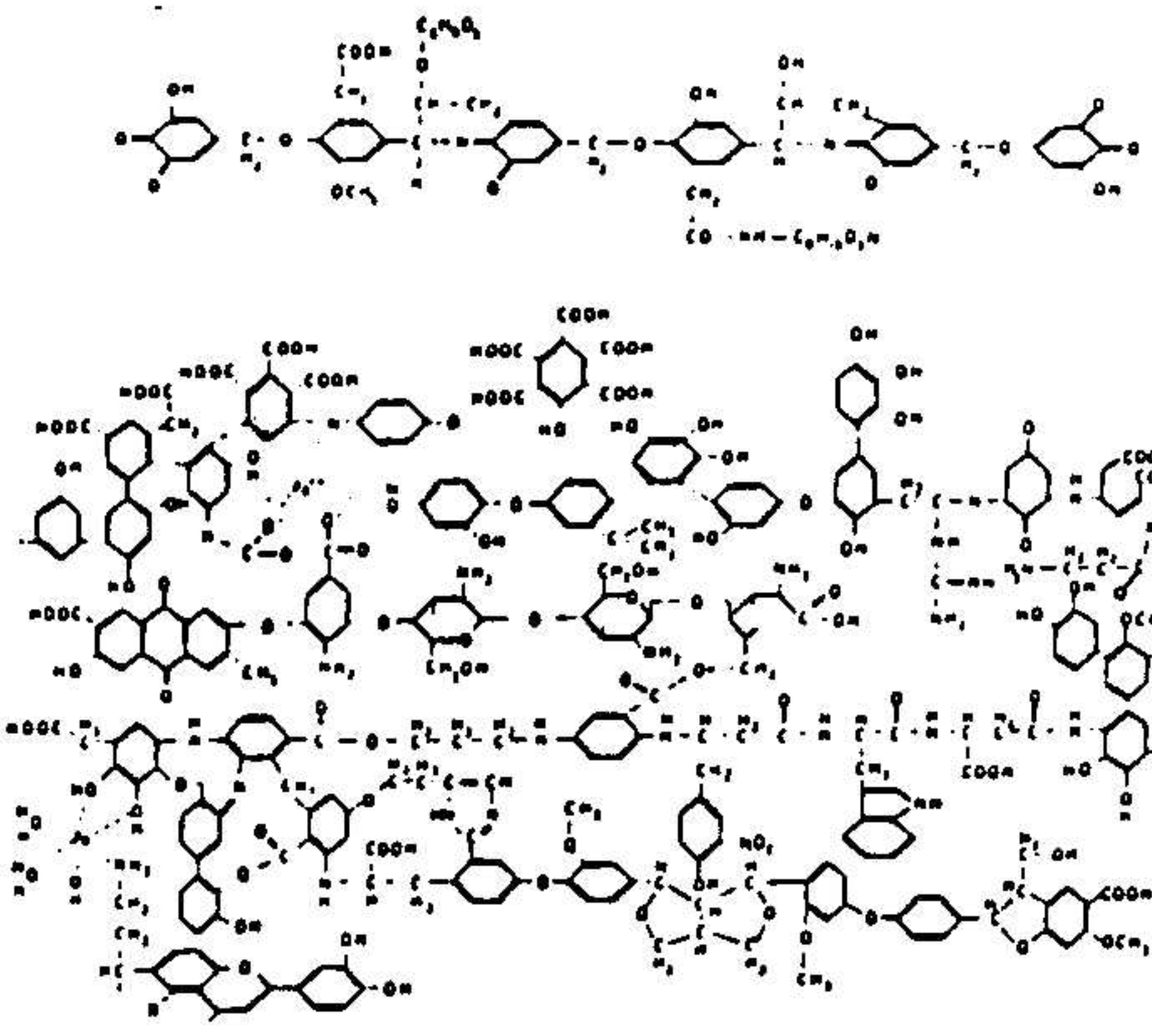

Figure #1: Tentative structures of humic acids
Upper: proposed by S. Dragunov
(Dragunov, 1961)
Lower: proposed by D. Kleinnempel
(Kleinhempel, in Rock, 1977)

For purposes of discussion, it is best to think of the structure of the humus molecule in the simplified form (Trussell and Umphres,1978) shown in Figure 2; that is a huge amorphous mass of polyhetero condensate with certain functional groups protruding from its surface that react with chlorine to produce THMs. The functional groups shown in Figure 2 are some of those that have been shown in the recent literature (Rook,1977; Morris,1978) to participate in this reaction.

Rook (1976) showed that m-dihydroxy aromatic compounds, common building blocks of humic materials, produce high levels of $CHCl_3$ during chlorination. Since they are present at high concentrations in most surface waters, there can be little doubt that humic substances are important precursors. The importance of methyl ketone as a haloform precursor is more speculative. Acetone (Corwin,1970) and trichloroacetone (Suffet, et.al,1976) potential haloform precursors, also have been found in natural water.

Other studies (Trussell and Umphres,1978) have recognized bromide as an important precursor in the formation of THMs. In the presence of chlorine, bromide is oxidized to intermediates (likely Br_2, HOBr, and OBr-, with some BrCl and

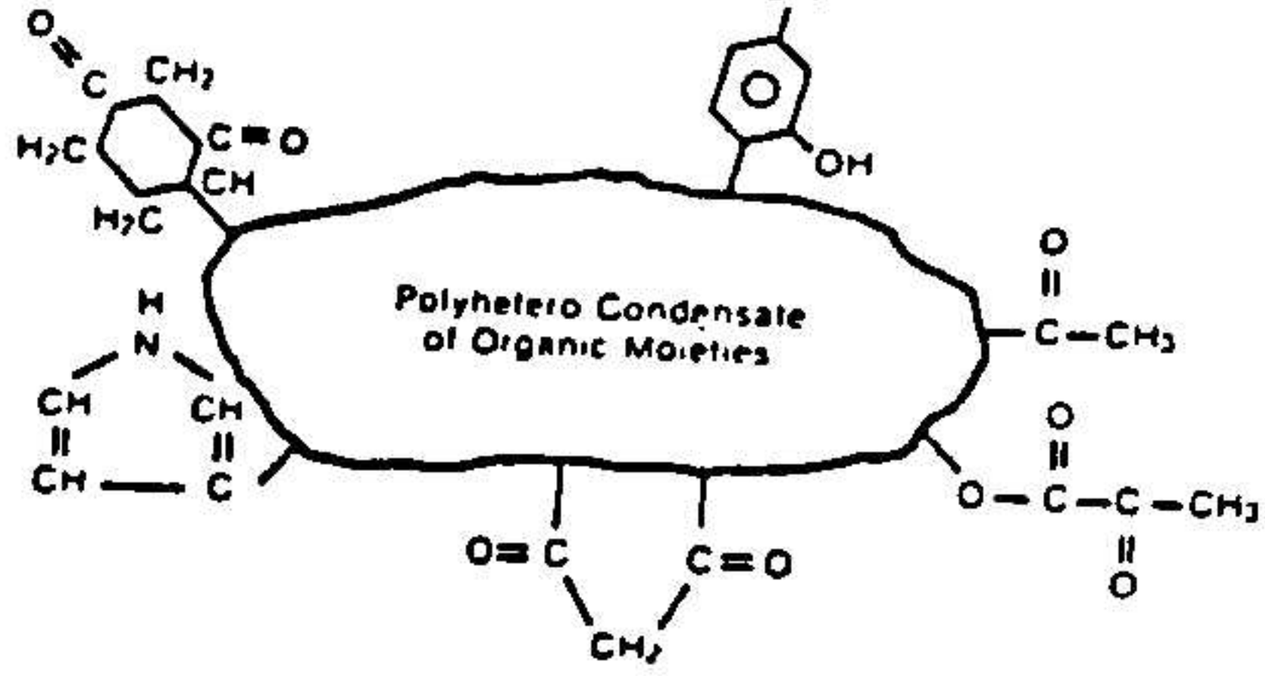

Figure #2: Model Humic Compound
(Trussell and Umphres, 1978)

$BrCl_5$) (Carpenter and Macalady, 1978), which apparently participate in the halogenation step of the THMs reaction sequence much more effectively than does chlorine. This effect was noted by Kleopfer (1976) and has also been observed by others (Lange and Kawczynski, 1978); Stevens, 1976). All of these researchers have observed that the presence of bromide increases the yield of THMs for a given chlorine dose.

Reaction of aqueous hypohalides with methyl ketones or compounds oxidizable to methyl ketones to yield haloform is a classic reaction of organic chemistry known since 1822. The pattern of the reaction is the successive replacement of hydrogen by chlorine on carbon alpha to a carbonyl group followed by eventual hydrolysis to produce CHX_3 and, generally, a carboxylate. The mechanism is believed to be an initial proton dissociation from the alpha-carbon, giving an enolate carbanion which is then subject to electrophilic attack by HOCl or OCl^-. Figure 3 gives a detailed schematic representation of the course of the haloform reaction with hypochlorous acid and acetone.

The haloform reaction is extremely sensitive to a great number of physicochemical parameters. The formation of

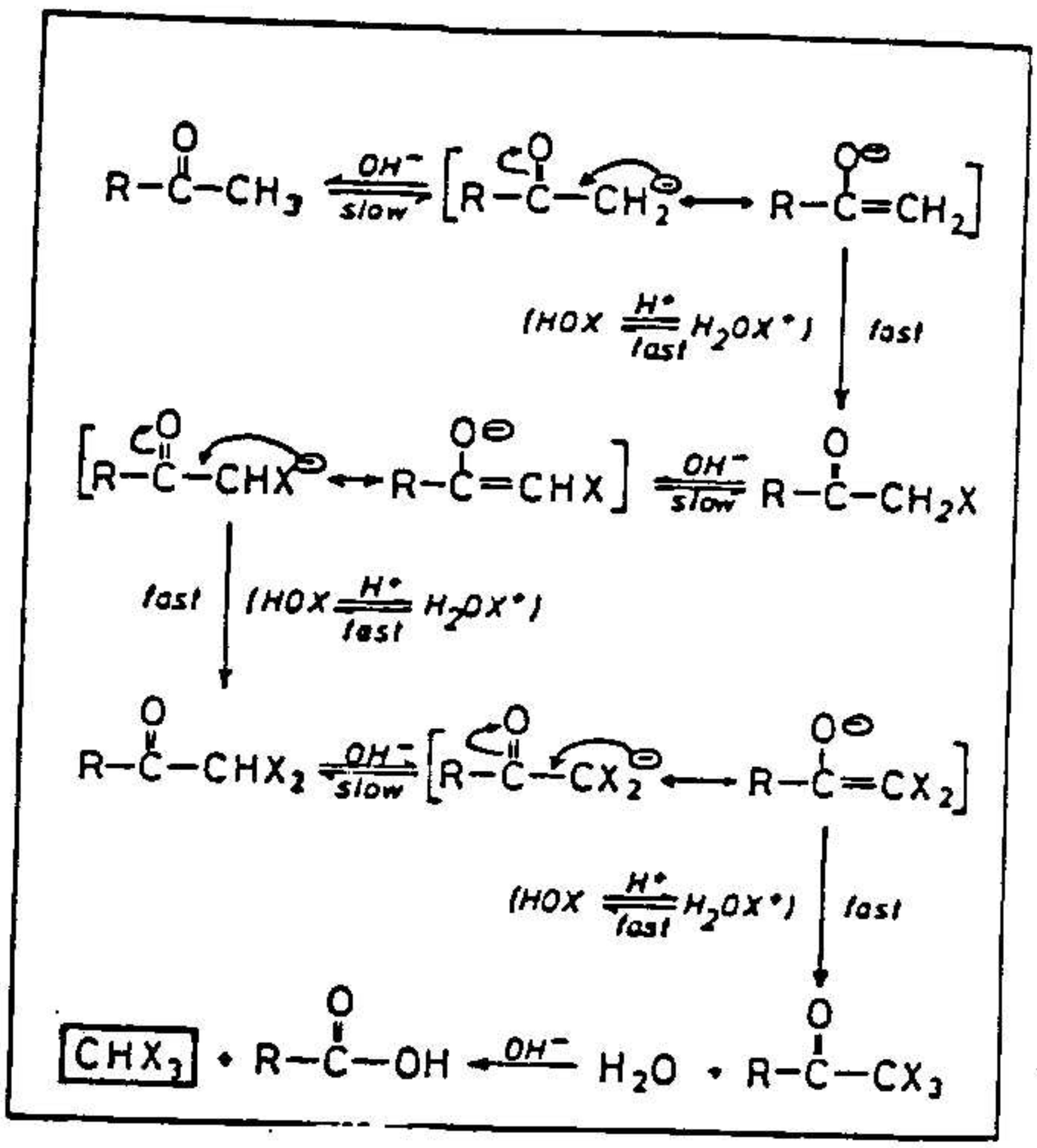

Figure #3: Haloform Reaction Pathway
(Trussell and Umphres, 1978)

trihalomethanes is a function of temperature, pH, and chlorine concentration. Ammonia and halides in treated water also have a significant effect on the quantity and the nature of the volatile organohalogenated products formed. In most cases, chloroform ($CHCl_3$), dichlorobromomethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$) are formed during chlorination (Stevens,1976); iodinated compounds are not often observed. Until Rook (1974) no one had looked for or found the haloform reaction occurring in connection with water chlorination.

Due to the important role of humic acids as THMs precursors, monitoring organic matter during plant performance is necessary. UV absorbance has been postulated as an excellent surrogate parameter for estimating the raw water concentrations of organic carbon (NVTOC-nonvolatile total organic carbon) in rivers and water reservoirs (Edwaltz, et.al.,1985).

Organic compounds that are aromatic or that have conjugated double bonds absorb light in the ultraviolet (UV) region. UV absorbance is a good technique for measuring the presence of naturally occurring matter, such as humic substances, because they contain aromatic moieties and are

the dominant form of organic matter in natural waters . Figure 4 and 5 show qualitatively that UV (254 nm) absorbance closely follows the variations in NVTOC concentrations. UV measurements can be made continuously by use of an on-line spectrophotometer, thus providing the plant operator with a real-time evaluation of performance.

Chlorine is added to the drinking water primarily to prevent the spread of the waterborne diseases such as hepatitis, poliomyelitis, typhoid and cholera(Varma, et.al.,1981). The reaction of chlorine (gas) in water can be described by the following chemical equations:

$$Cl_2 + H_2O = HOCl + H^+ + Cl^-$$

$$HOCl = H^+ + OCl^-$$

Hypochlorous acid (HOCl) is generally regarded as the active species which inactivates the microorganisms. The hydrolysis of HOCl is very fast (Aokl and Munemori, 1983). HOCl reacts with other water borne contaminants also. Because chlorine hardly exists as Cl_2 in water, the term aqueous chlorine has been coined to indicate HOCl, OCl^-, and other species such as NH_2Cl, $NHCl_2$. At pH 7.5 the activities of HOCl and OCl^- are approximately equal (see figure 6). Below this pH, HOCl

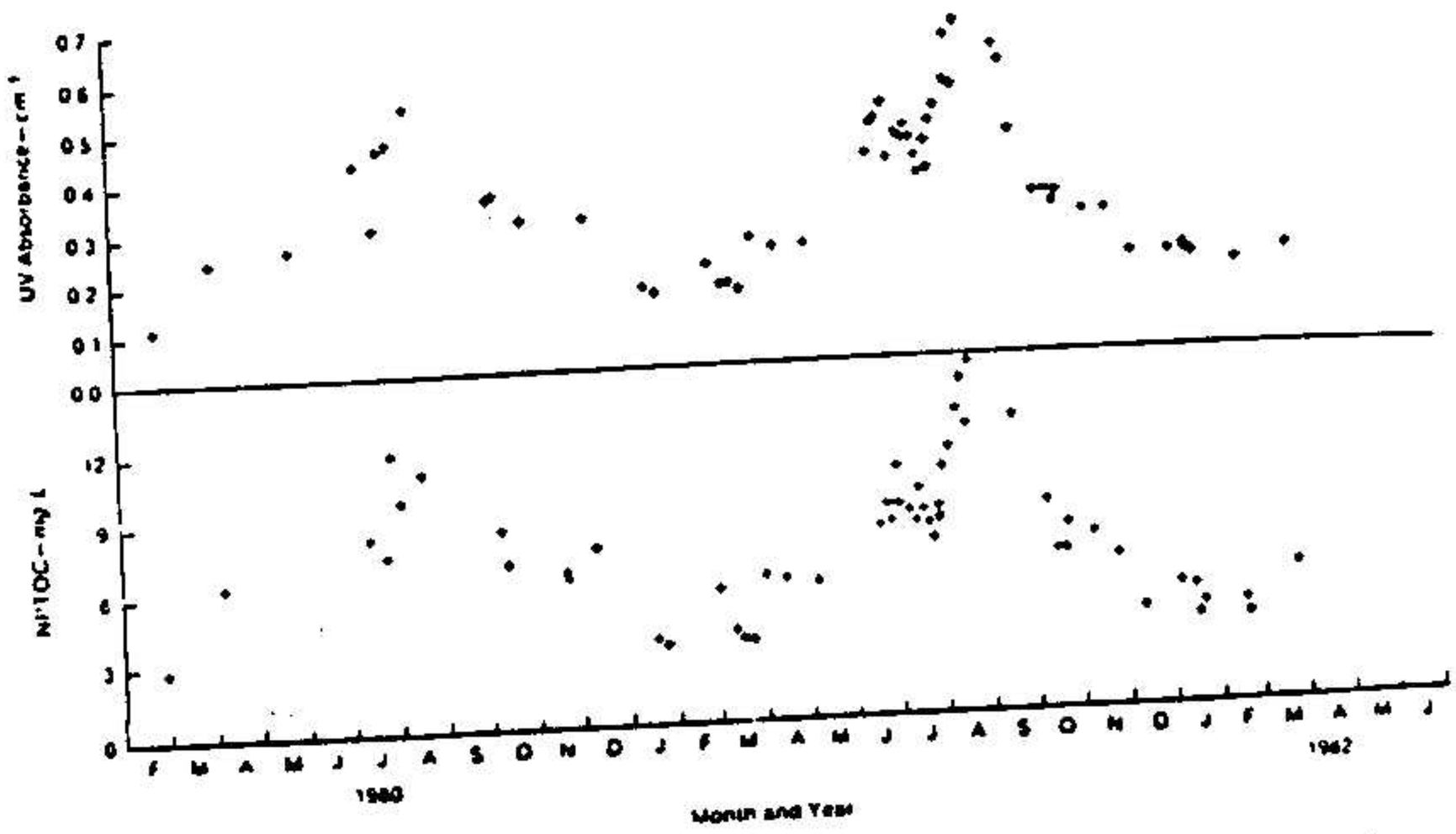

Figure #4: Seasonal Variation in UV (254 nm) and NVTOC for Grasse River (Edzwald et.al.,1985)

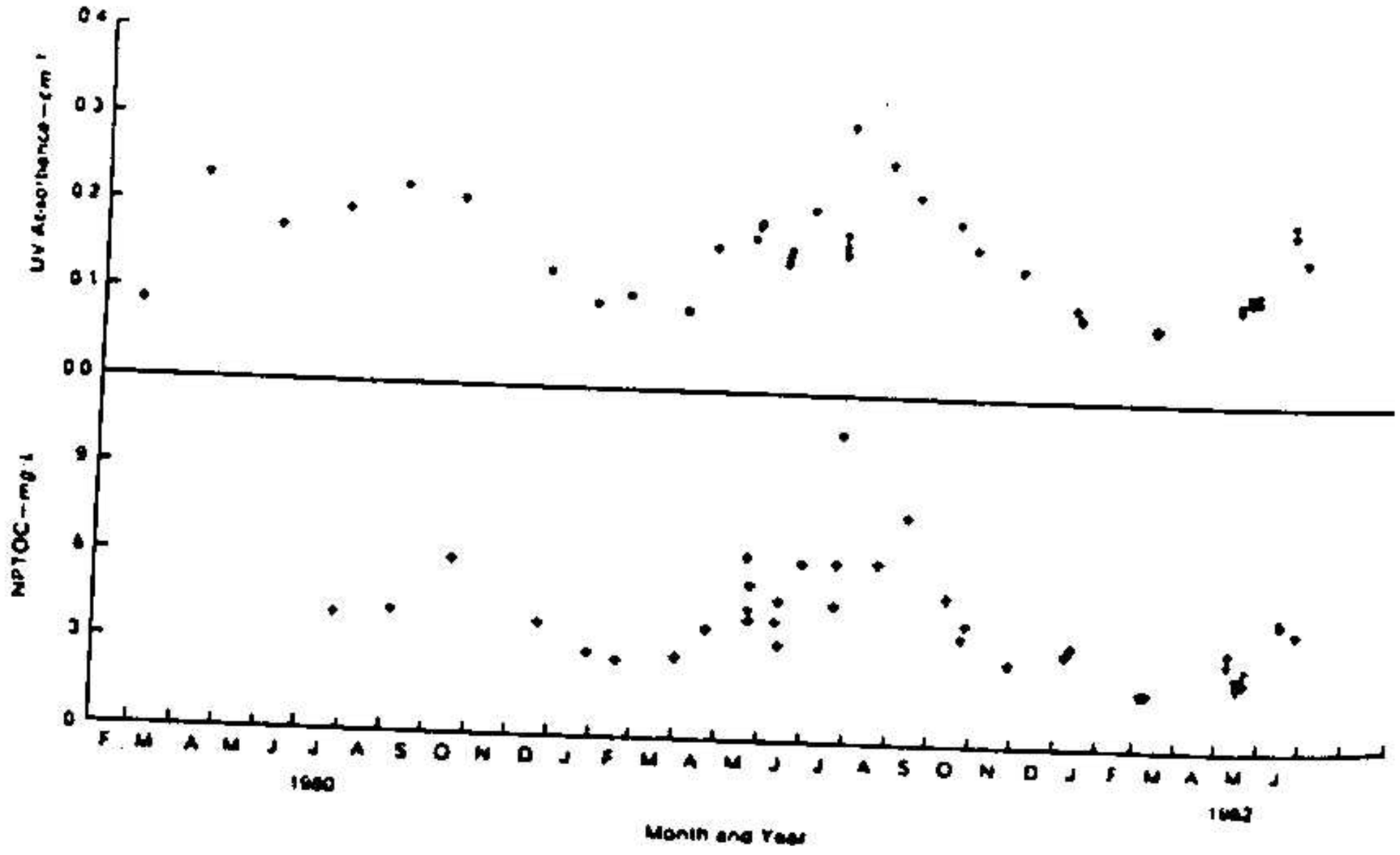

Figure #5: Seasonal Variation in UV (254 nm) and NVTOC for Glenmore Reservoir (Edzwald et.al.,1985)

predominates and above pH 7.5 OCl^- predominates. This phenomenon is very important in disinfection chemistry because, generally, HOCl is about 80 percent more effective in killing bacteria than OCl^-.

A variety of factors influence the THMs formation reaction, including precursor type, precursor concentration (expressed as non-volatile total organic carbon [NVTOC]), chlorine (Cl_2) dosage (expressed as the ratio of Cl_2 to NVTOC $[Cl_2]/[NVTOC]$), temperature, pH, halogen ion (bromide or iodide) concentration, and time. These factors can affect the total yield of THMs as well as the rate at which THMs are formed. The effects of these factors have been discussed previously in the literature (Rook,1976; Rook,1977; Carpenter and Macalady,1978; Young and Singer,1979).

Although there have been attempts to model the kinetics of the THM formation reaction, existing models typically exclude some important parameters (Trussell and Umphres,1978; Kavanaugh,1980; Moore,1979). Trussell and Umphres (1978) proposed a differential rate expression relating the rate of THM production to chlorine residual to the first power and the precursor concentration to the m^{th} power. The following was obtained:

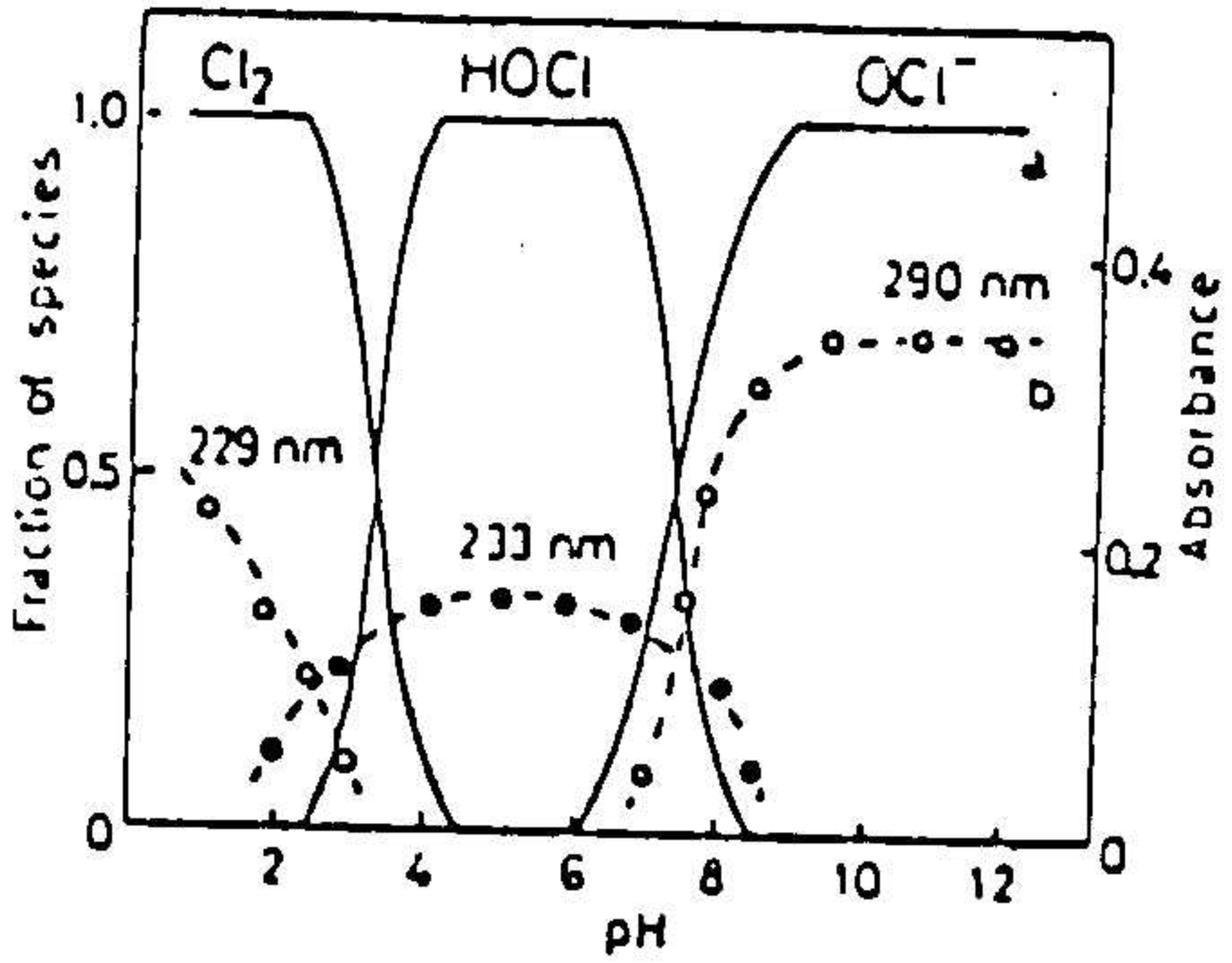

Figure #6: Calculated Fraction of Free Chlorine Species in Aqueous Solution (Aokl and Munemori, 1983)

$$d[THM]/\ dt = -\ dC/dt = K_2[Cl_2][C]^m$$

where m is the order of reaction with respect to the precursor concentration and C is the concentration of the organic precursor. A good fit of experimental data was observed when TOC was used as a surrogate parameter for precursor concentration and m was assumed to be 3. However, Trussell noted that this sort of relationship seems unlikely and suggested that more work be done.

Kavanaugh (1980) developed a semiempirical reaction rate model on the basis of overall reaction stoichiometry. The formation of THMs can be described by the overall stoichiometric expression:

$$3A + B \xrightarrow{K_n} C$$

where: A = HOCl, B = TOC, and C = TTHM, while K_n is the n-order overall rate constant for the reaction. He initially hypothesized a 3 parameter rate expression. This rate expression is given by:

$$dC/dt = K_n(B)(A_o - 3C/f)^n$$

This differential equation portrayed the rate of change in THM formation with respect to time as a function of free chlorine, TOC, and yield a parameter, f, which represented the moles of THMs formed per mole of free chlorine consumed. Also appearing in the rate expression was the rate constant and a reaction order with respect to chlorine, m. Under assumptions of a third-order reaction with respect to chlorine (i.e., m=3) and constant TOC levels, an integrated expression was developed to predict TTHMs as a function of free chlorine and f. The integrated expression becomes:

$$1/(A_o - 3C/f)_2 = 6K_3t/f + 1/A_o^2$$

where $k_3 = K_4(TOC)$, A_o is the initial chlorine dose, and concentrations are in the same molar units. The integrated expression, which represented a two-parameter kinetic model, satisfactorily fits experimental data for reaction times greater than 100 min but underestimated THM formation for shorter reaction times.

Moore (1979) used simple and multiple regression to study the characteristics of raw water, finished plant water, and distribution system water at nineteen Massachusetts communities. He found chlorine dosage to be the most reliable predictive parameter for chloroform levels in distribution systems. Modelling all nineteen cases, a simple linear

regression equation was developed in which chlorine dosage was related to chloroform concentration with a correlation coefficient of 77 %.

hours) samples (600 ml each) and were analyzed for precursors concentration, pH, residual chlorine and THMs formed.

4. THMs were measured using the purge and trap method. Reaction was stopped for each sample using a chemical agent: sodium thiosulfate.
5. The procedure was repeated in duplicate samples at three different temperatures: 5, 25 and 45°C.
6. Various kinetic models were proposed and tested, using the data obtained through non-linear regression techniques.

A.2 General Procedure for Natural Water Experiment:

1. Raw water was obtained from a local river. It was characterized in terms of THMs precursors concentration (humic acids and bromide ion) and pH. For the humic acid concentration a spectrophotometric method was used. Bromide concentration was determined by using a spectroscopic method and an ion selective electrode.
2. Water was chlorinated in a constant temperature bath using chlorine doses of 8 ppm of chlorine as Cl_2. Chlorine concentration was determined by means of

CHAPTER 3

EXPERIMENTAL PROCEDURES

A. Experimental Design:

This work consists of a kinetic study of THMs formation during water chlorination. Two samples were analyzed: Synthetic Water (formulated and prepared at the laboratory) and Natural Water (obtained from a local river).

A.1 General Procedure for Synthetic Water Experiment:

1. Synthetic water was formulated and prepared with the following characteristics: 0.7 ppm Humic Acids concentration, 0.5 ppm Bromide ion concentration and pH=7.3.
2. Water was chlorinated in a constant temperature bath using chlorine doses of 15 ppm of chlorine as Cl_2. Chlorine concentration was determined by means of iodometric methods(titration and an ion selective electrode).
3. The reaction was monitored by taking short-term (1,2,4 and 8 hours) and long-term (24,48,72 and 96

correspond to the purity specified on the specific methods . Reagents and equipment are described for each technique. All glassware was carefully cleaned and treated with acid wash solution before being used. Acid solutions were prepared at the laboratory from concentrate (available from Fisher).

For trihalomethanes determination, the system available uses the purge and trap method for sample concentration (Perkin Elmer LSC-2 liquid concentrator), a temperature programmed gas chromatographic separation (PE Sigma 3B Water Pollution Analyzer in combination with a PE LCI-100 Laboratory Computer Integrator), and detection by an electrolytic conductivity detector(Perkin Elmer model 700A Hall Detector). The column used was the packed column Carb B-Chrom Waw and the carrier gas was helium. Standards used were: bromoform-96%, bromodichloromethane-97% and chloroform-99% from Aldrich Chemical Company and chlorodibromomethane available form Columbia Chemical Inc. Distilled water was further treated to obtain organic-free water. Samples were collected on precleaned vials that followed EPA protocols. They are narrow mouth screw cap bottles with the TFE fluorocarbon face silicon septa cap liners (available from Wheaton) and the stabilizing agent: Sodium thiosulfate, ACS reagent grade from Fisher.

iodometric methods(titration and an ion selective electrode).

3. The reaction was monitored by taking short-term (1,2,4 and 8 hours) and long-term (24,48,72 and 96 hours) samples (600 ml each) and were analyzed for precursors concentration, pH, residual chlorine and THMs formed .
4. THMs were measured using the purge and trap method. Reaction was stopped for each sample using a chemical agent: sodium thiosulfate.
5. The procedure was repeated in duplicate samples at three different temperatures: 5, 25 and 45°C.
6. Various kinetic models were proposed and tested, using the data obtained through non-linear regression techniques.

B. Reagents and Equipment:

A constant temperature bath (Forma model 2061),a heating and refrigerating unit was used. It permitted a temperature control of ± 0.1°C and allowed the reaction to proceed away from light. Distilled and deionized water of high purity was used for the preparation of solutions and standards. Reagents used for the determination of precursors and products

273). The reference electrode used an inner filling solution:4M Potassium Chloride Saturated with Silver Chloride and an outer filling solution: Potassium Nitrate 1M, both obtained commercially from Fisher. The following solutions were obtained commercially: a standard solution: Sodium Bromide 1000 ppm as Bromide and Bromide ISA (Ion Strength Adjustor, Sodium Nitrate 5M).

Total Residual Chlorine was determined by two methods: electrochemical and wet chemistry. The electrochemical method used an Orion system that consist of an Orion Model 407A Ion Meter and an ion selective electrode (Orion Model 97-70), Orion Iodide and Acid Reagent as well as Residual Chlorine standard (which was commercially available). Titration facilities were established for chlorine determination by an iodometric method. Sodium Thiosulfate (ACS Certified) was obtained from Fisher. The Potassium Iodide used was a Baker Analyzed Reagent. Other reagents used were: Starch-Soluble (Certified ACS for Iodometry from Fisher), Salicylic Acid (Baker) and Potassium Dichromate, primary standard of high purity (101.14% purity).

pH measurement was performed on a Sargent-Welch (Model LS) pH meter. Commercial Buffer solutions (pH=4 and pH=10

On humic acids determination, a Perkin Elmer Lambda 4B UV/VIS Spectrophotometer was used (1 cm. quartz cells and 254 nm.). Humic acid, Na salt,tech. used was obtained from Aldrich chemicals. When humic acids are determined as non-volatile total organic carbon (NVTOC) the carbon analyzer used (O.I. 524C) consists of an ampule analyzing unit and a purging and sealing unit. Carbon free water was used, phosphoric acid, concentrate (from Fisher), anhydrous potassium biphthalate and potassium hydrogen phthalate, low nitrogen (both certified ACS reagent from Fisher), sodium carbonate and purified oxygen (CO_2 free) as purging gas.

Spectrophotometric and electrochemical facilities were developed for bromide concentration determination. A Spectronic 501 Bausch & Lomb spectrophotometer was used at 590 nm. The following reagents (Certified ACS) were used on bromide determination: Sodium Acetate Trihydrate and Chloramine-T, sodium p-toluenesulfonchloramide (from Sigma), phenol-sulfonephthalein sodium salt,sodium thiosulfate pentahydrate, and anhydrous Potassium Bromide (from Fisher). The Electrochemical facilities for Bromide determination include a Fisher Accumet Model 950 pH/ion meter, a Bromide Ion Selective electrode (Fisher 13-626-520) and a silver Chloride double-junction reference electrode (Fisher 13-620-

used over a concentration range of approximately 0.1 to 1500 micrograms per liter.

Humic acids were determined by using two methods: a spectrophotometric method and as non-volatile total organic carbon(NVTOC) using a wet oxidation method. UV absorbance at 254 nm is an excellent surrogate parameter for estimating the raw waters concentration of organic carbon (NVTOC). Organic compounds that are aromatic or have conjugated double bonds absorb light in the ultraviolet(UV) wavelength region. UV spectroscopy is a good technique for measuring the presence of naturally occurring organic matter, such as humic substances, because they contain aromatic moieties and are dominant forms of organic matter in natural waters. When humic acids are analyzed as NVTOC a carbon analyzer is used. The model consists of an ampule analyzing unit and a purging and sealing unit. The sample is acidified, purged to remove inorganic carbon, and oxidized with persulfate in an autoclave at a temperature of 250°F and 15 psig of pressure. The resultant carbon dioxide is measured by non-dispersive infrared spectrometry.

Bromide concentrations were analyzed by means of a spectrophotometric standard method and an ion selective

from Fisher) were used.

C. Analytical Techniques:

THMs concentrations were analyzed by means of chromatographic techniques. The system uses the purge and trap method for sample concentration (Perkin Elmer LSC-2 liquid sample concentrator), a temperature programmed gas chromatographic separation, and detection by an electrolytic conductivity detector (Perkin-Elmer model 700A). The purge and trap method extracts THMs from the aqueous sample by bubbling of an inert gas. The THMs are then carried away with the purge gas and collected on a short trapping column that is kept at ambient temperature. After the aqueous sample has been thoroughly purged, the trapped components are thermally desorbed and backflushed into the analytical column. The accuracy of this method has been certified by several investigators (Dressman, et.al.,1979).

The method is applicable to the determination of chloroform, bromodichloromethane, dibromochloromethane, and bromoform in drinking water or raw source water. The concentration of these four compounds may be added to determine total trihalomethanes (TTHM). The method can be

$$E = E^{\circ} + 2.3\ (S)\log(A)$$

E = measured electrode potential

E° = constant, the sum of several system potentials

S = electrode slope

A = bromide ion activity

At 25°C, the electrode slope is -59.2 mV per decade increase in bromide ion activity. Activity is related to the electrical force each ion in solution exerts with respect to every other ion. It is not the same as concentration. In practical operation, an ionic strength adjustor (ISA) is added to raise the ionic strength of standards and samples to high and essentially constant levels. In this matched situation, activity coefficients are equal, and working concentration curves can be prepared for the analysis of bromide ion.

Total residual chlorine was determined using an iodometric method by titration and by means of an ion selective electrode. Iodometry is an indirect process involving iodine. Excess iodine ion is added to an oxidizing agent, liberating iodine which then titrated with sodium thiosulfate. This analysis is based on the fact that chlorine

electrode. The principle of the spectrophotometric analysis consists on the fact that when a sample containing bromide ions(Br^-) is treated with a dilute solution of Chloramine-T in the presence of phenol red, the oxidation of bromide and subsequent bromination of the phenol red occurs readily. If the reaction is buffered to approximately pH 4.7, the color of the brominated compound will range from reddish to violet, depending on bromide concentration. Thus, a sharp differentiation can be made among various concentration of bromide. Materials present in ordinary tap water do not interfere, but oxidizing and reducing agents do interfere. Thus, this method was used only for samples before chlorination. The minimum detectable concentration of this method is: 0.1 mg Br^-/L.

The solid state electrode measured bromide ion concentration in aqueous solutions. The probe has a rugged, epoxy, solid state body. It was used with a silver chloride double junction reference electrode. The operation of the bromide electrode is based on the potential which develops across a single-crystal silver bromide membrane. This potential is proportional to the activity of bromide ions in contact with the membrane. The relationship between potential and bromide ion activity is set forth by the Nernst Equation:

will liberate free iodine from potassium iodide (KI) solutions at pH 8 or less.

$$Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$$

The liberated iodine is titrated with a standard solution of sodium thiosulfate ($Na_2S_2O_3^-$) with starch indicator solution. Iodine oxidizes thiosulfate to the tetrathionate ion:

$$I_2 + 2S_2O_3^- \longrightarrow 2I^- + S_4O_6^-$$

The reaction is rapid, goes well to completion and there are no side reactions. The equivalent weight of $Na_2S_2O_3.5H_2O$ is the molecular weight, 248.17, since one electron per molecule is lost. A solution (colloidal dispersion) of starch is employed, since the deep blue color of starch-iodine complex serves as a very sensitive test for iodine. The sensitivity is greater in slightly acid than in neutral solutions. The exact mechanism of the formation of the colored complex is not known. However, it is thought that molecules of iodine are held on the surface of beta-amylose, a constituent of starch. Titration was done at pH 3 to 4 because the reaction is not stoichiometric at neutral pH due to partial oxidation

of thiosulfate to sulfate. If the pH of the reaction is above 9, thiosulfate is oxidized partially to sulfate:

$$4I_2 + S_2O_3^- + 5H_2O \longrightarrow 8I^- + 2SO_4^{2-} + 10\ H^+$$

Acetic acid (glacial) was added to adjust the sample to the desired pH. A number of substances can be used as primary standards for thiosulfate solutions. Pure iodine is the most obvious standard, but is seldom used because of difficulties in handling and weighing. More often, use is made of a strong oxidizing agent like potassium dichromate which will liberate iodine from iodide, an iodometric process. Potassium dichromate can be obtained in a high degree of purity. The reaction with iodide is carried out in about 0.2 to 0.4M acid, and is complete in 5 to 10 minutes:

$$Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

The residual chlorine electrode allows total residual chlorine to be measured quickly and accurately. All forms of total residual chlorine are measured: free chlorine, hypochlorites, and chlorine bound to nitrogenous compounds. The electrode method is based on iodometric measurements of chlorine. Commercial iodide and acid reagents are added to

a sample, and the iodide reacts completely with the chlorine to form iodine:

$$Cl_2 + 2I^- \longrightarrow 2Cl^- + I^2$$

The iodine concentration after reaction is equal to the chlorine concentration before the reaction. Acid must be present for the conversion of chloroamines to iodine. The electrode contains a platinum (redox) sensing element and iodine-sensing reference element. The platinum element develops a potential that depends on the relative levels of iodine and iodide ion in solution:

$$E_1 = E_o + (S/2)\log([I_2]/[I^-]^2)$$

$$E_1 = E_o + (S/2)\log[I_2] - (S)\log[I^-]$$

where:

E_1 = potential developed by the platinum element

E_o = a constant

S = monovalent electrode slope(58 mV/decade at 20°C)

$[I_2]$ = Iodine concentration

$[I^-]$ = Iodide concentration

The iodide sensing element develops a potential that depends on the iodine level in solution,

$$E_2 = E_o' - (S)\log[I_2]$$

where:

E_2 = potential developed by the iodide sensing element

E_o' = a constant

The meter measures the difference between the potentials developed by the two elements:

$$E_1 - E_2 = E_o'' + S/2 \log[I_2]$$

The combination of the platinum and the iodide sensing elements thus measures the iodine concentration, which is equal to the total residual chlorine concentration before reaction with iodine reagent.

CHAPTER 4:

RESULTS

A. Experimental Results

A.1 Synthetic Water

Synthetic water was chlorinated, in duplicate runs, at 5°C, 25°C, and 45°C. Tables #1, #2, and #3 summarize the results obtained; in terms of TTHMs. UV absorbance, used here as a surrogate parameter for NVTOC concentration, is illustrated, as a function of time and temperature in figure 7. Chlorine and bromide concentration behavior are illustrated in Figures 8 and 9. Figure 10 shows that the pH remained essentially constant for all runs.

A.2 Natural Water

Raw river water was chlorinated, in duplicate runs also, at 5°C, 25°C and 45°C. Tables #4, #5, and #6 summarize the results obtained, in terms of TTHMs. Figures 11, 12, 13, 14 and 15 show THMs formation as a function of time, both as total (TTHMs) and individual species. Figure 16 illustrates

Table #1: Absorbance, Bromide, Chlorine, and TTHMs Measured for Synthetic Water, T = 5°C.

Run Number	Time (hrs)	UV (254 nm)	Br (μM)	Cl2 (μM)	TTHMs (μM)
0	0	0.207	0.0063	0.2115	0.116
1	1	0.177	0.0019	0.1637	0.301
1	1	0.181	0.0009	0.1798	0.265
2	2	0.171	0.0015	0.1637	0.368
2	2	0.178	0.0008	0.1763	0.334
3	4	0.168	0.0013	0.1587	0.437
3	4	0.177	0.0008	0.1704	0.371
4	8	0.168	0.0011	0.1563	0.550
4	8	0.166	0.0008	0.1675	0.412
5	24	0.155	0.0010	0.1482	0.637
5	24	0.156	0.0006	0.1575	0.516
6	48	0.139	0.0009	0.1393	0.813
6	48	0.155	0.0005	0.1522	0.540
7	72	0.146	0.0006	0.1388	0.761
7	72	0.153	0.0005	0.1462	0.640
8	96	0.147	0.0000	0.1331	0.873
8	96	0.143	0.0007	0.1413	0.662

Table #2: Absorbance, Bromide, Chlorine, and TTHMs Measured for Synthetic Water, T = 25°C.

Run Number	Time (hrs)	UV (254 nm)	Br (μM)	Cl2 (μM)	TTHMs (μM)
0	0	0.207	0.0063	0.2115	0.116
1	1	0.169	0.0008	0.1601	0.614
1	1	0.169	0.0008	0.1637	0.550
2	2	0.163	0.0008	0.1544	0.647
2	2	0.161	0.0007	0.1570	0.650
3	4	0.156	0.0009	0.1450	0.773
3	4	0.154	0.0007	0.1488	0.741
4	8	0.153	0.0006	0.1337	0.824
4	8	0.147	0.0010	0.1388	0.804
5	24	0.132	0.0008	0.1093	0.717
5	24	0.134	0.0008	0.1156	0.700
6	48	0.127	0.0006	0.0838	0.366
6	48	0.125	0.0007	0.0928	0.438
7	72	0.125	0.0001	0.0637	0.187
7	72	0.112	0.0004	0.0753	0.192
8	96	0.111	0.0006	0.0440	0.140
8	96	0.113	0.0007	0.0540	0.135

Table #3: Absorbance, Bromide, Chlorine, and TTHMs Measured for Synthetic Water, T = 45°C.

Run Number	Time (hrs)	UV (254 nm)	Br (μM)	Cl2 (μM)	TTHMs (μM)
0	0	0.207	0.0063	0.2115	0.116
1	1	0.156	0.0019	0.1331	1.037
1	1	0.154	0.0009	0.1458	1.196
2	2	0.147	0.0014	0.1250	1.269
2	2	0.143	0.0010	0.1369	1.192
3	4	0.140	0.0014	0.1172	1.246
3	4	0.137	0.0009	0.1285	1.395
4	8	0.134	0.0021	0.0982	0.951
4	8	0.131	0.0008	0.1125	1.115
5	24	0.123	0.0008	0.0581	0.426
5	24	0.117	0.0006	0.0784	0.569
6	48	0.115	0.0006	0.0247	0.140
6	48	0.107	0.0008	0.0457	0.257
7	72	0.109	0.0006	0.0041	0.047
7	72	0.100	0.0005	0.0200	0.090
8	96	0.111	0.0014	0.0000	0.000
8	96	0.102	0.0008	0.0113	0.000

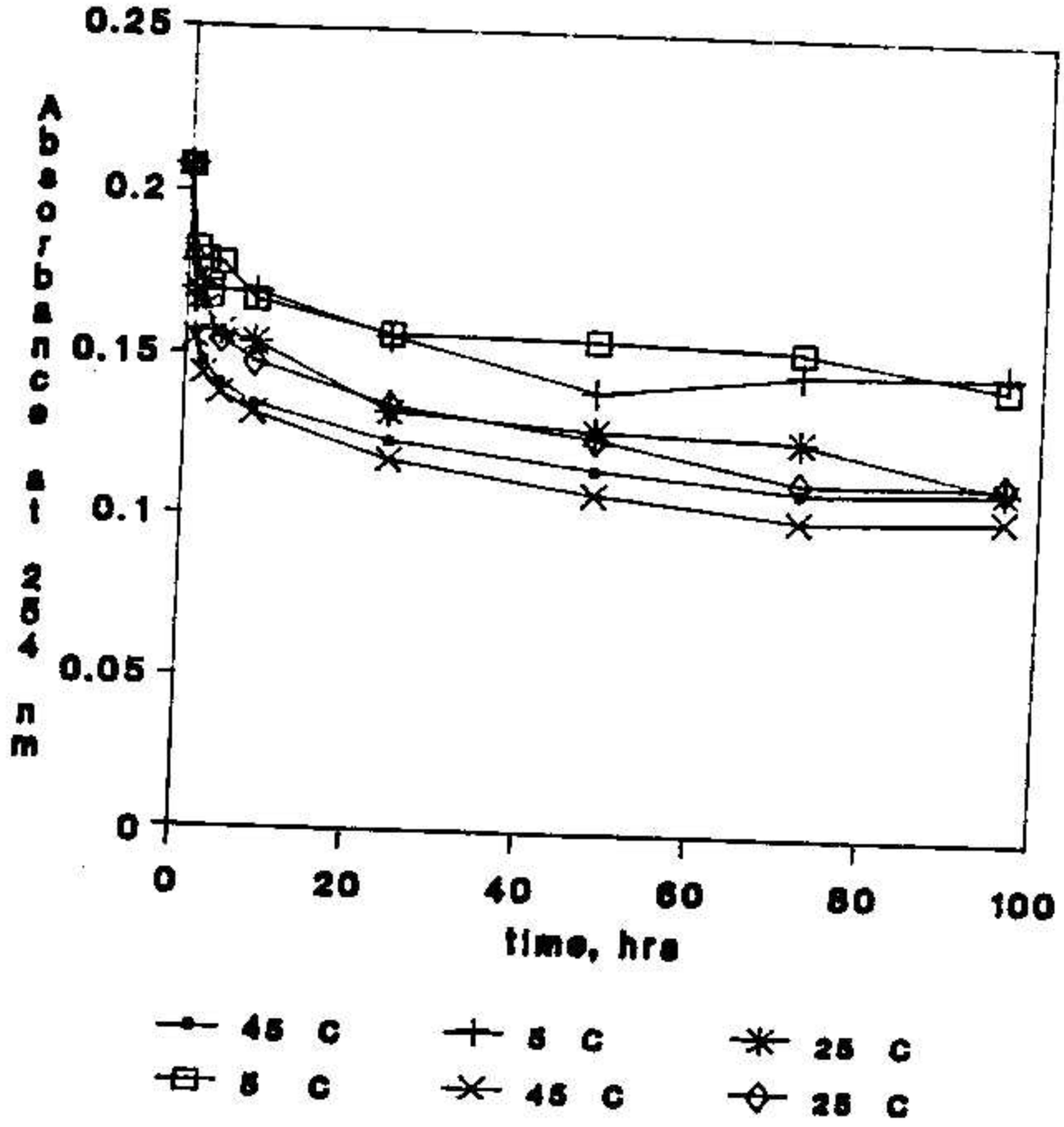

Figure 7: UV Measurements for Synthetic Water

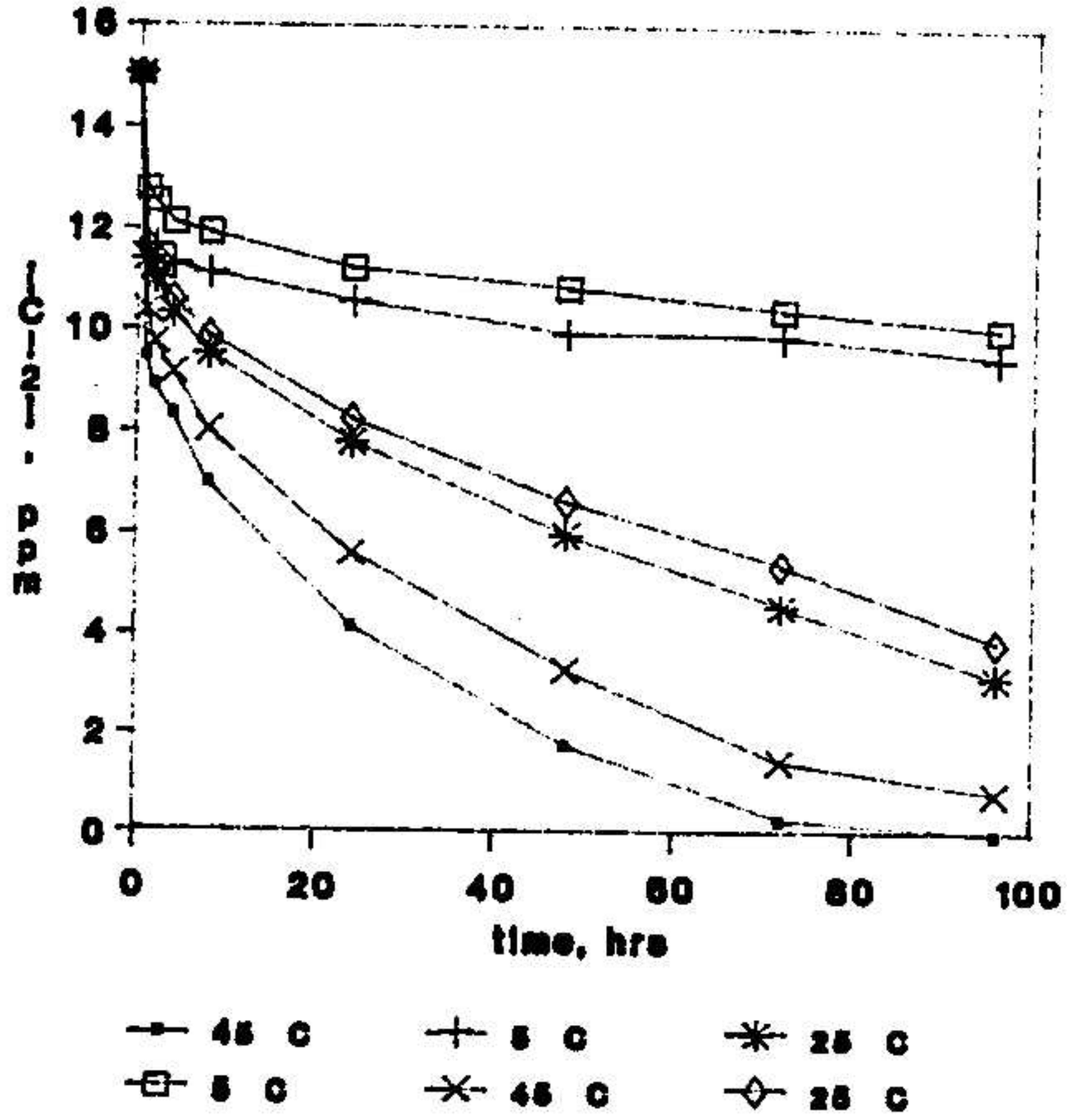

Figure 8: Chlorine Measurements for Synthetic Water

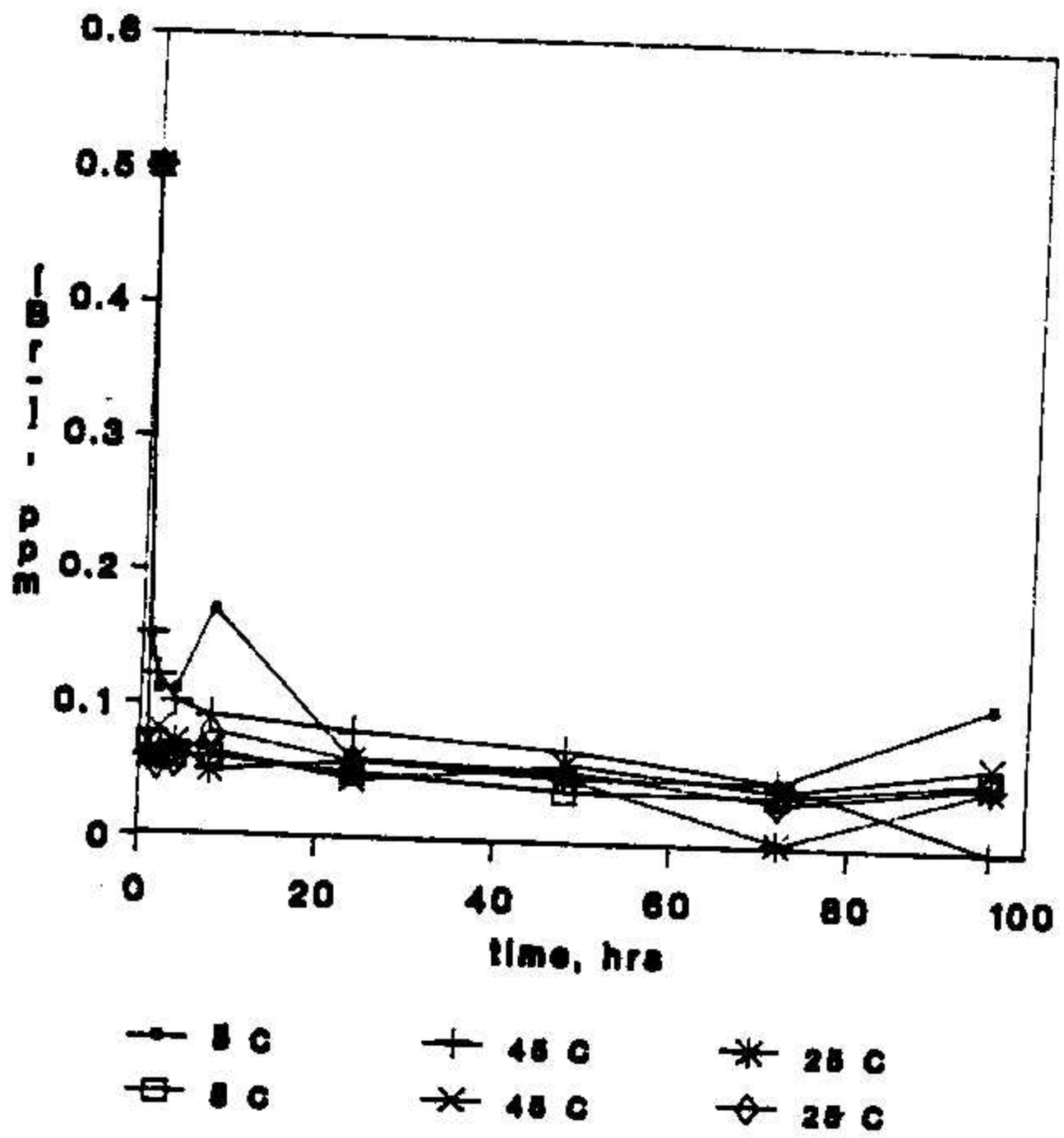

Figure 9: Bromide Measurements for Synthetic Water

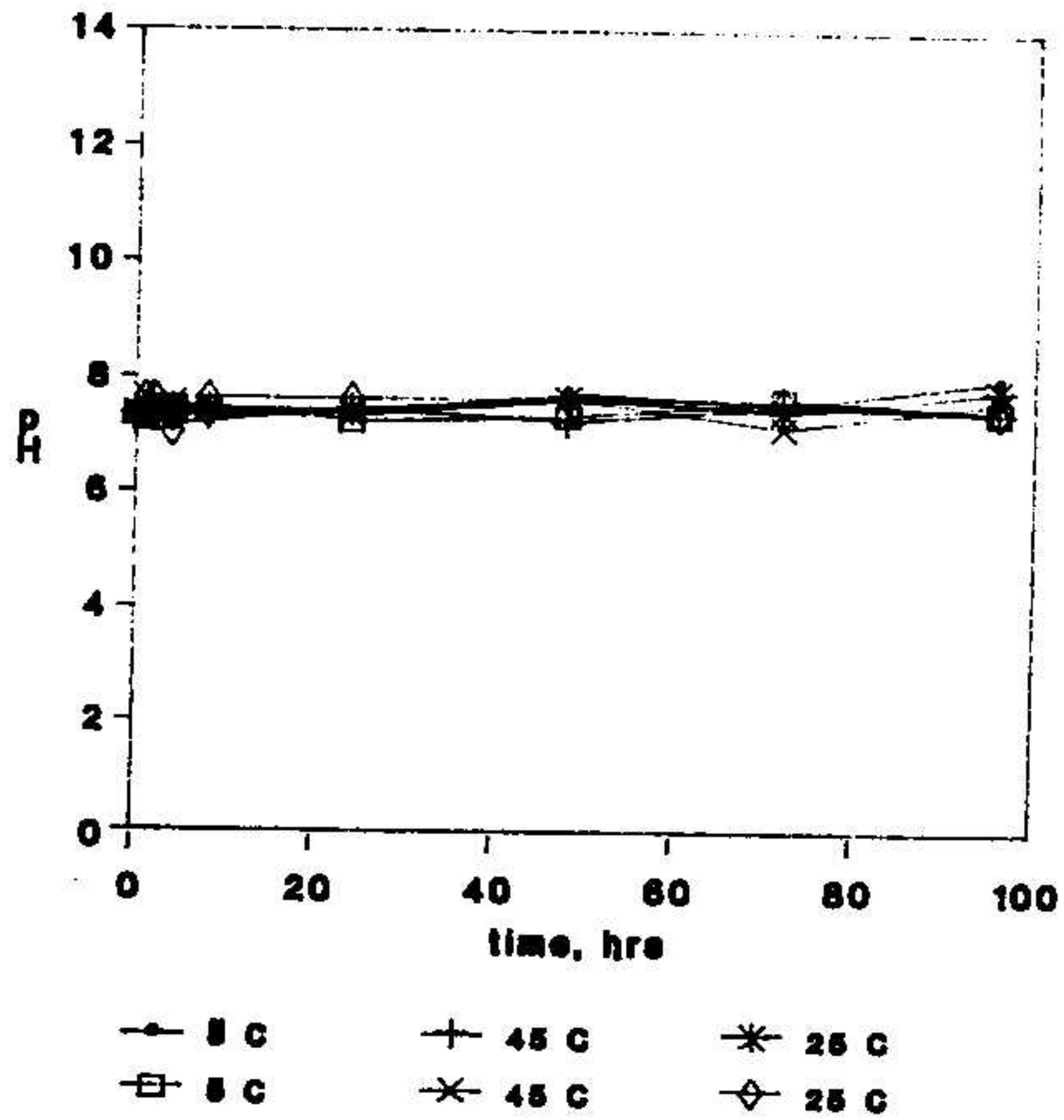

Figure 10: pH Measurements for Synthetic Water

Table #4: Asorbance, Bromide, Chlorine, and TTHMs Measured for Natural Water, T = 5°C.

Run Number	Time (hrs)	UV (254 nm)	Br (μM)	Cl2 (μM)	TTHMs (μM)
0	0	0.092	0.0063	0.1128	1.668
0	0	0.091	0.0063	0.1128	1.704
1	1	0.091	0.0013	0.0907	1.789
1	1	0.090	0.0025	0.0943	1.824
2	2	0.088	0.0012	0.0887	1.824
2	2	0.089	0.0024	0.0918	1.819
3	4	0.086	0.0011	0.0876	1.882
3	4	0.088	0.0020	0.0912	1.885
4	8	0.085	0.0013	0.0874	1.969
4	8	0.086	0.0024	0.0863	1.893
5	24	0.080	0.0009	0.0794	1.995
5	24	0.084	0.0013	0.0835	2.059
6	48	0.079	0.0015	0.0778	2.045
6	48	0.078	0.0019	0.0763	2.108
7	72	0.071	0.0016	0.0704	2.155
7	72	0.071	0.0019	0.0763	2.108
8	96	0.070	0.0014	0.0694	1.232
8	96	0.070	0.0019	0.0725	2.172

Table #5: Absorbance, Bromide, Chlorine, and TTHMs Measured for Natural Water, T = 25°C.

Run Number	Time (hrs)	UV (254 nm)	Br (μM)	Cl2 (μM)	TTHMs (μM)
0	0	0.091	0.0063	0.1128	1.721
0	0	0.088	0.0063	0.1128	1.762
1	1	0.086	0.0050	0.0938	2.009
1	1	0.085	0.0019	0.0925	2.015
2	2	0.085	0.0063	0.0907	2.086
2	2	0.081	0.0024	0.0905	2.078
3	4	0.084	0.0028	0.0872	2.169
3	4	0.079	0.0029	0.0856	2.078
4	8	0.081	0.0019	0.0807	2.270
4	8	0.079	0.0026	0.0800	2.234
5	24	0.071	0.0011	0.0681	1.134
5	24	0.067	0.0014	0.0687	2.343
6	48	0.069	0.0026	0.0594	2.261
6	48	0.059	0.0014	0.0592	2.479
7	72	0.066	0.0015	0.0564	2.487
7	72	0.057	0.0025	0.0556	2.513
8	96	0.062	0.0018	0.0534	2.614
8	96	0.054	0.0014	0.05142	2.605

Table #6: Absorbance, Bromide, Chlorine, and TTHMs Measured for Natural Water, T = 45°C.

Run Number	Time (hrs)	UV (254 nm)	Br (μM)	Cl2 (μM)	TTHMs (μM)
0	0	0.092	0.0063	0.1128	1.654
0	0	0.091	0.0063	0.1128	1.696
1	1	0.090	0.0023	0.0866	2.066
1	1	0.082	0.0019	0.0825	2.135
2	2	0.089	0.0011	0.0845	2.168
2	2	0.079	0.0019	0.0825	2.135
3	4	0.087	0.0019	0.0718	2.315
3	4	0.076	0.0021	0.0763	2.198
4	8	0.073	0.0013	0.0625	1.896
4	8	0.069	0.0014	0.0619	2.366
5	24	0.066	0.0038	0.0388	3.098
5	24	0.061	0.0024	0.0419	2.637
6	48	0.062	0.0010	0.0262	1.483
6	48	0.057	0.0019	0.0269	2.719
7	72	0.060	0.0021	0.0144	1.721
7	72	0.054	0.0024	0.0206	2.679
8	96	0.058	0.0014	0.0126	1.905
8	96	0.052	0.0035	0.0175	2.707

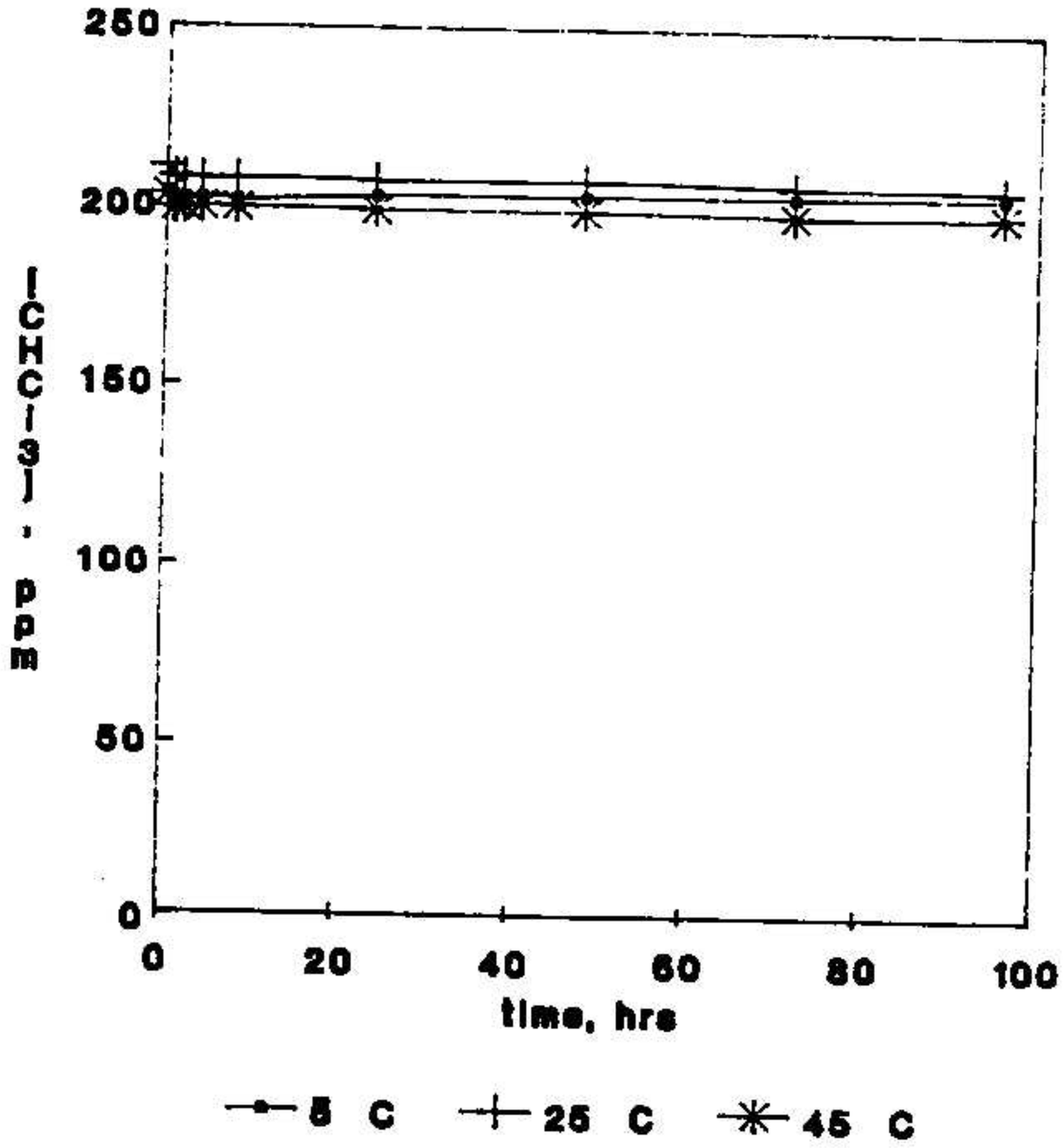

Figure 12: [Chloroform] at Different Temperatures for Natural Water

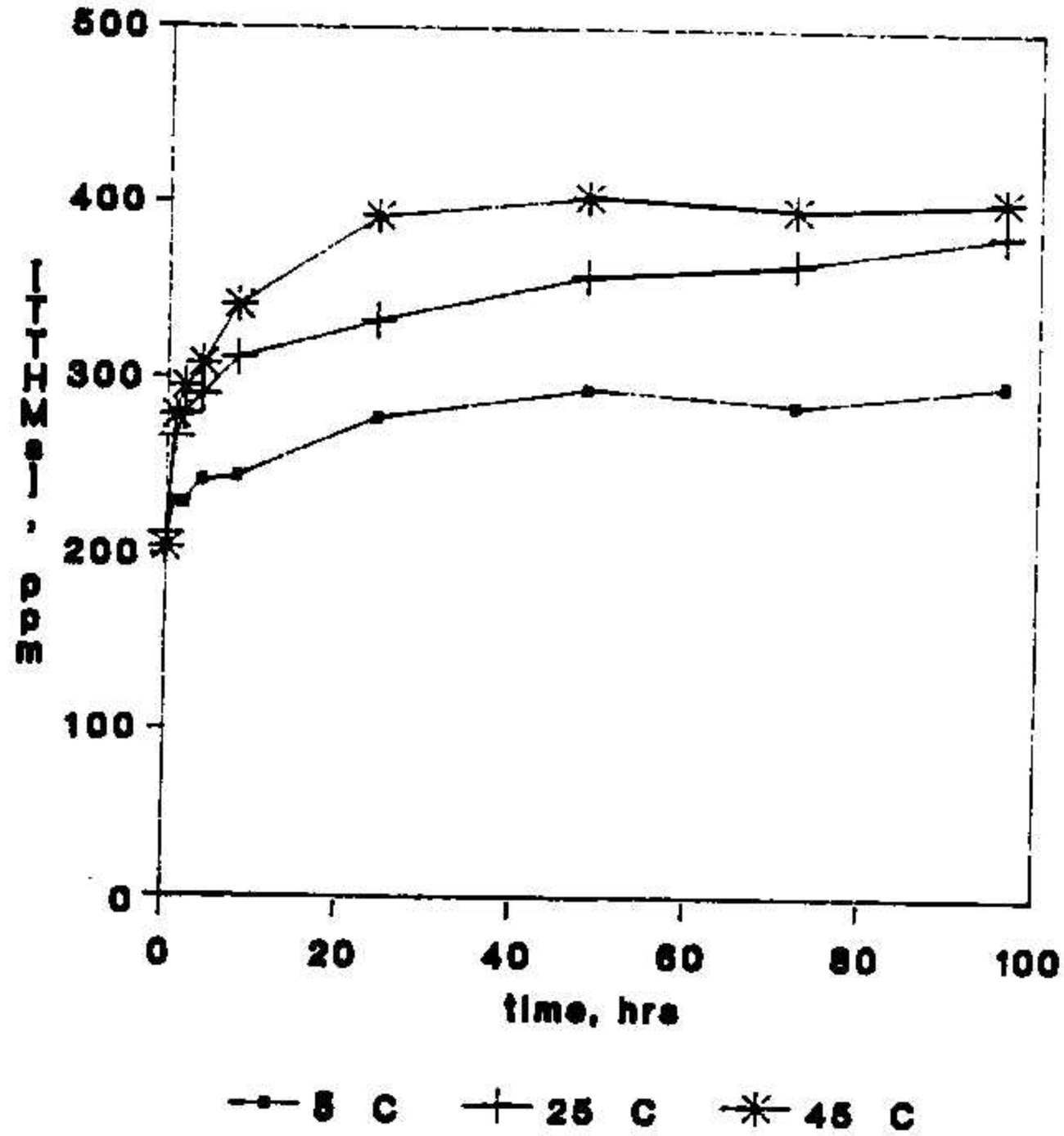

Figure 11: [TTHMs] at Different Temperatures for Natural Water

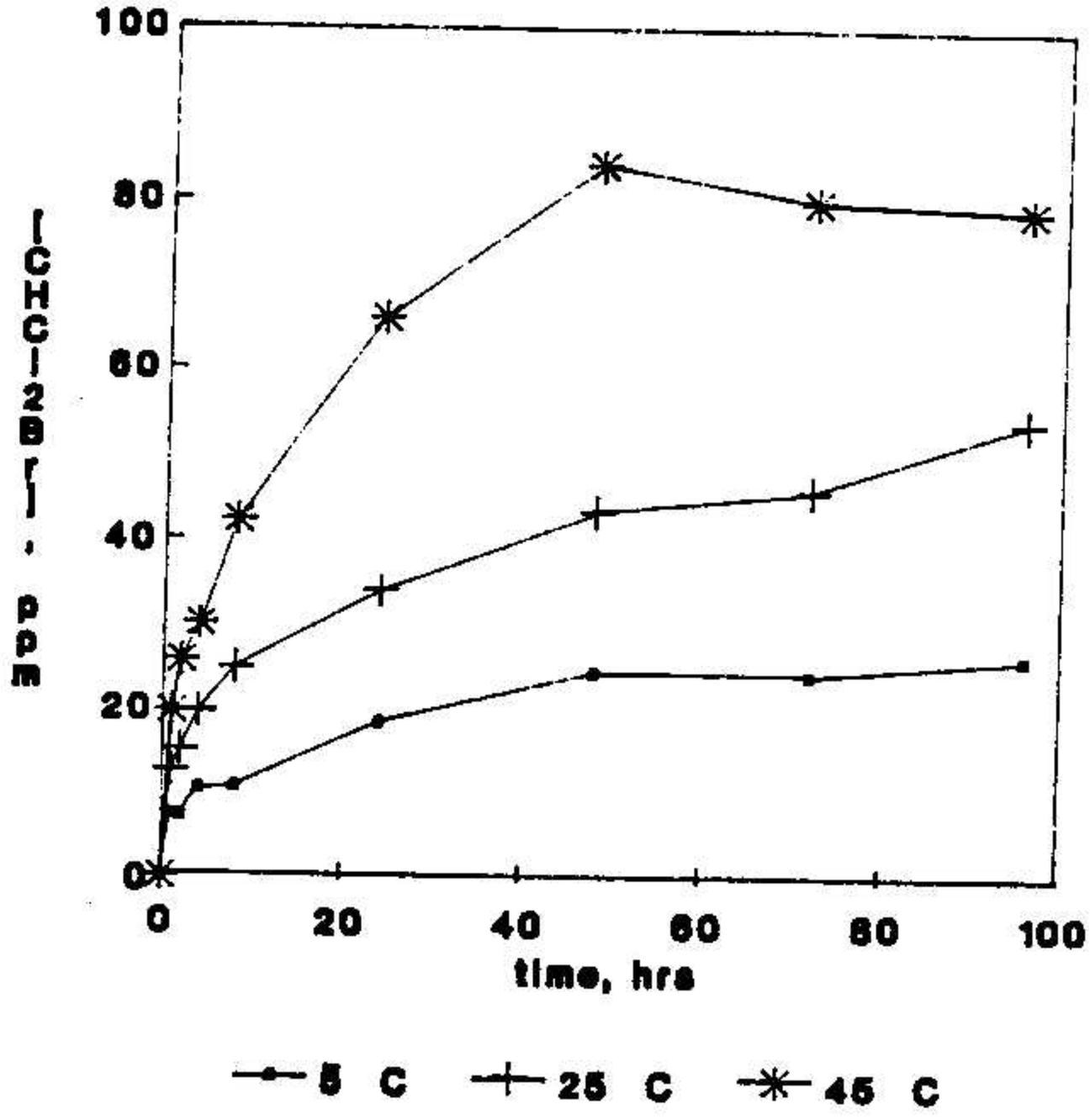

Figure 13:[Bromodichloromethane] at Different Temperatures for Natural Water

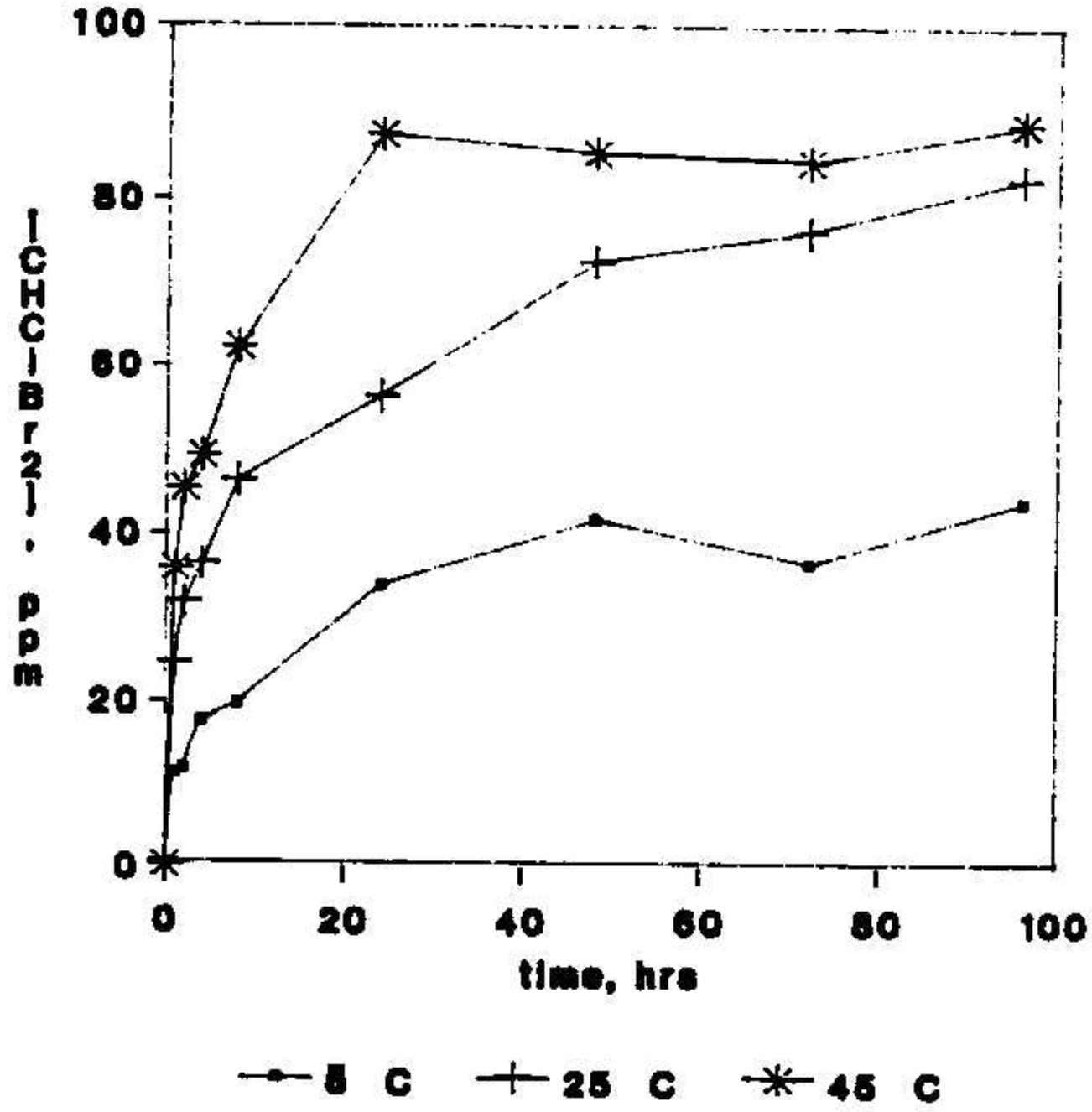

Figure 14: [Dibromochloromethane] at Different Temperatures for Natural Water

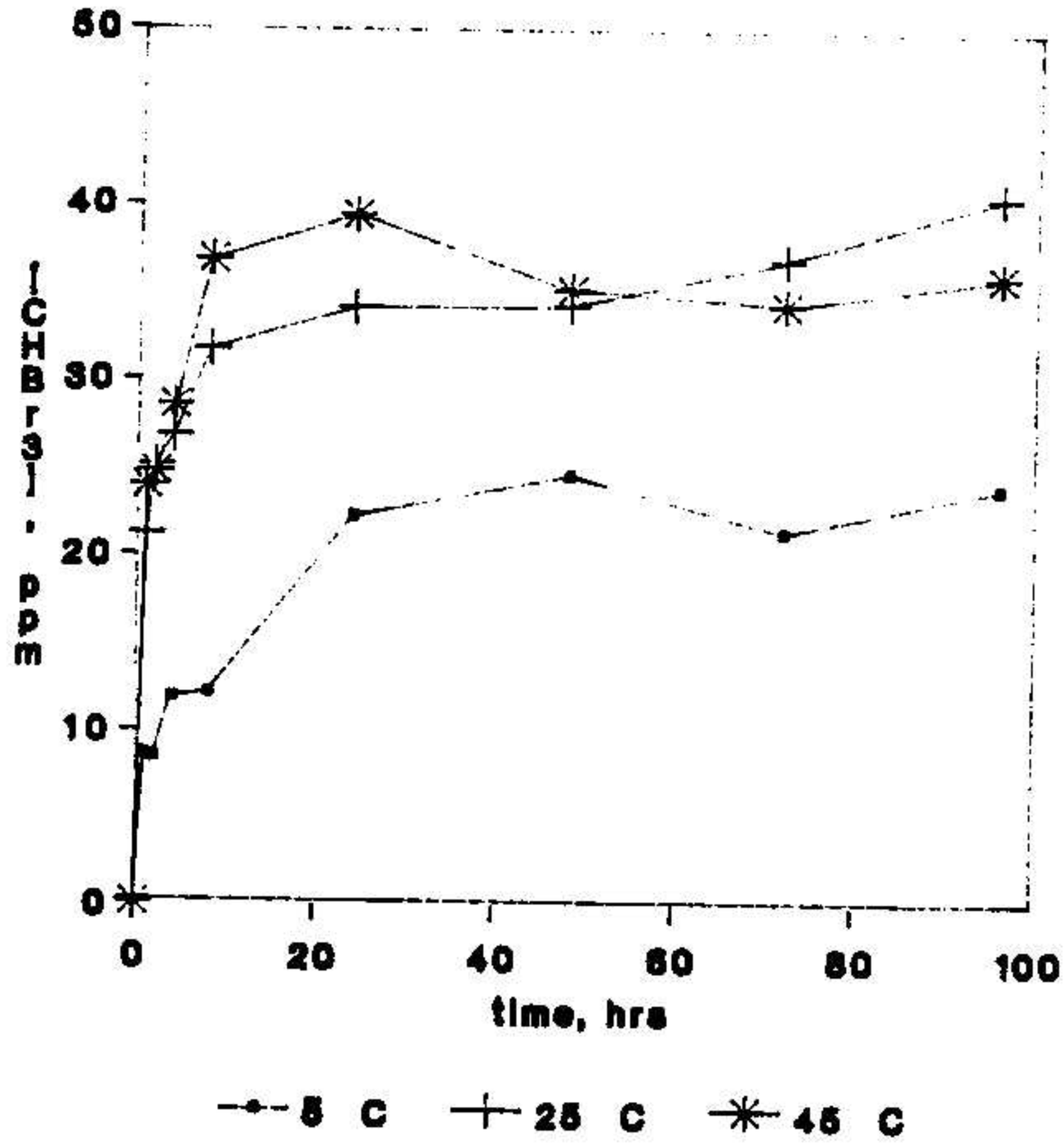

Figure 15: [Bromoform] at Different Temperatures for Natural Water

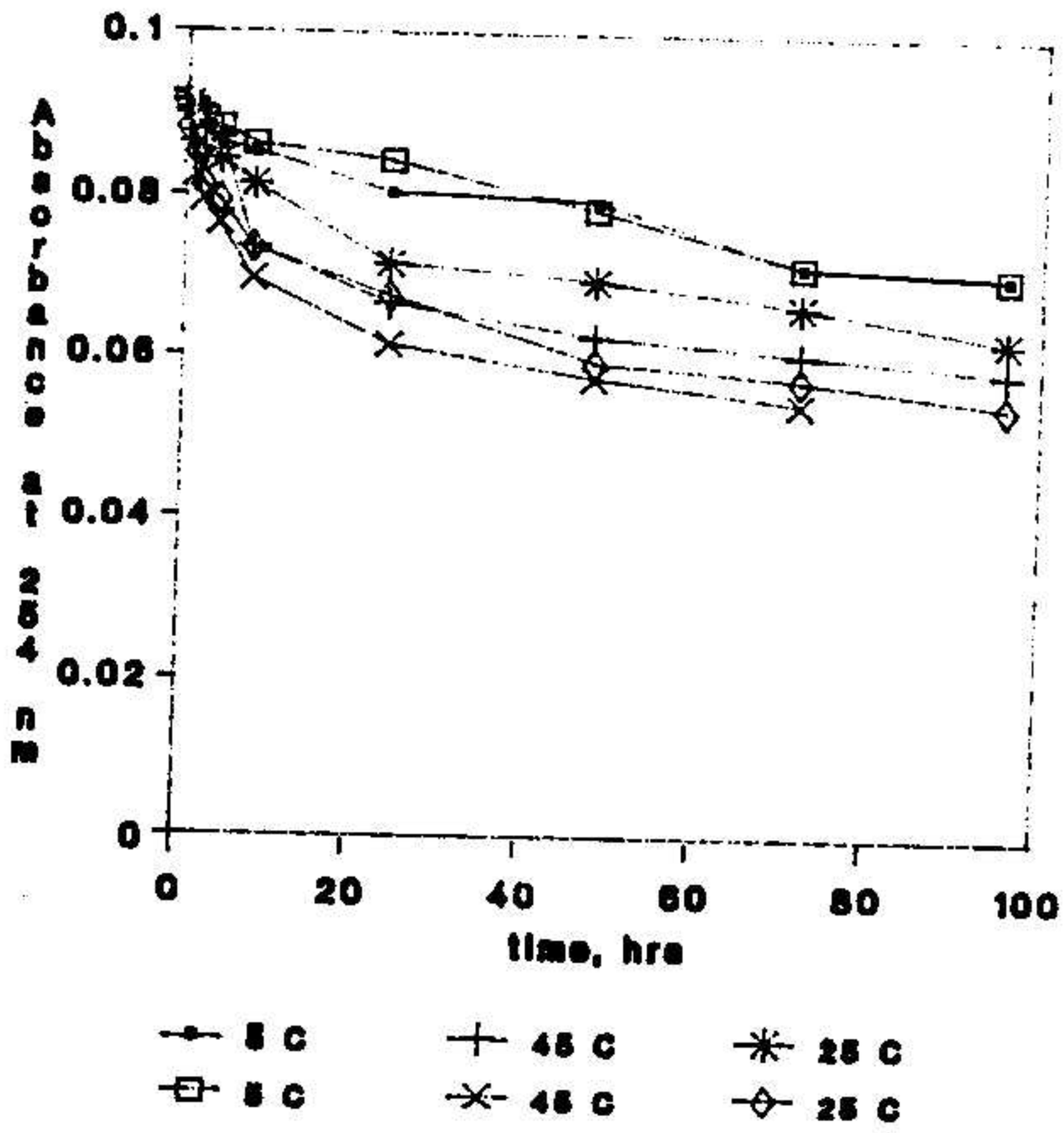

Figure 16: UV Measurements for Natural Water

UV absorbance as function of time and temperature. Figures 17 and 18 show chlorine and bromide concentration as functions of time and temperature. Figure 19 shows that pH remained essentially constant for all runs.

B. Kinetic Studies

B.1 Synthetic Water

A preliminary effort was undertaken for developing a kinetic model to describe the dynamics of the formation of TTHMs during the chlorination of synthetic water. Appendix E gives details about some of the models considered. The model selected as giving the best fit to the available data among those considered is of the form:

$$dY_1/dt = b_1 Y_2 Y_3^2 + b_2$$

$$dY_2/dt = -b_1 Y_2 Y_3^2 - b_3 Y_2$$

$$dY_3/dt = -b_1 Y_2 Y_3^2$$

where:

Y_1 = TTHMs concentration, expressed in μmole/L,

Y_2 = chlorine concentration, in μmole/L,

Y_3 = precursors concentration, expressed in terms of UV absorbance, cm^{-1}

t = time, in hours.

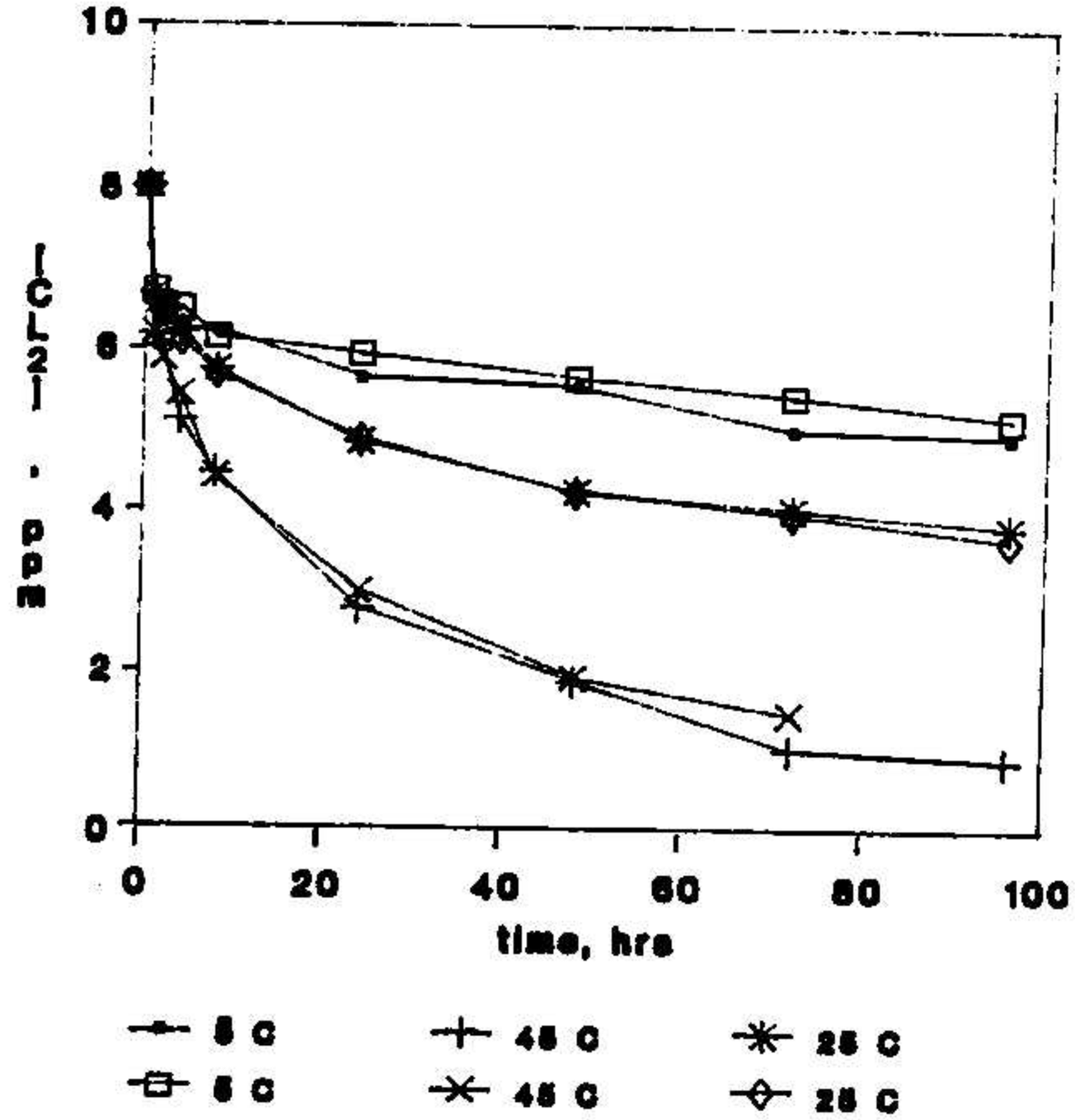

Figure 17: Chlorine Measurements for Natural Water

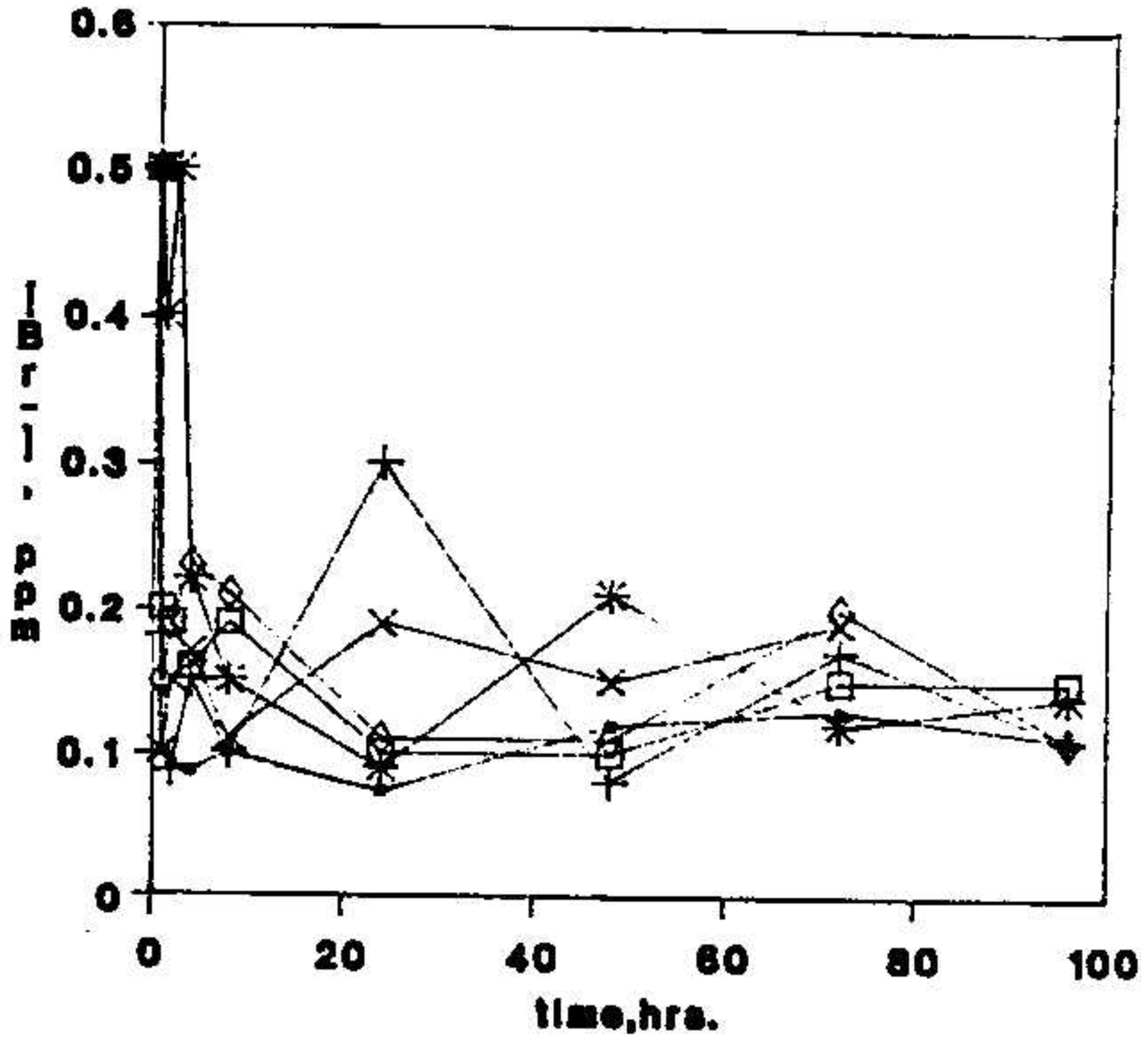

Figure 18: Bromide Measurements for Natural Water

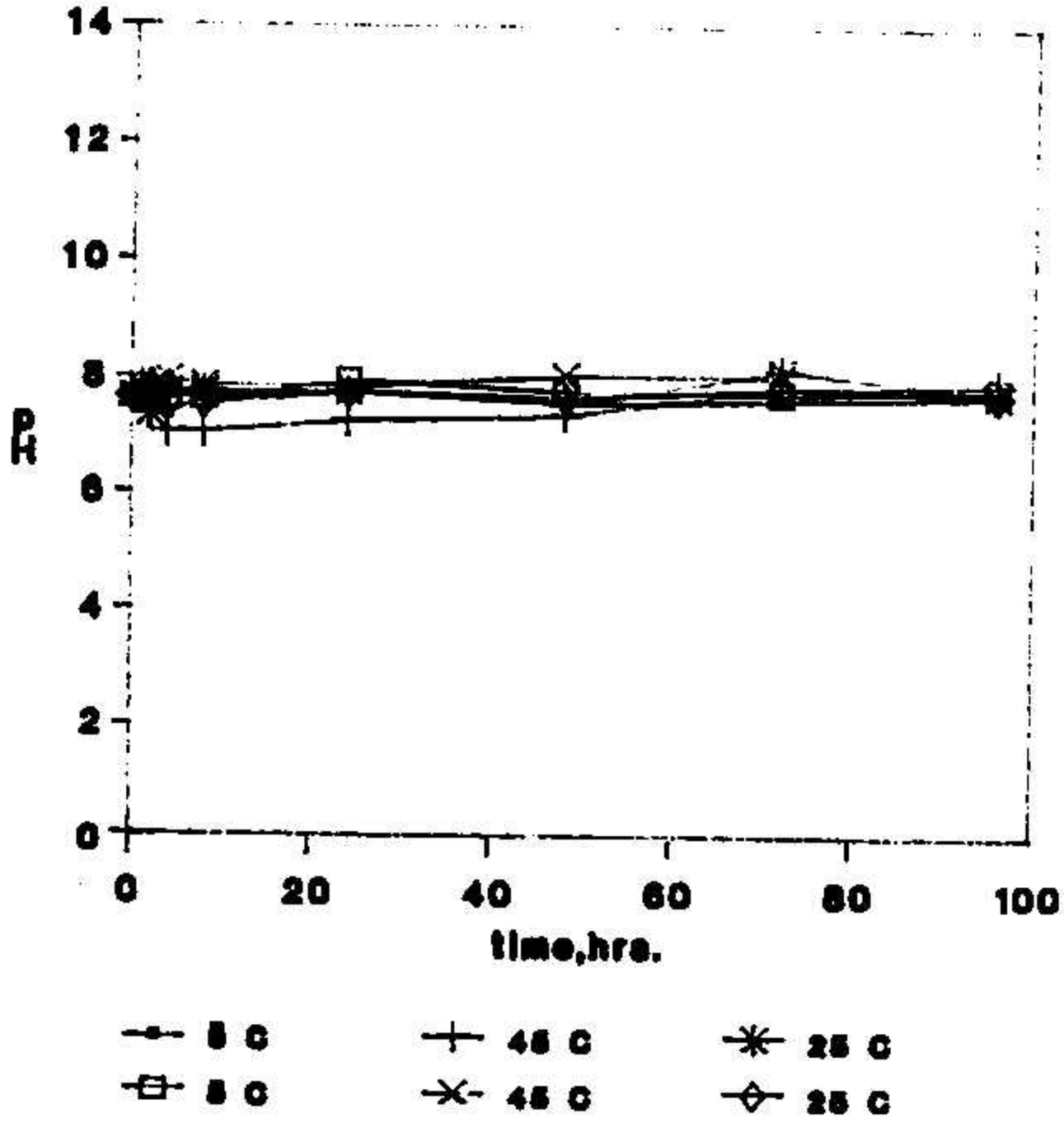

Figure 19: pH Measurements for Natural Water

The same model was found to be appropriate to describe the reaction kinetics both for the short-term conditions (less than 8 hours) and for the long-term results (greater than 24 hours). However, the values of the parameters were found to be very different for the short and long-term.

To determine the appropriateness of the models and obtain the best estimates of the parameters, a nonlinear regression model (NLR) developed by Constantinides (1987) was used. This model combines the Marquardt algorithm for nonlinear regression with the fourth order Runge-Kutta numerical integration techniques to, simultaneously, integrate the rate equations and evaluate the parameters which result in the best statistical fit to the experimental data. Appendix F gives a brief description of the computer program developed by Constantinides to implement the regression model. No program listing is included because of the length of the source code.

The proposed model was fitted to the synthetic water data available at 5°C. The best estimates of the parameters, with 95% confidence intervals, for the short-range are presented in Table #7.

Table #7: Short-range kinetic model parameter estimates for synthetic water at 5° C

Parameter	Best Estimate*	95% Confidence interval
b_1	1.1070	0.9421 - 1.2720
b_2	0.0492	0.0380 - 0.0605
b_3	0.0119	0.0017 - 0.0222

* Units are consistent with those used to define the variables previously.

Best parameter estimates for the long-term kinetic model of chlorination of synthetic water at 5°C are presented in Table #8.

Table #8: Long-range kinetic model parameter estimates for synthetic water at 5° C

Parameter	Best Estimate	95% Confidence Interval
b1	0.1900	0.1480 - 0.2318
b2	0.00735	0.00451 - 0.0102
b3	0.000604	-0.00058 - 0.0179

Figures 20 and 21 present the predicted short-term and long-term behavior of TTHMs respectively.

Modelling of synthetic water data at 25°C and 45°C was not attempted because the behavior of these data was erratic.

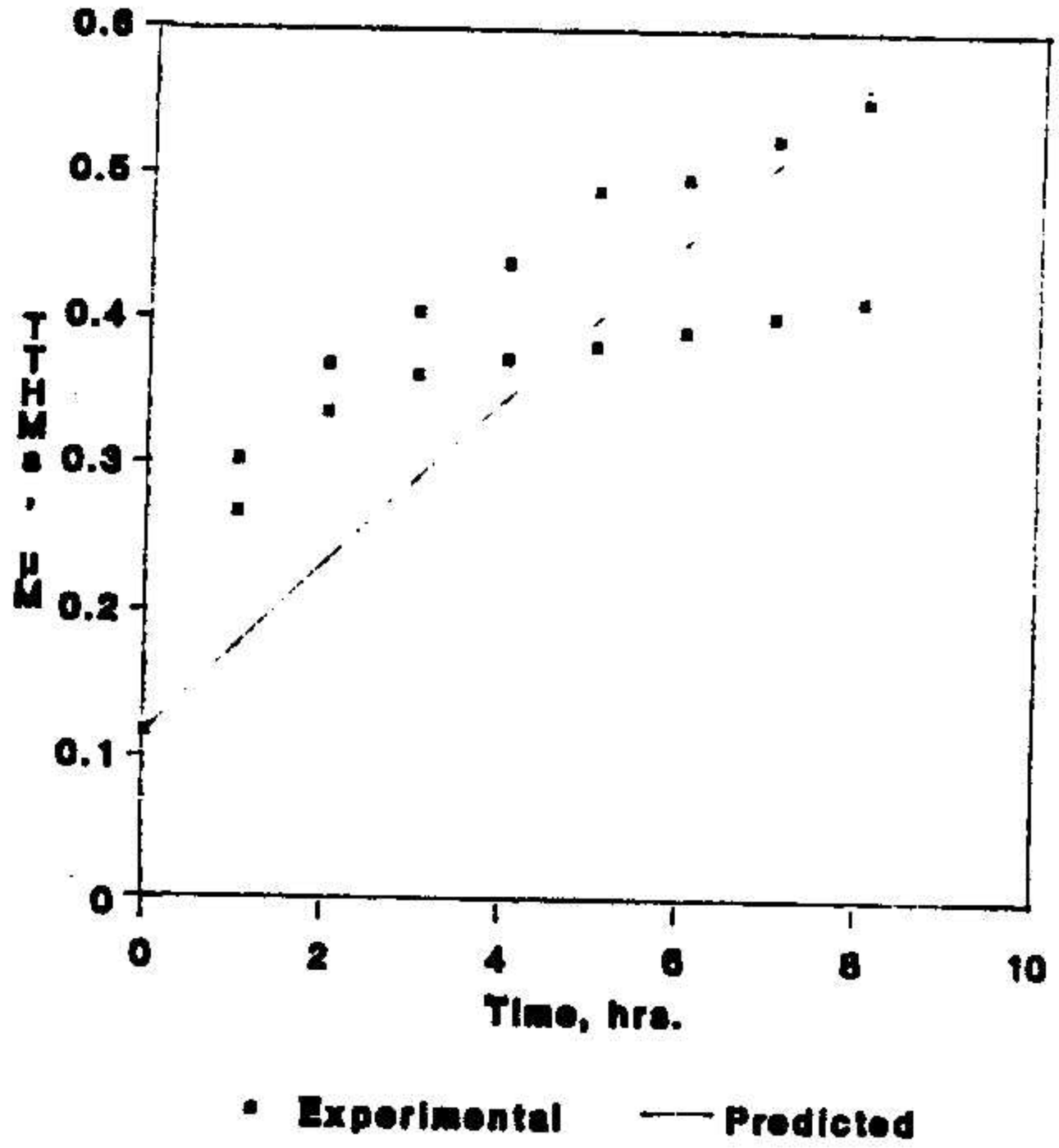

Figure 20: Predicted Short-Term Behavior of [TTHMs] for Synthetic Water at 5 C

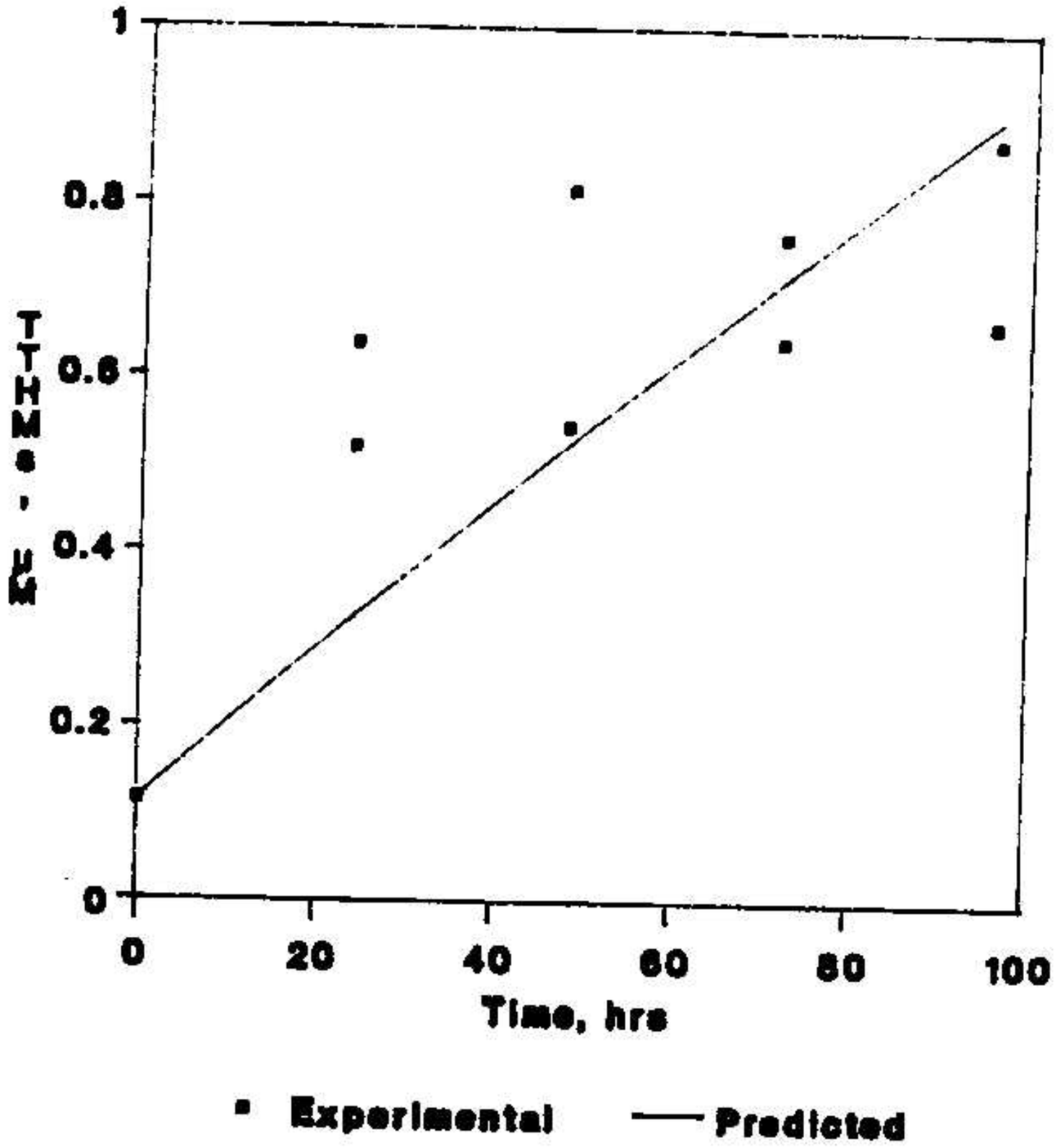

Figure 21: Predicted Long-Term Behavior of [TTHMs] for Synthetic Water at 5 C

B.2 Natural Water

The model used for synthetic water at 5°C was found to be appropriate for natural water at 5°C and 25°C. Again, the modelling effort was divided into a short-term and a long-term effect. Tables 9 and 10 present best short-range parameter estimates at 5°C, and 25°C, respectively.

Figures 22 and 23 show the predicted short-term behavior of TTHMs at 5°C, and 25°C, respectively.

Table #9: Short-range parameter estimates for natural water at 5° C

Parameter	Best Estimate	95% Confidence interval
b_1	1.2710	0.9119 - 1.6310
b_2	0.0378	0.03105 - 0.0445
b_3	0.0355	0.0289 - 0.0420

Table #10: Short-range parameter estimates for natural water at 25° C

Parameter	Best Estimate	95% confidence interval
b_1	7.8340	3.8730 - 11.8000
b_2	0.0754	0.0640 - 0.0869
b_3	0.0107	-0.0061 - 0.0275

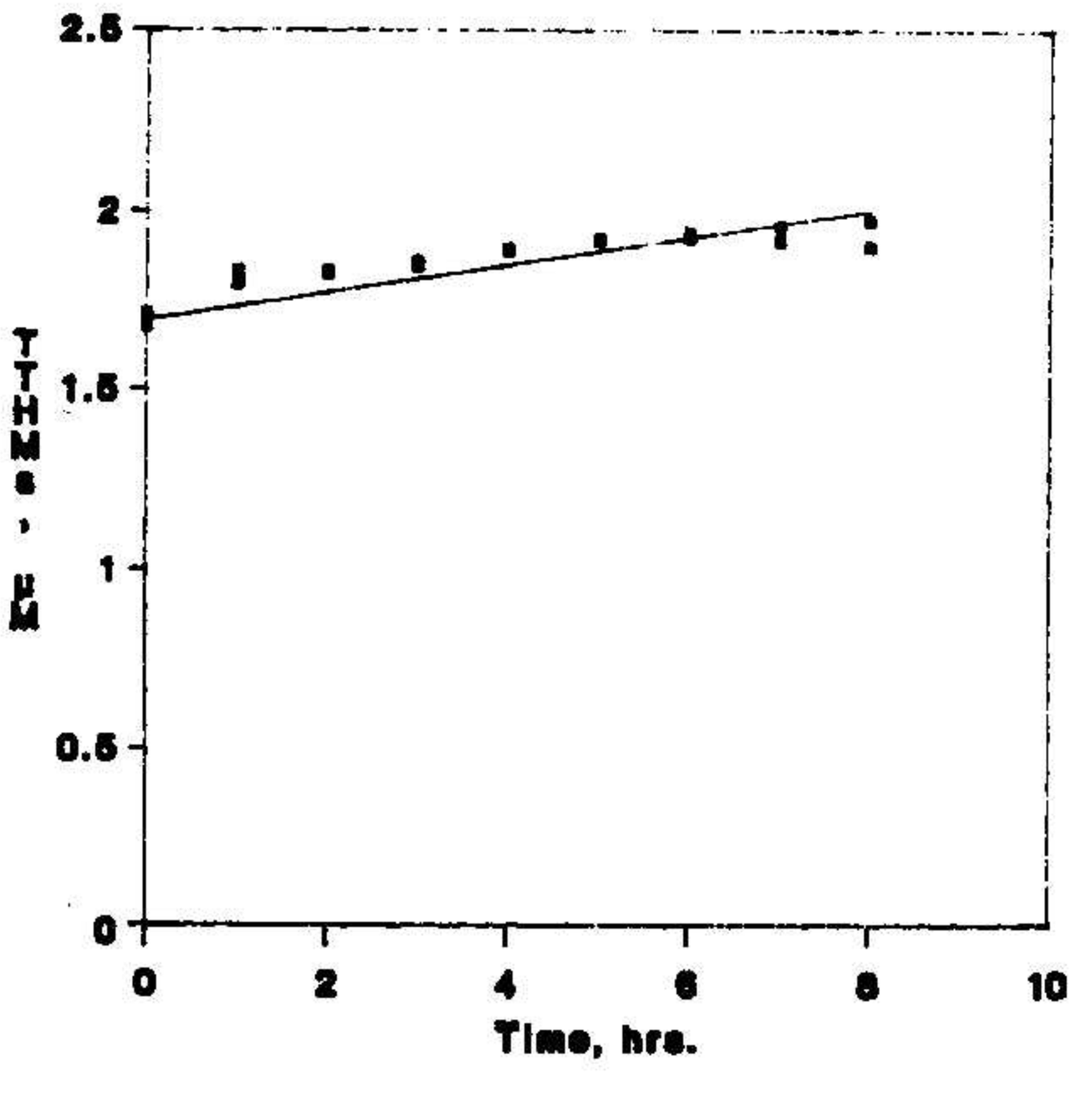

Figure 22: Predicted Short-Term Behavior of [TTHMs] for Natural Water at 5 C

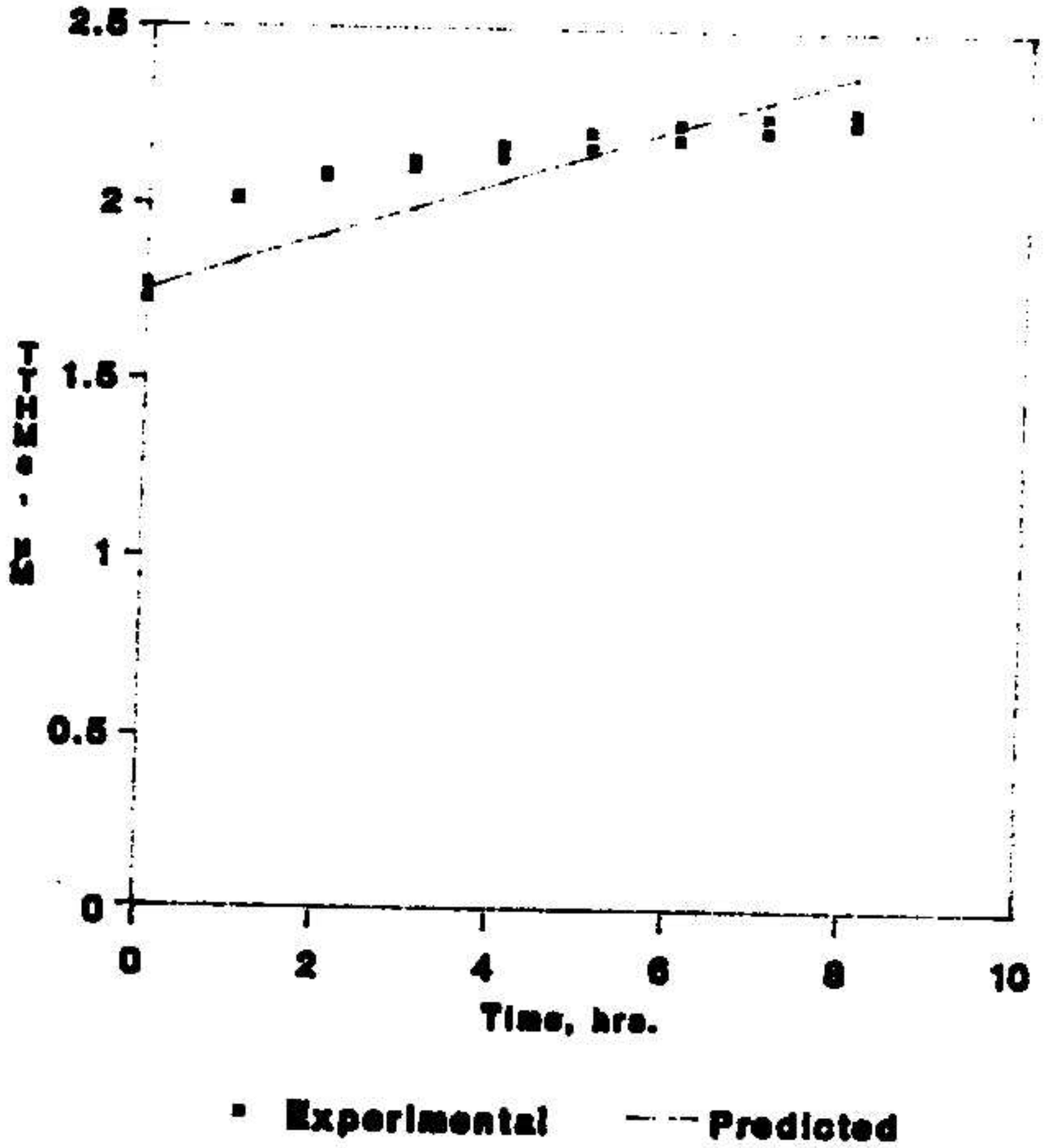

Figure 23: Predicted Short-Term Behavior of [TTHMs] for Natural Water at 25 C

Tables 11 and 12 present long-range parameter estimates at 5°C, and 25°C, respectively.

Table #11: Long-range parameter estimates for natural water at 5° C

Parameter	Best Estimate	95% confidence interval
b_1	0.4458	0.3350 - 0.5367
b_2	0.00176	0.00010 - 0.00342
b_3	0.00329	0.00220 - 0.00439

Table #12: Long-range parameter estimates for natural water at 25° C

Parameter	Best Estimate	95% confidence interval
b_1	4.1046	3.5992 - 4.6083
b_2	0.00960	0.00581 - 0.01340
b_3	0.0	-0.001 - 0.001

Figures 24 and 25 show the predicted long-term behavior of TTHMs at 5°C, and 25°C respectively.

Arrhenius-type relationships were developed for the models parameters. Activation energies and frequency factors were calculated. Table 13 presents the results obtained for the short-term model. Table 14 presents the same results for the long-term model.

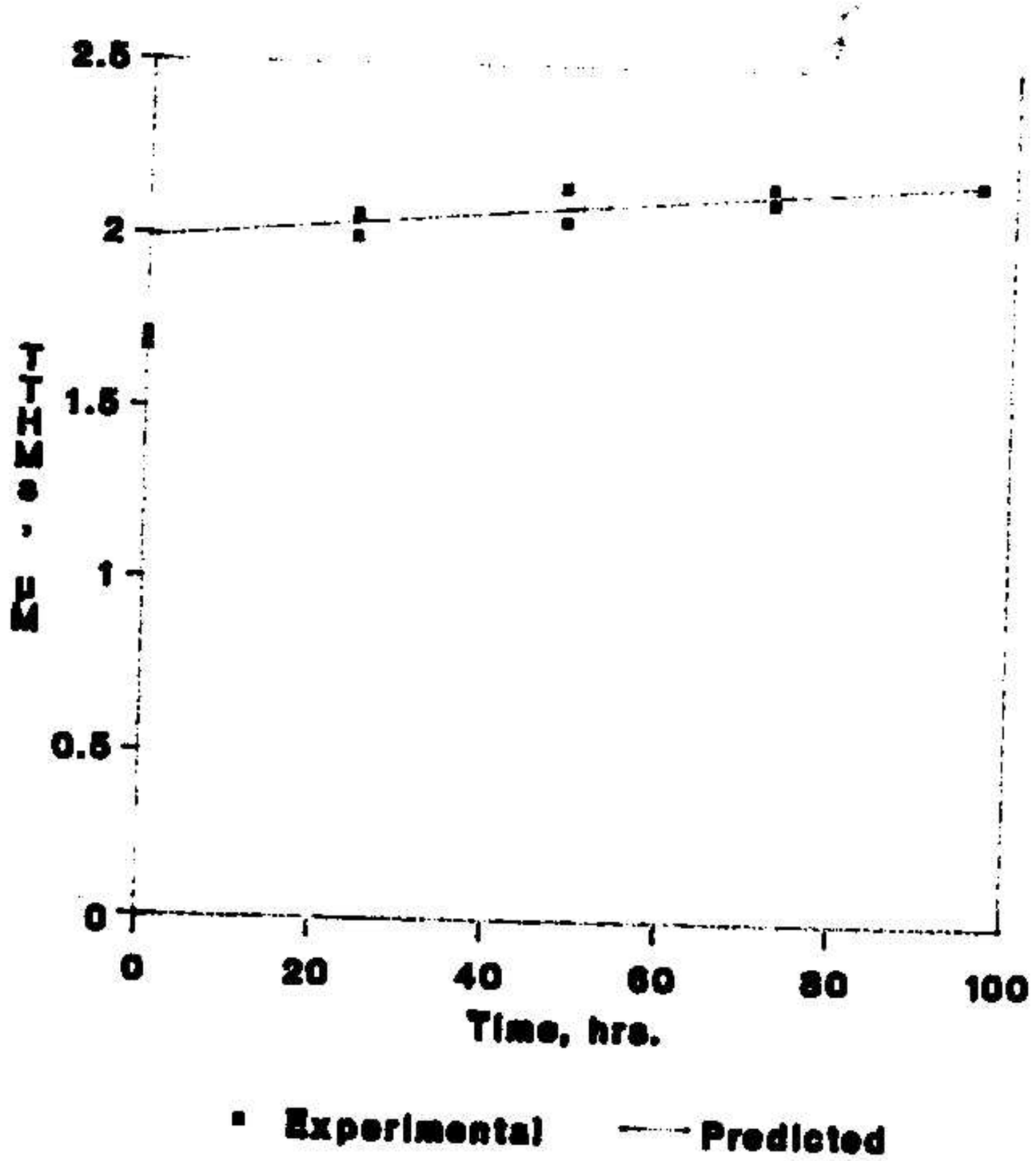

Figure 24: Predicted Long-Term Behavior of [TTHMs] for Natural Water at 5 C

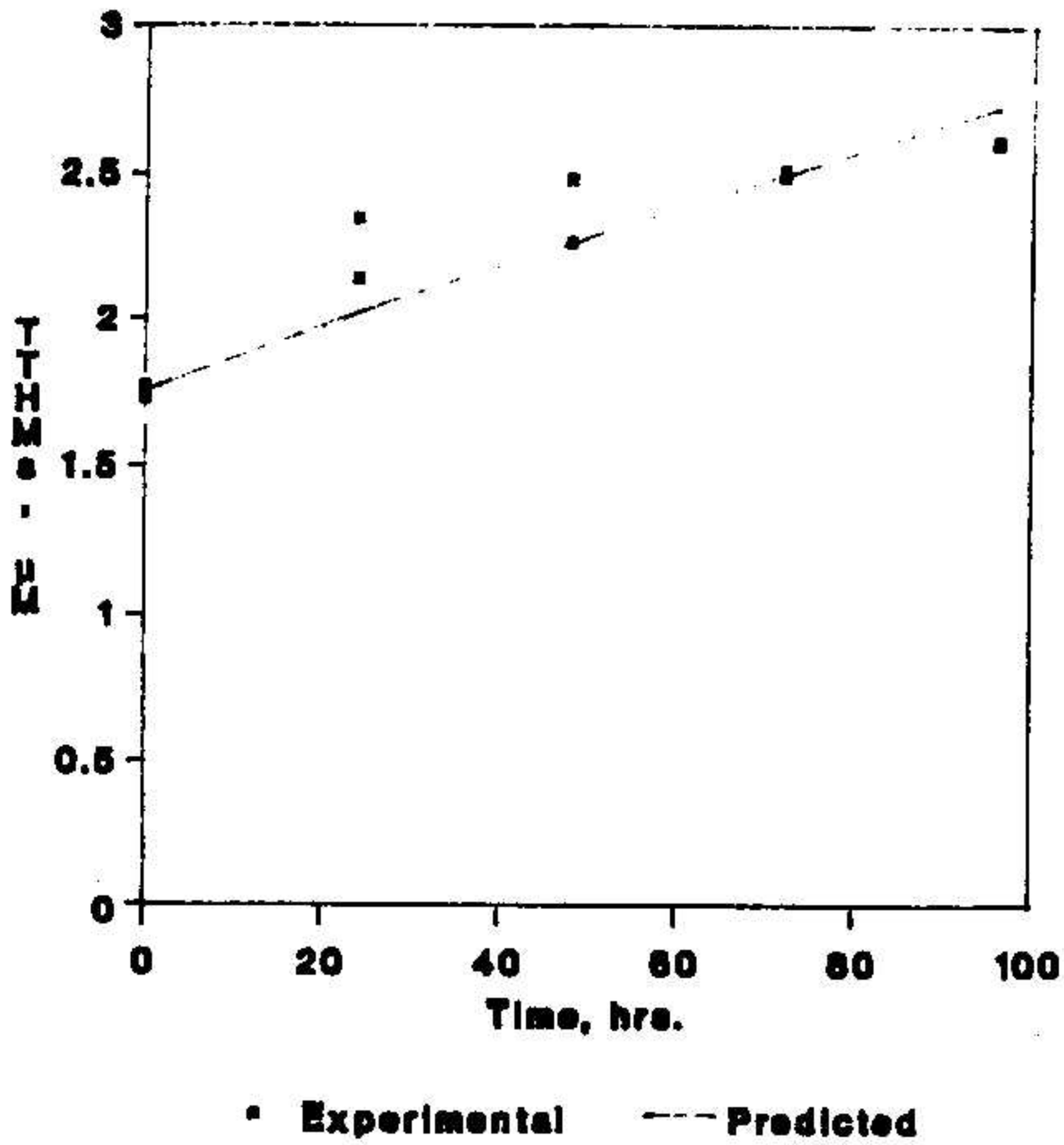

Figure 25: Predicted Long-Term Behavior of [TTHMs] for Natural Water at 25 C

Table #13: Arrhenius parameters for short-term kinetic model with natural water

Parameter	Frequency factor*	Activation energy, E/R, Kelvin
b_1	7.89×10^{11}	7550
b_2	1130.4	2865

* Units: $b_1(hr^{-1})$, $b_2(\mu M/hr)$

Table #14: Arrhenius parameters for long-term kinetic model with natural water

Parameter	Frequency factor	Activation energy, E/R, Kelvin
b_1	1.097×10^{14}	9212
b_2	1.745×10^{8}	7039

C. Discussion of Results

The kinetic data obtained in this work is, generally, highly reliable and reproducible. This is particularly true for the natural water data at low and intermediate temperatures. On the other hand, the data for synthetic water were obtained first, and they are not as reliable as those for natural water. Therefore, they are of limited value,

particularly at high temperatures. For the natural water, the data obtained at 45°C were found to be unreliable. Apparently some of the THMs were volatized at this temperature, in spite of our efforts to try to minimize volatilization losses.

Good data were obtained for both the synthetic and natural waters at 5°C. Therefore, after kinetic modelling, their behavior could be compared. It was found that both types of water could be appropriately described with the same kinetic model. However, the values of the parameters estimates were significantly different for the two waters, particularly those for the long-term models. It should be remembered that the synthetic water was prepared using a commercial source of humic acid, which is probably different from the humic and fulvic acids naturally present in local waters. This result points out again to the site-specific nature of THMs formation.

The nonlinear regression model used proved to be an excellent tool for kinetic modelling of experimental data. Because of its numerical integration scheme, it allows the researcher to test different rate models of varying complexity.

Although the kinetic models developed in this work are only of preliminary nature, they describe the experimental data with good precision as shown in Figure 26.

The reason for viewing our modelling efforts as preliminary is that they are based only in TTHMs formation. Enough data were collected during the course of this work to allow for a detailed kinetic study for each of the four species that make up total trihalomethanes. In such a model, the contribution of bromide could be explicitly incorporated, something that is missing in our model. We suspect that, in our model, the bromide effect is incorporated indirectly in the constant term, b_2, in the TTHMs rate of formation equation.

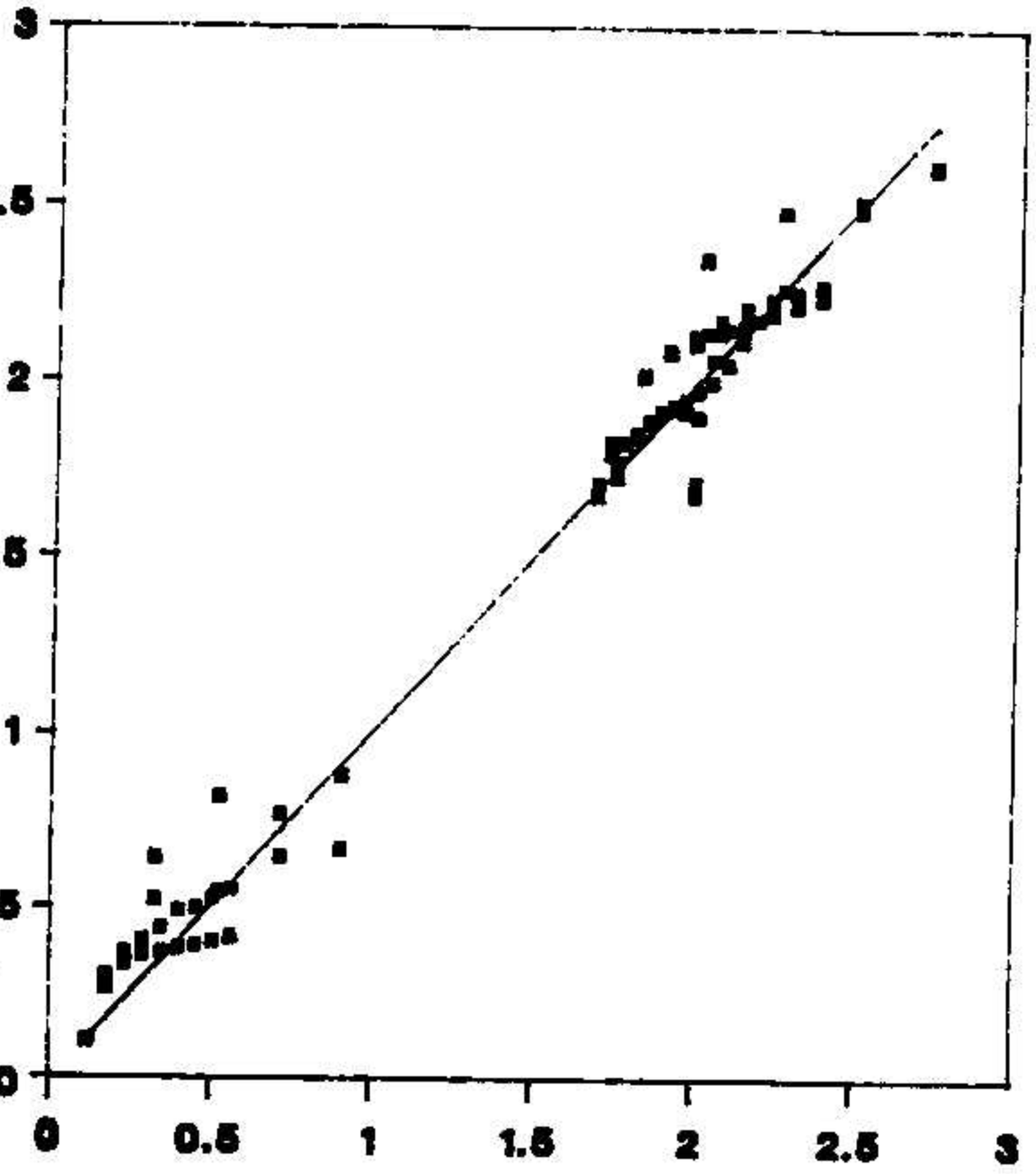

Figure 26: Measured versus Predicted TTHMs Concentrations

CHAPTER 5

Conclusions and Recommendations

The following conclusions and recommendations follow from this work:

a. The kinetic data obtained during chlorination of synthetic and natural waters are, generally, highly reliable and reproducible.

b. During chlorination at 5°C, the kinetic behavior of THMs formation in synthetic water was found to be significantly different from that observed in local natural waters at the same temperature, particularly at long-term.

c. After exhaustive statistical testing, a kinetic model was found to appropriately describe the formation of TTHMs during chlorination of natural waters at 5°C and 25°C. That model was divided into a short-term (less than 8 hours) one, and a long-term model (24-96 hrs).

d. Model parameters were found to follow an Arrhenius-type relationship with temperature. Corresponding activation energies and frequency factors were estimated.

e. The nonlinear regression model used to analyze the data was found to be an excellent tool for reaction kinetics studies.

f. A more intensive modelling effort should be undertaken using the data obtained in this work. Reaction kinetics for each of the four trihalomethanes, individually, should be studied.

CHAPTER 6

BIBLIOGRAPHY

Aokl T. and M. Munemori,1983. Continuos Flow Determination of Free Chlorine in Water. Anal. Chem. 55(1):209.

Bellar T.A., J.J. Lichtenberg and R.C. Kroner,1974. The Occurence of Organohalides in Chlorinated Drinking Water. J AWWA.,66(12):703.

Carpenter J. and D. Macalady,1978. Chemistry of Halogens in Sea Water. Water Chlorination: Chemistry, Environmental Impact and Health Effects. Ann Arbor, MI, Ann Arbor Science Publishers, Inc.Vol.1 pp.106-180.

Constantinides,A., 1987. Applied Numerical Methods with Personal Computers.Mc. Graw Hill Publishing Co., New York, N.Y.

Corwin J.F.,1970. Organic Matter in Natural Waters.D.W. Hood, Ed. Inst. of Marine Sci. Occasional Publ. no.1, Univ. of Alaska, College, Aka.

De Leer E.W.B., J.S. Sinninghe Diamsté and L. De Galan,1984. Formation of Aryl-Chlorinated Aromatic Acids and Precursors for Chloroform in Chlorination of Humic Acid. Water Chlorination: Chemistry, Environmental Impact and Health Effects. Ann Arbor, MI, Ann Arbor Science Publishers, Inc.Vol.5 pp:843-857.

Dore M., N. Merlet, J. De Laat and J. Goichon,1982. Reactivity of Halogens with Aqueous Micropollutants: A Mechamism for the Formation of Trihalomethanes. J AWWA 74(2):103.

Dragunov S,1961. Soil Organic Matter. M.M. Kononova, Ed., Pergamon, New York, N.Y.

Dressman R.C., A.A. Stevens, J. Fair and B. Smith,1979. Determination of Trihalomethanes in Drinking Waters. J AWWA 71(7):392.

Edwaltz J.K., W.C.Becker, and K.L.Wattier,1985.Surrogate Parameters for Monitoring Organic Matter and THM Precursors. J AWWA 77(4):122.

Federal Register, November 29,1979.44,no.231,68624-68707; March 11,1980.45,no.49,15542-15547

Jolley R.L.,1981. Treatment Techniques for Controlling Trihalomethanes in Drinking Water. Water Chlorination: Chemistry, Environmental Impact and Health Effects. Ann Arbor, MI, Ann Arbor Science Publishers, Inc. Vol.2 pp:1-21

Kavanaugh M.,1980. Empirical Kinetic Model of Trihalomethane Formation: Application to Meet the Proposed THM Standard. J AWWA 80(10):578.

Kleopfer R.,1976. Identification and Analysis of Organic Pollutants in Water. Analysis of Drinking Water for Organic Compounds, L.Leith, Ed. Ann Arbor, MI, Ann Arbor Science Publishers Inc. pp:399-450.

Lange A. and E. Kawczynski,1978. Experiences at Contra Costa County Water District. Presented at Calif.-Nevada Sct. of AWWA, Water Treatment Forum no. VII.

Moore G.S.,1979. A Statistical Model for Predicting Chloroform Levels in Chlorinated Surface Water Supplies. J AWWA 71(1):37.

Morris J.C.,1975. Formation of Halogenated Organics by Chlorination of Water Supplies.A Review,NTIS PB-24511 Ofce. Res. Develop.USEPA, Washington D.C.

Morris J. and B. Baum,1978. Precursors and Mechanisms of Haloform Formation in the Chlorination of Water Supplies. in Drinking Water. Water Chlorination: Chemistry, Environmental Impact and Health Effects. Ann Arbor, MI, Ann Arbor Science Publishers, Inc. Vol. 2 pp: 29-48.

Parra P., E. Martínez, C. Suñol, F. Artigas, J.M. Tusell, E. Gelpi and J. Albaigés,1986. Analysis, Accumulation and Central Effects of Trihalomethanes.I.Bromoform. Toxicol. and Environ. Chem.,24(1):79.

Rook J.J.,1974. Formation of Haloforms During Chlorination of Natural Waters. J. Wtr. Trtmt. Exam. 23(2):234.

Rook J.J.,1976. Haloforms in Drinking Water. J AWWA 68(3):168.

Rook J.J.,1977. Chlorination Reactions of Fulvic Acids in Natural Waters. Envir. Sci. and Technol. 11(5):478.

Schnitzer N. and S.U. Khan,1972. Humic Substances in the Environment. Marcel Deckker, New York, N.Y.

Stevens A.A.,1979. Formation of Non-Polar Organo-Chloro Compounds as By Products of Chlorination. Proceedings-Oxidation Techniques in Drinking Water Treatment. September 11-13,1978, Karlsruhe, F.R.G., EPA-570/9-79020, USEPA, Washington, D.C. pp.145-160, NTIS accession no. PB 301313/AS.

Stevens A.A.,1976. Chlorination of Organics in Drinking Water. J AWWA 68(11):615.

Stevens A.A. and J.M. Symons,1978. Formation and Measurement of Trihalomethanes in Drinking Water. Proceedings-Control of Organic Chemical Contaminants in Drinking Water. USEPA, Washington, D.C.

Suffet I.H., L. Brenner and B. Silver,1976. Identification of 1,1,1-Trichloroacetone in two Drinking Waters. Envir. Sci. Technol. 10(3):1273.

Trussell R.R. and M.D. Umphres,1978. The formation of Trihalomethanes. J AWWA 70(11):604.

United States Environmental Protection Agency,1979. The Analysis of Trihalomethanes in Finished Waters by Purge and Trap Method.Method 501.1,USEPA, EMSL, Cincinnati, OH.

Varma M.M., R.C. Chawla, A. Barlam and H.M. Katz, 1981. Kinetics of Trihalomethane Formation in Lyophilized Potomac Water. The American Institute of Chemical Engineers. 77(209):220.

Young J.S. and P. Singer,1979. Chloroform Formation in Public Water Supplies: A Case Study. J AWWA 71(2):87.

APPENDIX A

ANALYTICAL TECHNIQUES, PROCEDURES AND DETAILS

A.1 Analysis of Trihalomethanes (THMs) by the Purge and Trap Method:

This analysis was performed by using method 502.1 prepared by the staff of research and development of EPA (EPA # 600/4-81-059). This method is applicable in the determination of four trihalomethanes: chloroform, dichlorobromomethane, dibromochloromethane, and bromoform in finished drinking water, raw source water, or drinking water in any stage of treatment. The concentration of these four compounds is totalled to determine total trihalomethanes (TTHM). The method can be used over a concentration range of approximately 0.5 to 1500 ppb.

A.1.1 Procedure

Trihalomethanes are extracted by an inert gas(He) which is bubbled through the aqueous sample. The THMs, along with other organic constituents which exhibit low water solubility and a vapor pressure significantly greater than water, are efficiently transferred from the aqueous phase to the gaseous phase. These compounds are swept from the purging device and are trapped in a short column containing a suitable adsorbent. After a predetermined period of time, the trapped

components are thermally desorbed and backflushed onto the head of a gas chromatographic column and separated onto programmed conditions:

Initial temperature: 45°C

Time: 3 min

Rate: 8°C/min

Final temperature: 220°C

Injector temperature: 220°C

Detector temperature: 250°C

Measurement is accomplished with a halogen specific detector such as electrolytic conductivity (700A PE Hall Detector).

A.1.2 Calculations:

1. Locate each trihalomethane in the sample chromatogram.
2. Calculate the concentration of the samples by comparing the peak height of the samples to the standard peak height . Round off the data to the nearest ug/L or two significant figures.

$\mu g/L = [(PHS)/(PHSTD)](CSTD)$

where:

PHS = peak height sample

PHSTD = peak height standard

CSTD = concentration standard, μg/L

3. Calculate the total trihalomethane concentration (TTHM) by summing the 4 individual trihalomethane concentrations in μg/L.

$$TTHM = [CHCl_3] + [CHBrCl_2] + [CHBr_2Cl] + [CHBr_3]$$

A.2 Determination of Humic Acids

A.2.1 Spectrophotometric Procedure:

1. Preparation of Humic Acids Standards: Stock Humic Acids Solution, 100 ppm: 0.1000 g Humic Acid, sodium salt diluted to 1000 ml with distilled water.
2. Humic Acid Standards: Five standards: 3,6,9,12 and 15 ppm were prepared by diluting 3.00, 6.00, 9.00, 12.00, and 15.00 ml stock humic acids solution to 100.00 ml distilled water.
3. Treatment of Standards and Samples: UV absorbance of standard and sample solutions was

measured at 254nm using a 1-cm quartz cell and the humic acids values were determined from a calibration curve for Humic Acids concentration in ppm against absorbance.

In the table A.1 is presented the data for the calibration curve (figure A.1). From the figure or through a regression model the concentration of the sample can be obtained (see Table A.2).

Table A.1: Data of the Calibration Curve for Humic Acids

Standard Concentration (ppm), X_h	Absorbance Measurement (254 nm), Y_h
3.0	0.088
6.0	0.178
9.0	0.268
12.0	0.354
15.0	0.444

Regression Model: $Y_h = 0.0296X_h$
Coefficient of correlation: 0.9999

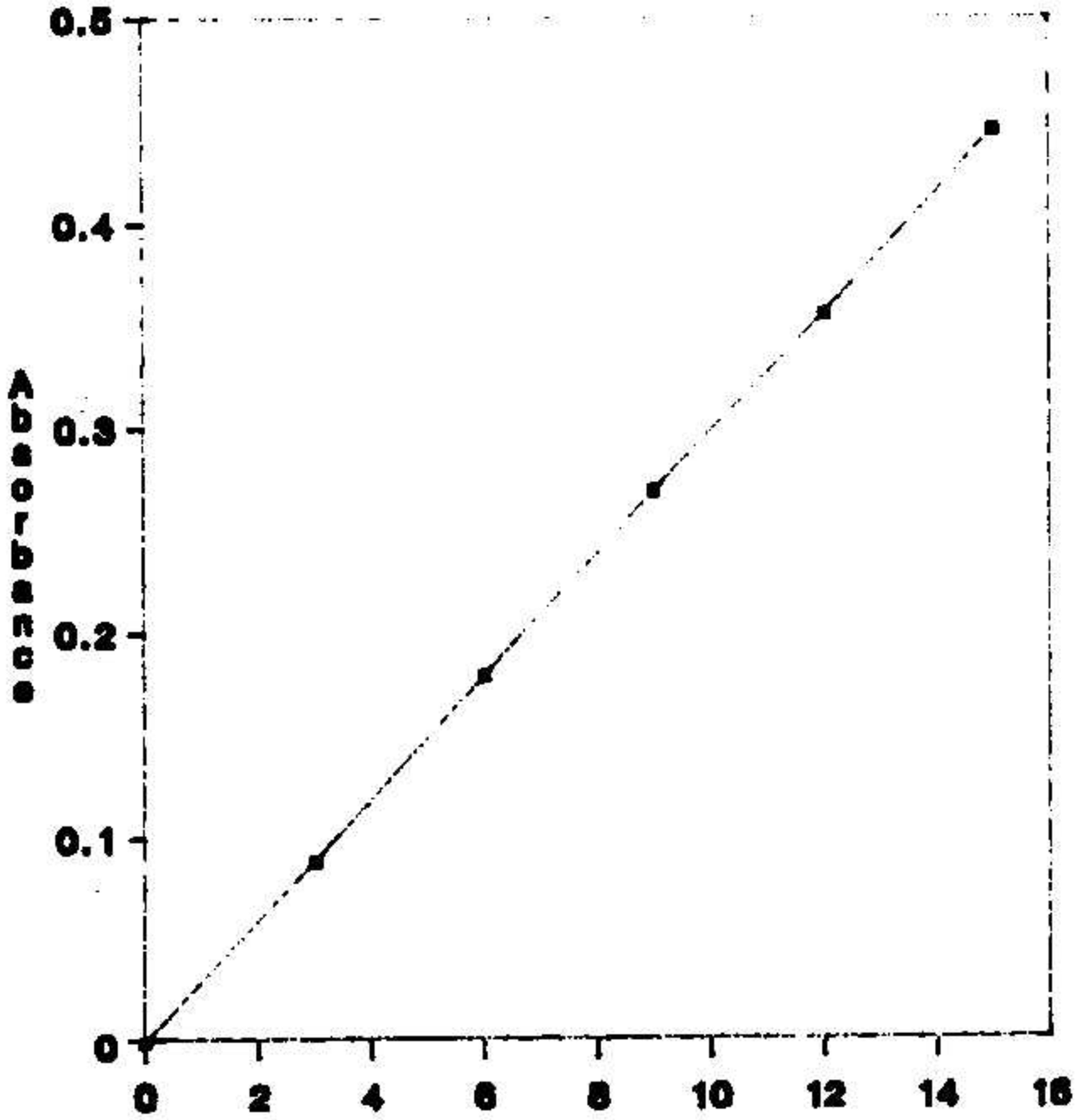

Figure A.1: Calibration Curve for Humic Acids

Table A.2: Humic Acids Concentration for Samples

Sample	Absorbance (254 nm)	Concentration (ppm)
Synthetic Water	0.204	6.89
Natural Water	0.091	3.07 *

* This is an estimated value because the humic acids in natural water may exhibit a different concentration-absorbance relation.

A.2.2 Non-Volatile Total Organic Carbon Analysis Procedure

1. Preparation of standard carbon dioxide curve: The following procedure was used in making the standard solution: take 2.126 grams of potassium biphthalate (KHP) and dilute to 1000 ml with distilled water in a volumetric flask. Take 16,12,10,6,4,1 ml of the 1000 ppm solution and dilute volumetrically to a solution which has organic carbon concentration as KHP of 16,12,10,6,4,1 ppm.
2. Calibration curve (Figure A.2) was prepared using the information of Table A.3 in which measurements of standard solutions concentrations are presented.

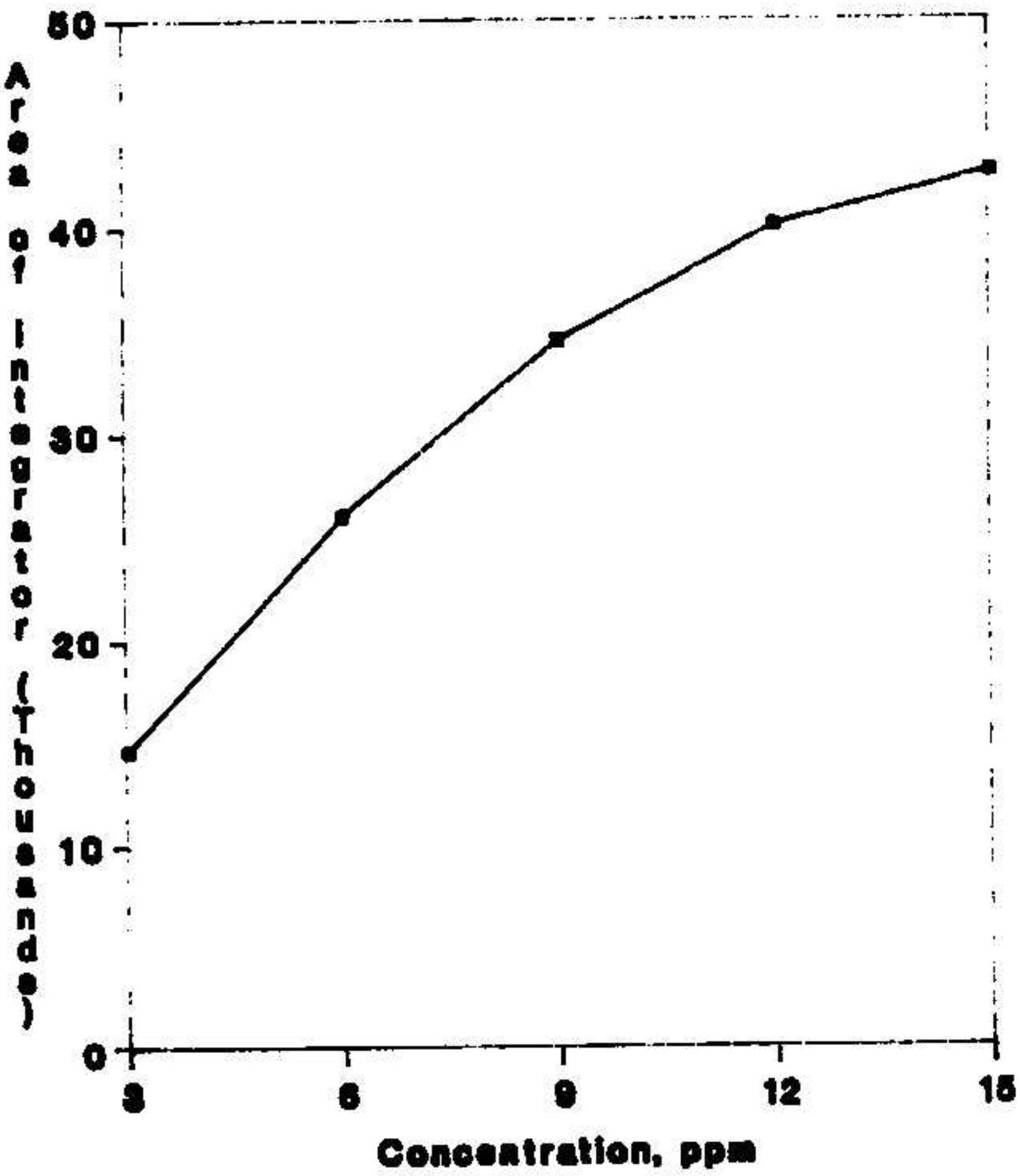

Figure A.2: Calibration Curve for NVTOC

Table A.3: Data of Calibration Curve for NVTOC

Standard Concentration X_n (ppm)	Integrator Area Y_n	Integrator Area Corrected $Y_{n,c}$
1	16502	17777
4	42063	41297
6	58180	55661
10	80034	81230
12	90415	92436
16	112894	111687

The regression model for NVTOC determination is presented on Table A.4.

Table A.4: Regression Model for NVTOC Determination

Parameter	Calibration Curve
A	9409.933
B	8498.263
C	-131.621

Coefficient Correlation: 0.9957
Regression Model: $Y_n = A + B*X_n + C*X_n^2$

3. Sample Concentration Measurement: From results Table A.4 and Figure A.2 was obtained the measured concentration for each sample. Table A.5 presents the results.

Table A.5: Concentration of NVTOC

Sample*	Integrator Area	Concentration (ppm)
3	15709	0.75
6	25916	2.01
9	34832	3.15
12	38169	3.58
15	43607	4.31
Blank	4517	-0.57

* These samples are the standard solutions used for calibration curve of Humic Acids Determination by Spectroscopic Method. Concentration of Humic Acid is given in ppm.

A relationship between Integrator Area (from Total Carbon Analyzer) and humic acids concentration (in ppm) is represented in figure A.3.

From figure A.3 or regression model on table A.7 value for a 7 ppm solution was determined and corresponds to the value of 29096. With this value and graph A.3 or regression

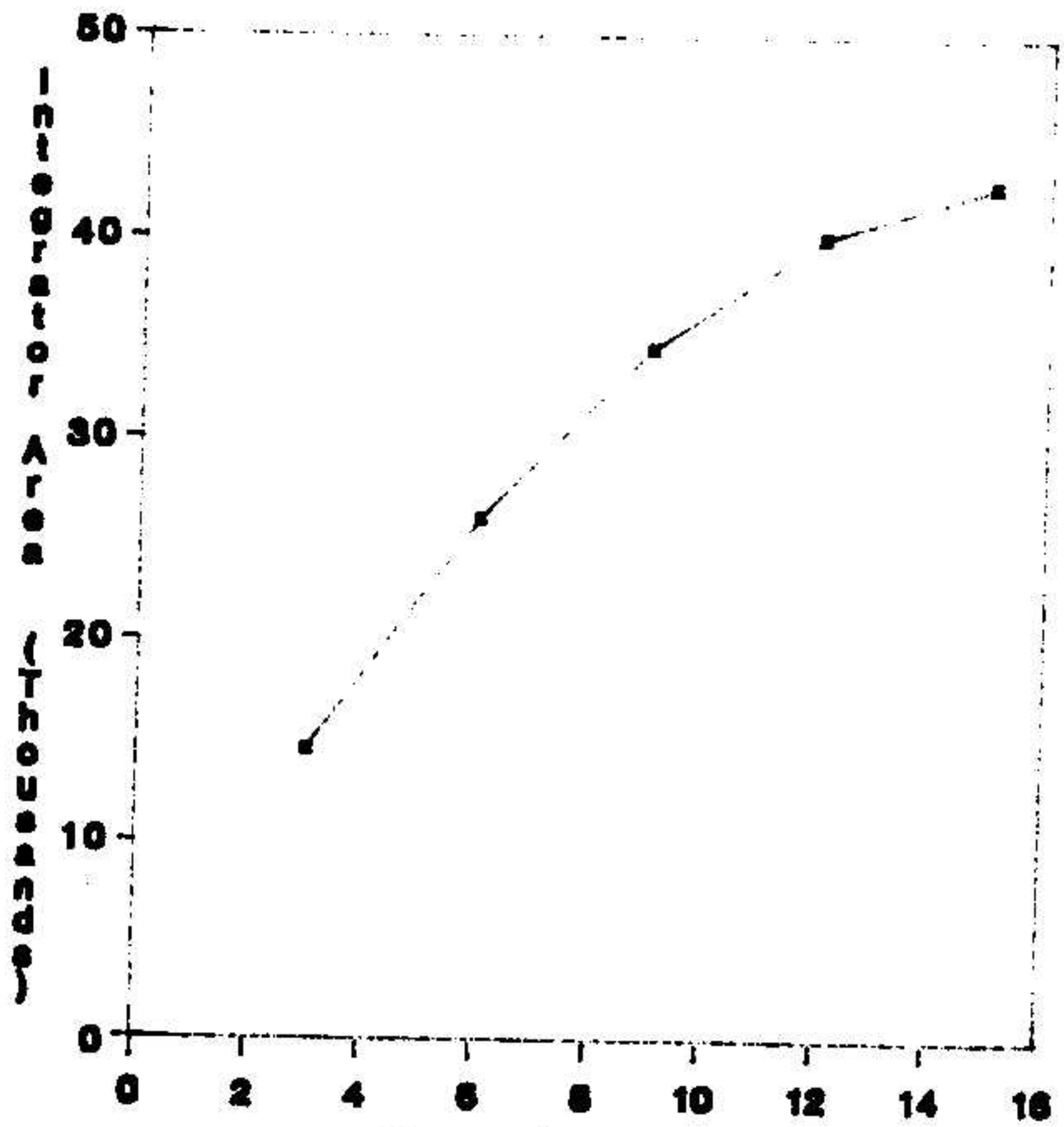

Figure A.3: Integrator Area versus Humic Acids

model on table A.7, NVTOC concentration was estimated as 2.406 ppm.

Table A.6: NVTOC Data for Regression Model

Sample	Integrator Area	Integrator Area Corrected
3	15709	14442
6	25916	25925
9	34832	34451
12	38169	40018
15	43607	42627

Table A.7: Integrator Area Against Humic Acids Curve

Parameter	Curve
a	5306.293
b	-164.341

Coefficient Correlation: 0.9989
Regression Model: $Y_I = aX_I + bX_I^2$

A.3 Bromide Concentration Measurement

A.3.1 Spectrophotometric Method

This analysis was performed by using technique 405 described on Standard Methods for the Examination of Water and Wastewater, 16th Edition, pp.278-279. The procedure is:

1. The following reagents were prepared: Acetate buffer solution with a final pH of 4.6, phenol red indicator solution, chloramine-T solution, sodium thiosulfate, 2M.
2. Preparation of Bromide Standards:
   a. Stock Bromide Solution: 744.6 mg anhydrous KBr were dissolved in distilled water and make up to 1000 ml.
   b. Standard Bromide Solution: 10.00 ml stock bromide solution was diluted to 1000 ml with distilled water.
   c. Six standards, 0,0.20,0.40,0.60,0.80 and 1.00 mg Br^-/L, by diluting 0.0,2.00,4.00,6.00,8.00, and 10.00 ml standard bromide solution to 50.00 ml with distilled water.
3. Treatment of Standards and Samples:

To 50.00 ml sample or standard, 2 ml Buffer solution, 2 ml phenol red solution, and 0.5 ml chloramine-T solution were added and mixed thoroughly after each addition. Twenty minutes after adding chloramine-T, it was dechlorinated by adding 0.5 ml thiosulfate solution. The sample were read against a reagent blank in a spectrophotometer at 590 nm.

The Bromide values were determined from a calibration curve of mg Br^-/L against absorbance. In the Table A.8 are presented the data for the calibration curve (Fig. A.4). From this figure or through a regression model the sample concentration can be obtained (see Table A.9).

Table A.8: Data of the Calibration Curve for Bromide

Standard Concentration (ppm), X_b	Absorbance Measurement (590nm), Y_b
0.0	0.000
0.2	0.040
0.4	0.082
0.6	0.120
0.8	0.166
1.0	0.203

Regression Model: $Y_b = 0.204\ X_b - 3.81\ X\ 10^{-4}$
Coefficient of correlation: 0.9997

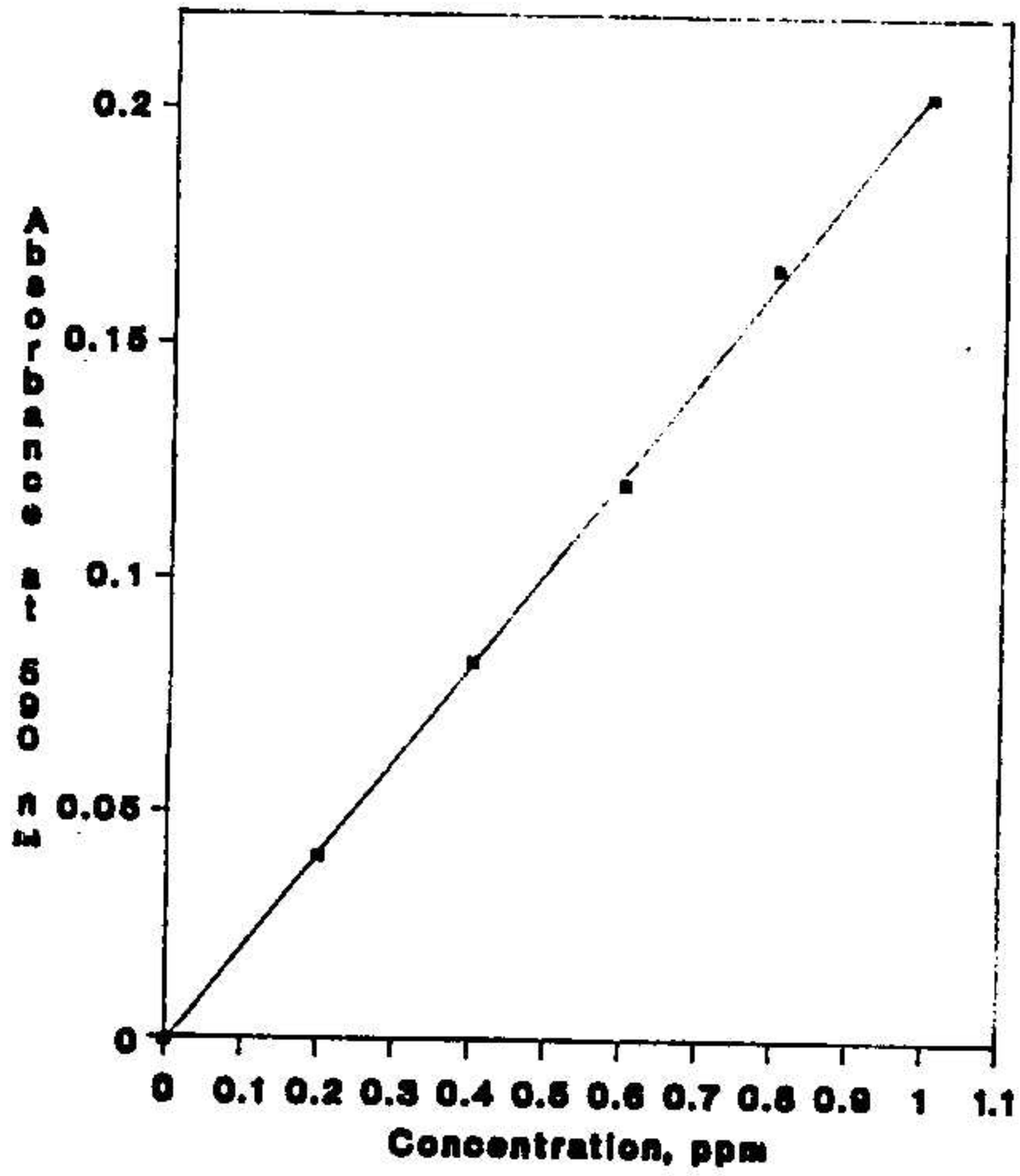

Figure A.4:Calibration Curve for Bromide

Table A.9: Bromide Concentration for Samples

Sample	Absorbance (590nm)	Concentration (ppm)
Synthetic Water	0.102	0.50
Natural Water	0.039	0.19

A.3.2 Bromide Ion Selective Electrode Procedure:

1. Preparation of Standards:

   a. From a commercial Bromide stock solution,1000 ppm conc., a Bromide standard solution,10 ppm was prepared.

   b. Five standards, 0.1,0.3,0.5,0.7 and 1.0 mg Br-/L were prepared by diluting 1.00, 3.00, 5.00, 7.00 and 10.00 ml of standard bromide solution with distilled water up to a 100.00 ml volume.

2. Instrumental Calibration: A concentration multi-point(5 points) standardization was performed as

follows:

a. After entering multi-point calibration program, inmerse the electrodes in a standard solution(100 ml of standard and 2 ml of commercial Bromide Ion Strength Adjustor Solution (ISA).

b. Enter the concentration of the standard and the mV reading once it has stabilized.

c. Do the same for the remaining four solutions.

d. Enter efficiency and slope values if acceptable (eff= -1.00 ± .08, slope= -59 ± 4 mV)

e. Recalibrate every 1 to 2 hours.

3. Treatment of Samples

a. Place a 100 ml sample in a 150 ml beaker

b. Add 2 ml ISA solution

c. Stir the sample during measurement

A.4 Total Residual Chlorine Determination

A.4.1 Iodometric Method

This analysis was performed by using technique 408A described on Standard Methods for the Examination of Water and Wastewater, 16th Edition, pp 298-299. The minimum detectable concentration approximates 1 mg/L. The procedure is as follows:

1. Reagents preparation:

   a. Standard Sodium Thiosulfate, 0.1N was prepared by dissolving 25 g $Na_2S_2O_3.5H_2O$ in 1L freshly boiled distilled water and standardized against potassium dichromate after 3 weeks storage.

   b. Standard Sodium Thiosulfate titrant,0.0025 N was prepared by diluting the aged 0.1N solution.

   c. Starch indicator solution was prepared using soluble commercial starch.

   d. Potassium Dichromate Standard Solution, 0.1000N was prepared dissolving 4.904 g (anhydrous of primary standard quality) in distilled water and diluting to 1000 ml.

2. Preparation for Titration:

A sample volume of 100 ml was collected. 5 ml acetic acid were placed in a 250 ml-erlenmeyer, 1 g potassium iodide was added and then the sample was poured and mixed with a stirring rod. Thiosulfate titrant was added from a buret until the yellow color of the liberated iodine almost disappears. Then 1 ml starch solution was added and titrated until blue color disappears.

3. Calculations for determining total available residual chlorine:

To determine total available residual chlorine in water sample:

$$\text{mg Cl as } Cl_2/L = A \times N \times 35450 / \text{ml sample}$$

where:

A = ml titration sample

N = normality of thiosulfate titrant

A.4.2 Total Residual Chlorine Electrode

This electrode method is EPA approved for drinking water and wastewater. The electrode has a slope of about +29 mV per decade change in concentration. The procedure is (as

follows):

A.2.1 Checking Electrode Slope:

Prepare chlorine water(approximately 100 ppm Cl_2) by diluting 1 ml hypochlorite solution to 500 ml with distilled water and follow the procedure using 407A specific ion meter.

1. Place 100 ml distilled water in a 150 ml beaker. Add 1 ml iodide reagent and 1 ml acid reagent.
2. Add 1 ml chlorine water to beaker and stir gently for 2 min.
3. Turn the meter function switch to X^{++}. Set the slope indicator dial to 100% and temperature compensator to 20°C.
4. Place electrode in solution. Turn calibration control until the needle points "1" on the red logarithmic scale.
5. Add 10 ml chlorine water to the beaker and stir for 2 min. Then the needle should point to "10". If necessary, turn the temperature compensator knob to set needle to "10".

A.2.2 Procedure for samples between 0.2 and 20 ppm:

1. Standard solution(1 ppm) Preparation:

   a. Pipet 1 ml residual chlorine standard(100 ppm as Cl_2), 1 ml iodide reagent, and 1 ml acid reagent into a 150 ml beaker. Use only 1 ml of each solution, and do not add water. Swirl for two minutes to allow complete reaction.
   b. Add 99 ml of distilled water and mix thoroughly.
   c. Store this 1 ppm standardizing solution in the storage bottle for calibration. Prepare solution daily.

2. Measurement using 407A meter:

   a. Turn the function switch to X**. Set the slope indicator dial to 100% slope. Turn the temperature compensator knob to 20°C.
   b. Place the electrode in the 1 ppm standardizing solution so that the reference element is submerged.

c. Turn the calibration control knob until the needle points to "1".

d. Remove the electrode from the solution. Blot dry.

e. Transfer a 100 ml sample to a 150 ml beaker. Add 1 ml each of iodide reagent and acid reagent. Mix and let stand for 2 min.

f. Place the electrode in sample so that the reference element is submerged. The reading on the red logarithmic scale is equal to the sample total residual chlorine concentration.

g. Recalibrate every 2 hours.

A.5 pH Measurement:

This analysis was performed by using a Sargent-Welch (Model LS) pH meter. The meter was adjusted by a 2 point calibration using buffers pH=4 and pH=10. The term pH is convenient to use to express hydrogen ion concentrations. The term pH is defined in such a way as to convert a negative power of ten into a small positive number: is the negative logarithm of the hydrogen ion concentration,

$$pH = - \log (H_3O^+) = \log 1/(H_3O^+) .$$

Table A.10 presents sample initial pH conditions.

Table A.10: Sample pH Initial Conditions

Sample	pH	Adjustment*
Synthetic Water	7.3	Yes
Natural Water	7.6	No

* Adjustment with 0.025M H_2SO_4 solution

APPENDIX B:
EXPERIMENTAL DATA FOR SYNTHETIC WATER

Table B.1: Experimental Data for Synthetic Water, T = 5°C.

Sample Run	Time (hrs)	UV	pH	Br^- (ppb)	Cl_2 (ppb)	TTHMs (ppm)
0	0	0.207	7.3	0.500	15.00	14.7
1	1	0.177	7.3	0.150	11.61	48.8
1	1	0.181	7.3	0.070	12.75	43.4
2	2	0.171	7.3	0.120	11.61	60.8
2	2	0.178	7.4	0.060	12.50	54.5
3	4	0.168	7.3	0.100	11.25	71.3
3	4	0.177	7.4	0.060	12.08	61.5
4	8	0.168	7.3	0.090	11.08	91.2
4	8	0.166	7.4	0.060	11.88	68.4
5	24	0.155	7.4	0.080	10.51	104.3
5	24	0.156	7.2	0.050	11.17	84.7
6	48	0.139	7.2	0.070	9.88	133.1
6	48	0.155	7.3	0.040	10.79	88.6
7	72	0.146	7.5	0.050	9.84	123.0
7	72	0.153	7.6	0.040	10.37	104.2
8	96	0.147	7.4	0.001	9.44	143.6
8	96	0.143	7.4	0.056	10.02	108.3

Table B.2 : THMs Data for Synthetic Water, T = 5°C.

Time (hrs)	$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)	$CHClBr_2$ (ppb)	$CHBr_3$ (ppb)	TTHMs (ppb)	TTHMs (μM)
0	11.7	3.0	0.0	0.0	14.7	0.116
1	14.4	14.4	16.0	4.0	48.8	0.301
1	11.9	13.2	14.5	3.8	43.4	0.265
2	15.9	18.3	21.1	5.5	60.8	0.368
2	14.9	17.5	17.7	4.4	54.5	0.334
3	20.0	21.8	23.7	5.8	71.3	0.437
3	14.8	21.0	20.8	4.9	61.5	0.371
4	22.4	29.0	32.8	7.0	91.2	0.550
4	15.9	23.9	23.7	4.9	68.4	0.412
5	27.4	34.2	35.7	7.0	104.3	0.637
5	21.4	28.9	29.0	5.4	84.7	0.516
6	34.5	44.7	44.5	9.4	133.1	0.813
6	21.6	32.2	29.3	5.5	88.6	0.540
7	34.5	41.9	37.7	8.9	123.0	0.761
7	27.5	36.4	33.0	7.3	104.2	0.640
8	35.1	51.4	46.9	10.2	143.6	0.873
8	27.3	38.7	35.0	7.3	108.3	0.662

Note:

$$\text{TTHM (in ppm)} = [CHCl_3] + [CHBrCl_2] + [CHBr_2Cl] + [CHBr_3]$$

$$\text{TTHM (in } \mu\text{M)} = [CHCl_3]/119.378 + [CHBrCl_2]/163.834 + [CHBr_2Cl]/208.290 + [CHBr_3]/252.746$$

Table B.3 : Experimental Data Synthetic Water, T = 25°C.

Sample Run	Time (hrs)	UV	pH	Br^- (ppb)	Cl_2 (ppb)	TTHMs (ppm)
0	0	0.207	7.3	0.500	15.00	14.7
1	1	0.169	7.4	0.060	11.35	102.8
1	1	0.169	7.6	0.060	11.61	92.6
2	2	0.163	7.3	0.060	10.95	107.2
2	2	0.161	7.6	0.053	11.13	109.4
3	4	0.156	7.4	0.070	10.28	126.8
3	4	0.154	7.0	0.055	10.55	123.7
4	8	0.153	7.4	0.050	9.48	134.7
4	8	0.147	7.6	0.079	9.84	132.4
5	24	0.132	7.4	0.060	7.75	112.9
5	24	0.134	7.6	0.060	8.20	112.2
6	48	0.127	7.6	0.050	5.94	54.7
6	48	0.125	7.6	0.055	6.58	67.6
7	72	0.125	7.4	0.005	4.52	26.9
7	72	0.112	7.6	0.035	5.34	28.0
8	96	0.111	7.8	0.050	3.12	19.0
8	96	0.113	7.4	0.053	3.83	18.1

Table B.4 : THMs Data for Synthetic Water, T = 25°C.

Time (hrs)	$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)	$CHClBr_2$ (ppb)	$CHBr_3$ (ppb)	TTHMs (ppb)	TTHMs (μM)
0	11.7	3.0	0.0	0.0	14.7	0.116
1	23.5	33.1	37.9	8.3	102.8	0.614
1	20.1	30.3	34.6	7.6	92.6	0.550
2	25.7	36.0	37.0	8.7	107.3	0.646
2	24.0	36.1	40.3	9.0	109.4	0.650
4	32.2	43.6	41.6	9.4	126.8	0.773
4	28.0	42.4	44.1	9.2	123.7	0.741
8	34.4	47.7	43.4	9.2	134.7	0.824
8	32.3	46.7	44.4	9.0	132.4	0.804
24	36.3	37.9	33.2	5.5	112.9	0.717
24	32.5	39.1	34.2	6.4	112.2	0.700
48	22.7	18.4	12.1	1.5	54.7	0.366
48	23.6	23.5	18.2	2.3	67.6	0.438
72	13.2	8.1	5.6	0.0	26.9	0.187
72	12.5	9.5	6.0	0.0	28.0	0.192
96	12.0	4.8	2.2	0.0	19.0	0.140
96	11.8	4.5	1.8	0.0	18.1	0.135

Note:

$$\text{TTHM (in ppm)} = [CHCl_3] + [CHBrCl_2] + [CHBr_2Cl] + [CHBr_3]$$

$$\text{TTHM (in } \mu\text{M)} = [CHCl_3]/119.378 + [CHBrCl_2]/163.834 + [CHBr_2Cl]/208.290 + [CHBr_3]/252.746$$

Table B.5 : Experimental Data Synthetic Water, T = 45°C.

Sample Run	Time (hrs)	UV	pH	Br^- (ppb)	Cl_2 (ppb)	TTHMs (ppm)
0	0	0.207	7.3	0.500	15.00	14.7
1	1	0.156	7.3	0.150	9.44	172.0
1	1	0.154	7.6	0.080	10.34	201.4
2	2	0.147	7.2	0.110	8.86	209.8
2	2	0.143	7.4	0.080	9.71	199.4
3	4	0.140	7.1	0.110	8.31	204.2
3	4	0.137	7.5	0.070	9.11	231.5
4	8	0.134	7.2	0.170	6.96	153.4
4	8	0.131	7.4	0.064	7.98	182.2
5	24	0.123	7.4	0.060	4.12	64.9
5	24	0.117	7.3	0.045	5.56	89.7
6	48	0.115	7.7	0.050	1.75	19.8
6	48	0.107	7.6	0.060	3.24	38.6
7	72	0.109	7.5	0.050	0.29	6.1
7	72	0.100	7.1	0.043	1.42	12.5
8	96	0.111	8.0	0.110	0.00	0.0
8	96	0.102	7.6	0.065	0.80	46.5

Table B.6 : THMs Data for Synthetic Water, T = 45°C.

Time (hrs)	$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)	$CHClBr_2$ (ppb)	$CHBr_3$ (ppb)	TTHMs (ppb)	TTHMs (μM)
0	11.7	3.0	0.0	0.0	14.7	0.116
1	39.0	63.0	58.0	12.0	172.0	1.037
1	43.1	66.8	77.7	13.8	201.4	1.196
2	45.6	84.8	65.8	13.6	209.8	1.269
2	44.5	67.0	73.7	14.2	199.4	1.192
4	47.5	81.0	63.6	12.1	204.2	1.246
4	50.6	87.8	79.2	13.9	231.5	1.395
8	43.8	51.3	47.8	10.5	153.4	0.951
8	45.7	67.1	57.4	12.0	182.2	1.115
24	24.0	23.4	15.0	2.5	64.9	0.426
24	28.5	31.0	26.1	4.1	89.7	0.569
48	10.2	6.5	3.1	0.0	19.8	0.140
48	12.6	20.4	5.6	0.0	38.6	0.257
72	4.4	1.7	0.0	0.0	6.1	0.047
72	7.0	4.0	1.5	0.0	12.5	0.090
96	0.0	0.0	0.0	0.0	0.0	0.000
96	0.0	0.0	0.0	0.0	0.0	0.000

Note:

$$\text{TTHM (in ppm)} = [CHCl_3] + [CHBrCl_2] + [CHBr_2Cl] + [CHBr_3]$$

$$\text{TTHM (in } \mu\text{M)} = [CHCl_3]/119.378 + [CHBrCl_2]/163.834 + [CHBr_2Cl]/208.290 + [CHBr_3]/252.746$$

APPENDIX C:
EXPERIMENTAL DATA FOR NATURAL WATER:

Table C.1 : Experimental Data for Natural Water, T = 5°C.

Sample Run	Time (hrs)	UV	pH	Br^- (ppb)	Cl_2 (ppb)	TTHMs (ppm)
0	0	0.092	7.6	0.500	8.00	199.1
0	0	0.091	7.6	0.500	8.00	203.3
1	1	0.091	7.5	0.100	6.43	197.3
1	1	0.090	7.6	0.200	6.69	201.9
2	2	0.088	7.7	0.092	6.29	197.0
2	2	0.089	7.6	0.190	6.51	201.2
3	4	0.086	7.3	0.087	6.21	199.0
3	4	0.088	7.6	0.160	6.47	201.7
4	8	0.085	7.6	0.100	6.20	199.1
4	8	0.086	7.6	0.190	6.12	201.1
5	24	0.080	7.7	0.074	5.63	197.6
5	24	0.084	7.9	0.100	5.92	202.6
6	48	0.079	7.5	0.120	5.52	197.5
6	48	0.078	7.7	0.100	5.63	202.8
7	72	0.071	7.6	0.130	4.99	199.1
7	72	0.071	7.7	0.150	5.41	203.1
8	96	0.070	7.7	0.110	4.92	94.8
8	96	0.070	7.8	0.050	5.14	203.7

Table C.2 : THMs Data for Natural Water, T = 5°C.

Sample Number	$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)	$CHClBr_2$ (ppb)	$CHBr_3$ (ppb)	TTHMs (ppb)	TTHMs (μM)
1	199.1	0.0	0.0	0.0	199.1	1.668
28	203.3	0.0	0.0	0.0	203.3	1.703
2	197.3	6.9	13.4	7.6	225.2	1.789
29	201.9	7.3	11.2	8.6	229.0	1.824
3	197.0	8.7	15.3	12.0	233.0	1.824
30	201.2	7.2	11.8	8.4	228.6	1.819
4	199.0	11.4	20.0	12.4	242.8	1.882
31	201.7	10.4	17.6	11.9	241.6	1.885
5	199.1	12.6	29.8	20.5	262.0	1.969
32	201.1	10.7	19.7	12.2	243.7	1.893
6	197.6	16.2	32.0	22.0	267.8	1.995
33	202.6	18.4	33.7	22.2	276.9	2.059
7	197.5	19.6	36.3	24.4	277.8	2.045
34	202.8	24.4	41.6	24.5	293.3	2.144
8	199.1	24.4	44.5	31.4	299.4	2.155
35	203.1	24.2	36.3	21.3	284.9	2.108
9	106.1	17.3	34.1	18.6	176.1	1.232
36	203.7	26.3	43.9	23.9	297.8	2.172

Note:

$$\text{TTHM (in ppm)} = [CHCl_3] + [CHBrCl_2] + [CHBr_2Cl] + [CHBr_3]$$

$$\text{TTHM (in } \mu\text{M)} = [CHCl_3]/119.378 + [CHBrCl_2]/163.834 + [CHBr_2Cl]/208.290 + [CHBr_3]/252.746$$

Table C.3 : Experimental Data for Natural Water, T = 25°C.

Sample Run	Time (hrs)	UV	pH	Br^- (ppb)	Cl_2 (ppb)	TTHMs (ppm)
0	0	0.091	7.6	0.500	8.00	205.5
0	0	0.088	7.6	0.500	8.00	210.4
1	1	0.086	7.7	0.400	6.65	266.5
1	1	0.085	7.8	0.150	6.56	265.5
2	2	0.085	7.3	0.500	6.43	281.1
2	2	0.081	7.8	0.190	6.42	278.8
3	4	0.084	7.7	0.220	6.18	299.0
3	4	0.079	7.8	0.230	6.07	289.5
4	8	0.081	7.7	0.150	5.72	319.9
4	8	0.073	7.5	0.210	5.67	309.8
5	24	0.071	7.7	0.090	4.83	292.7
5	24	0.067	7.7	0.110	4.87	330.8
6	48	0.069	7.5	0.210	4.21	317.0
6	48	0.059	7.6	0.110	4.20	356.8
7	72	0.066	8.1	0.120	4.00	360.8
7	72	0.057	7.8	0.200	3.94	364.2
8	96	0.062	7.7	0.140	3.79	384.2
8	96	0.054	7.7	0.110	3.63	382.1

Table C.4: THMs Data for Natural Water, T = 25°C.

Time (hrs)	$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)	$CHClBr_2$ (ppb)	$CHBr_3$ (ppb)	TTHMs (ppb)	TTHMs (μM)
0	205.5	0.0	0.0	0.0	205.5	1.721
0	210.4	0.0	0.0	0.0	210.4	1.762
1	203.8	14.1	27.9	20.7	266.5	2.009
1	207.6	12.4	24.4	21.1	265.5	2.015
2	204.2	19.9	34.1	22.9	281.1	2.086
2	207.3	14.9	31.6	25.0	278.8	2.078
4	203.5	23.4	43.5	28.6	299.0	2.169
4	207.2	19.5	36.1	26.7	289.5	2.134
8	204.0	28.1	50.3	37.5	319.9	2.270
8	207.3	24.8	46.1	31.6	309.8	2.234
24	200.7	24.6	42.4	25.0	292.7	2.134
24	206.7	33.9	56.2	34.0	330.8	2.343
48	201.7	34.0	50.2	31.1	317.0	2.261
48	207.0	43.1	72.3	34.1	356.5	2.479
72	202.1	48.2	73.8	36.7	360.8	2.487
72	205.8	45.6	76.0	36.8	364.2	2.513
96	203.0	57.5	86.2	37.5	384.2	2.614
96	205.4	53.8	82.4	40.5	382.1	2.605

Note:

$$\text{TTHM (in ppm)} = [CHCl_3] + [CHBrCl_2] + [CHBr_2Cl] + [CHBr_3]$$

$$\text{TTHM (in } \mu\text{M)} = [CHCl_3]/119.378 + [CHBrCl_2]/163.834 + [CHBr_2Cl]/208.290 + [CHBr_3]/252.746$$

Table C.5 : Experimental Data for Natural Water, T = 45°C.

Sample Run	Time (hrs)	UV	pH	Br^- (ppb)	Cl_2 (ppb)	TTHMs (ppm)
0	0	0.092	7.6	0.500	8.00	197.4
0	0	0.091	7.6	0.500	8.00	202.5
1	1	0.090	7.6	0.180	6.14	288.3
1	1	0.082	7.8	0.100	6.16	277.5
2	2	0.089	7.3	0.087	5.99	306.0
2	2	0.079	7.7	0.150	5.85	294.1
3	4	0.087	7.0	0.150	5.09	336.1
3	4	0.076	7.9	0.170	5.41	306.4
4	8	0.073	7.0	0.100	4.43	302.2
4	8	0.069	7.8	0.110	4.39	339.6
5	24	0.066	7.2	0.300	2.75	480.7
5	24	0.061	7.8	0.190	2.97	390.7
6	48	0.062	7.3	0.080	1.86	245.4
6	48	0.057	8.0	0.150	1.91	402.2
7	72	0.060	7.8	0.170	1.02	282.3
7	72	0.054	8.0	0.190	1.46	395.5
8	96	0.058	7.9	0.110	0.89	318.5
8	96	0.052	8.1	0.280	1.24	401.3

Table C.6 : THMs Data for Natural Water, T = 45°C

Time (hrs)	$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)	$CHClBr_2$ (ppb)	$CHBr_3$ (ppb)	TTHMs (ppb)	TTHMs (μM)
0	197.5	0.0	0.0	0.0	197.5	1.654
0	202.5	0.0	0.0	0.0	202.5	1.696
1	190.6	20.2	46.2	31.3	288.3	2.066
1	198.6	19.5	35.6	23.8	277.5	2.048
2	193.9	26.6	49.2	36.6	306.3	2.168
2	198.7	25.6	45.1	24.6	294.0	2.135
4	193.5	35.6	63.0	44.0	336.1	2.315
4	199.1	29.9	49.0	28.4	306.4	2.198
8	119.1	45.7	89.6	47.8	302.2	1.896
8	198.9	42.0	62.1	36.7	339.7	2.366
24	191.7	80.9	122.2	104.1	498.9	3.098
24	198.3	65.8	87.3	39.3	390.7	2.637
48	76.4	51.7	75.6	41.7	245.4	1.487
48	198.2	83.8	85.2	35.0	402.2	2.719
72	89.9	61.5	88.4	42.5	282.3	1.721
72	197.4	79.6	84.3	34.2	395.5	2.679
96	89.8	75.5	100.8	52.2	318.5	1.905
96	198.1	78.6	88.7	35.9	401.3	2.707

Note:

$$\text{TTHM (in ppm)} = [CHCl_3] + [CHBrCl_2] + [CHBr_2Cl] + [CHBr_3]$$

$$\text{TTHM (in } \mu\text{M)} = [CHCl_3]/119.378 + [CHBrCl_2]/163.834 + [CHBr_2Cl]/208.290 + [CHBr_3]/252.746$$

APPENDIX D

Chemical Kinetics

Chemical Kinetics is the branch of physical chemistry that deals with the rates of chemical reactions and of the factors on which the rates depend. One reason for the great importance of this subject is that it provides most of the information needed to arrive at the mechanism of a reaction.

If a reaction is of stoichiometry:

$$aA + bB \longrightarrow yY + zZ,$$

the rate of consumption of A is defined as $-d[A]/dt$, and the rate of formation of Y is defined as $d[Y]/dt$. These quantities are not necessarily the same for different reactants and products, and it is convenient to have a quantity that applies to the reaction and is the same for all reactants and products. This is done by making use of the concept of extent of reaction.

For some reactions the rate is related to reactant concentrations by an equation of the form:

$$v = k[A]^{\alpha}[B]^{\beta} \ldots$$

where α and ß are known partial orders: α is the order with respect to A and ß the order with respect to B. The sum of all the partial orders is known as the overall order. The coefficient k that appears in this equation is known as the rate constant or the rate coefficient.

The effect of temperature T on the rate constant is expressed by Arrhenius equation:

$$k = Ae^{-E/RT}$$

where R is the gas constant, E is the activation energy, and A is the preexponencial factor.

The first task in the kinetic investigation of chemical reaction is to measure rates under a variety of experimental conditions and to determine how the rates are affected by the concentrations of reactants, products of reaction, and other substances that may affect the rate.

There are two main methods for dealing with such problems; they are the method of integration and the differential method. In the method of integration we start with a rate equation that we think may be applicable. For

reaction, we start with:

$$-dc/dt = kc$$

where c is the concentration of reactant. By integration we convert this into an equation giving c as a function of t and then compare this with the experimental variation of c with t. If there is a good fit, we can then, by simple graphical procedures, determine the value of the rate constant. If the fit is not good, we must try another rate equation and go through the same procedure until the fit is satisfactory. The method is something of a hit-and-miss one, but it is nevertheless very useful, especially when no special complications arise.

The second method, the differential method, employs the rate equation in its differential, unintegrated, form. Values of dc/dt are obtained from a plot of c against t by taking slopes, and these are directly compared with the rate equation. The main difficulty with this method is that slopes cannot always be obtained very accurately. In spite of this drawback the method is on the whole the more reliable one , and unlike the integration method it does not lead to any

particular difficulties when there are complexities in the kinetic behavior.

Considering the method of integration in more detail, a first-order reaction may be of the type:

$$A \longrightarrow Z$$

Suppose that at the beginning of the reaction (t=0) the concentration of A is a_o, and that of Z is zero. If after time t the concentration of Z is x, that of A is $a_o - x$. The rate of change of the concentration of Z is dx/dt, and thus for a first order reaction,

$$dx/dt = k(a_o - x),$$

After separation of variables, integration and evaluation using the boundary condition that x=0 when t=0 is obtained:

$$\ln(a_o/ a_o) - x = kt$$

The first order equations can be tested and the constant evaluated using a graphical procedure. A plot of $\ln a_o/a_o - x$ against t will give a straight line if the order is the

first. the rate constant is the slope.

Second order reactions can be treated in a similar fashion. There are now two possibilities: the rate may be proportional to the product of two equal concentrations or to the product of two different ones. The first case must occur when a single reactant is involved as in the process,

$$2A \longrightarrow Z,$$

It may also be found in reactions between two different substances,

$$A + B \longrightarrow Z,$$

provided that their initial concentrations are the same. In such situations the rate may be expressed as:

$$dx/dt = k(a_o - x)^2$$

The result of integration, with boundary condition t=0,x=0, is:

$$x / a_o(a_o - x) = kt$$

Graphical methods can again be employed to test this equation and to obtain the rate constant k.

If the rate is proportional to the concentrations of two different reactants, and these concentrations are not initially the same, the integration proceeds differently. Suppose that the initial concentrations are a_o and b_o; the rate after an amount x has reacted is:

$$dx/dt = k(a_o-x)(b_o-x)$$

This equation can be tested by plotting the left-hand side against t; if a straight line is obtained, its slope is k. These are the common orders; reactions of other orders can be treated in a similar manner.

In the differential method, the procedure is to determine rates directly by measuring tangents to the experimental concentration-time curves and to introduce these into the equations in their differential forms. The theory of the method is as follows. The instantaneous rate of a reaction of the n^{th} order involving one reacting substance is proportional to the n^{th} power of its concentration:

$$v = -da/dt = ka^n$$

Therefore

$$\log_{10} v = \log_{10} k + n\log_{10} a$$

A plot of $\log_{10}$ v against $\log_{10}$ a therefore will give a straight line if the reaction is of simple order; the slope k is the order n.

In order to test the Arrhenius equation, we take logarithms of both sides:

$$\ln k = \ln A - E/RT$$

If the Arrhenius law applies, a plot of ln k against 1/T will be a straight line, and the slope will be -E/R.

In order to develop a kinetic model for trihalomethane formation some models were tested. Some examples of the work done is presented as follows:

The following reaction equations were established:

$$\text{PRECURSORS} + Cl_2 \xrightarrow{k_1} \text{TTHMs}$$

$$\text{PRECURSORS} + Cl_2 \xrightarrow{k_2} \text{by products}$$

In the first model tested (model 1) the rate was related to reactant concentrations by equations of the form:

$$dC_1/dt = k_1C_2C_3$$

$$dC_2/dt = -k_1C_2C_3 - k_2C_2$$

$$dC_3/dt = -k_1C_2C_3 - k_2C_3$$

where:

C_1 = [TTHM]

C_2 = $[Cl_2]$

C_3 = [PRECURSORS] as UV absorbance measurement

A non-linear regression program (NLR) was used to evaluate each model. The model equations introduced to the program are of the form:

APPENDIX E

Analysis of Kinetics Models

$$dY_1/dt = b_1Y_2Y_3 \qquad (1)$$

$$dY_2/dt = -b_1Y_2Y_3 - b_2Y_2 \qquad (2)$$

$$dY_3/dt = -b_1Y_2Y_3 - b_3Y_3 \qquad (3)$$

Corresponding variational equations were developed for each model equation.

To improve data adjustment, an additional parameter, was added to equation 1 and the precursor dependence (Y_3) was defined as one of order = 2. The $-b_3Y_3$ term on equation 3 was eliminated. Models were tested with and without the $b_1Y_2Y_3$ term on equation 1.

The second model (model 2) presents these changes and tests the option without the $b_1Y_2Y_3$ term on equation 1. The equations of model 2 introduced to the program are of the form:

$$dY_1/dt = b_1$$

$$dY_2/dt = -b_2Y_2Y_3^2 - b_3Y_2$$

$$dY_3/dt = -b_2Y_2Y_3^2$$

The third model (model 3) presents the second option: $b_1Y_2Y_3^2$ as a term on the first model equation. They were introduced to the NLR program as:

$$dY_1/dt = b_1Y_2Y_3^2 + b_2$$

$$dY_2/dt = -b_1Y_2Y_3^2 - b_3Y_2$$

$$dY_3/dt = -b_1Y_2Y_3^2$$

After exhaustive statistical testing, model 3 was found to be the one that best fitted the experimental data.

APPENDIX F:

The Nonlinear Regression Program

THE NONLINEAR REGRESSION PROGRAM

A Brief Overview

The Nonlinear Regression Program (NLR) has been designed to fit a set of differential or algebraic equations to multiresponse data to determine a number of unknown parameters. The parameter estimation is linked with statistical analysis routines to form a single self-contained package. The input to the program is accomplished through a series of menus.

Parameter Estimation

The Marquardt algorithm, which utilizes an interpolation technique to combine the Gauss-Newton and steepest descent methods, is used in this program.

Statistical Analysis

A set of statistical tests accompanies the regression analysis. These are:

1) A linear 95% confidence interval for each parameter is calculated and a t-test is performed to check if the value of the parameter is significantly different than zero. The 95% confidence limits for each variable are calculated.
2) The correlation matrix of the parameters is calculated and the matrix components are tested at the 95% and 99% significance levels to determine the extent of correlation between the parameters.
3) The correlation coefficient matrix defines a hyperellipsoid in parameter space. A sum of squares search is performed in the direction of the major and minor axes of the hyperellipsoid to ascertain whether the minimum sum of squares has been located.
4) A Runs test is performed on the deviations between the experimental and predicted values of the state variables to ensure random distribution, i.e. to test the null hypotheses that the residuals are randomly distributed.
5) Analysis of variance is performed. The F-test is applied on the ratio of the residual variance to the experimental data variance to determine if more scatter exists than can be explained by experimental error.

Description of the program

The Nonlinear Regression Program consists of the MAIN program, 12 subprograms which are called from the MAIN program through CHAIN commmands, 6 data files, and one equations file. These are described below:

PROGRAM	DESCRIPTION
MAIN.BAS	The main program calls all the other programs and performs the Marquardt method.
INPUT.BAS	This program enters all the data, constants and equations for the nonlinear regression.
COMPAR.BAS	Compares the variance due to lack-of-fit with the variance due to experimental error, and performs the F-tests.
DATIN.BAS	Determines the variance of the experimental data and the weighting factors.
GJLNB.BAS	Uses the Gauss-Jordan reduction method to obtain the parameter increment vector.
JSRKB.BAS	This routine evaluates the state and variational equations which are specified by the user through the INPUT.BAS program. If the model contains differential equations, the 4th order Runge-Kutta method is used for the integration.
MUS.BAS	Calculates the residuals between the group means of the experimental points and the predicted curve.
PHLPA.BAS	A matrix inversion routine to determine the inverse of the ATA matrix.
RUNS	This performs a two sided Runs test at the 0.05 significance level. (This routine has been embedded within the main program).
SA12V.BAS	A statistical analysis routine that performs a series of tests on the predicted parameters.

- Combined residual variance of the data.
- Standard errors and covariances of the coefficients.
- 95% confidence limits of the coefficients using the Student t distribution, and significance tests.

SETPAR.BAS — Searches the sum of squares space at the end of the axes of the hyperellipsoid.

SUMS.BAS — This routine calculates the residuals between the experimental and the predicted points, and the weighted sum of squared residuals.

SUMS1.BAS — Similar to SUMS, but for unweighted residuals.

OUTPUT.BAS — Prints tables and draws graphs (on screen or using an HP 7475A Plotter) of final values of variables and data.

OTHER FILES ON THE DISKETTE

CONS.DAT — Random access file for all nonlinear regression constants.

DATA.DAT — Random access file that contains all the experimental data and weights.

DIST.DAT — Read-only file that contains the F-distribution table.

GUESS.DAT — Sequential file that contains the initial parameter guesses.

INITCOND.DAT — Sequential file for all the initial conditions of the differential equations.

OUTPUT.DAT — Sequential output file for the matrix A which contains the profiles of the state and variational variables over the entire integration interval.

MODEL.EQU — File containing the state and variational equations.

READ.ME — Text file containing this description. Can be read using the command TYPE READ.ME

Use of the program

The entire program is written in interpretive BASIC and will run under the IBM PC Advanced Basic Interpreter (BASICA). The program MAIN is responsible for the whole package, and it will call upon the appropriate subprogram as needed. NLR is menu driven for data input and adjustment. All the data are stored on the diskette in files with the extension .DAT. The state and variational equations may be entered from the keyboard. These are stored in a file called MODEL.EQU. Whenever new data and/or a new model are used, the previous set of files are overwritten by the new data and model. If the user wants to retain the old data and model, the user must first rename the files, or transfer them to another diskette, before entering the new information.