Agency
Region IV, Athens, GA 3061[illegible]
7/28/80

INTRODUCTION TO TRIHALOMETHANES (THM'S)

A. THM Formation

Aqueous chlorine + precursor* ⟶

(1) Chloroform + other THM's

* - Humic substances (humic and fulvic acids)

Other THM's normally found:

(2) bromodichloromethane, (3) dibromochloromethane, and (4) bromoform.

The following iodo compounds have also been reported where iodide was present in the raw water: dichloroiodomethane and bromochloroiodomethane.

B. Factors Influencing THM Formation

1. Temperature - Increasing temperature increases THM formation. (See Figure 1.)

2. Bromide Ion - Bromide ion is more reactive than chloride; therefore, a small amount of bromide will create a proportionately higher concentration of brominated compounds in the presence of larger amounts of chloride ion(see Figures 2 and 3).

3. pH - Increasing pH increases the rate of THM formation (see Figure 4). Increasing pH also increases THM formation of simple ketones that normally react very slowly with Cl_2 (see Figure 5).

4. Characteristics and Concentration of Precursors - Increasing the same precursor increases THM concentration (see Figure 6). However, precursor substances vary from one location to another; therefore, rate curves vary (see Figures 7 and 8).

5. Chlorine Dose Rate - Increasing chlorine dose rate increases THM formation (see Figure 9).

C. Factors Influencing THM Measurement during Treatment Evaluations

Introduction of Trihalomethane Formation Potential Concept

Because their formation is not instantaneous, THM concentrations increase in the water as it flows through a water-treatment plant (unless removed during treatment) to reach some value higher than that which would be observed if an analysis for THM species were performed immediately after sampling at the first point of chlorination. Further, the consumer is likely to receive water with THM concentrations higher than those leaving the plant because the reaction proceeds in the distribution system. This also occurs during sample storage and, in each case, the concentration is time-dependent. The formation rates vary according to all of the reaction conditions described in the previous section. These factors will be discussed again in the context of the THM measurement. To evaluate treatment success, four definitions are important:

1. Instantaneous THM (InstTHM) concentration - the concentration of THM in the water at the moment of sampling.

For InstTHM concentration measurement, the reaction of chlorine with precursor materials must be halted at the time of sampling with the goal being to measure only trihalomethanes present at the time of sampling. A small amount of reducing agent is added to the sample to react with the chlorine and, thus, render the chlorine unavailable for oxidation or substitution reactions. A small increase in trihalomethane concentrations upon storage after addition of reducing agent usually is observed. This is probably caused by a slow hydrolysis of certain trihalointermediates. The hydrolysis step does not require the presence of chlorine. The distinction should be made between this minor effect on the InstTHM concentration and the continued THM formation reaction when no reducing agent is added. The increase in THM concentration during storage after the addition of a reducing agent has amounted to only a few percent of the total value.

2. Terminal THM (TermTHM) concentration - the concentration of THM that occurs at the termination of the measurement of this parameter.

   TermTHM concentration is equally important as a parameter for evaluating consumer risk as is the InstTHM concentration, but because this parameter is a measure of the sum of the amounts of THM species already present (instantaneous) and those formed during the reaction time, a third parameter must be defined that is useful for evaluating unit-process performance for removal of unreacted precursor.

3. THM formation potential (THMFP)-measured as the increase in THM concentration that occurs during the storage period in the determination of the TermTHM concentration. The THMFP is obtained by subtraction of the InstTHM concentration from the TermTHM concentration either when TTHM or when the individual species data are used. THMFP is a measure of the portion of the total precursor material (of most concern to the consumer) remaining in the water at a given point in the treatment train. (See Figure 10.)

4. Total precursor - A distinction between THMFP and a total precursor is important. Total precursor concentration is the concentration of all organic THM precursor materials present in the water that could react with halogen species under conditions that maximize the yield of trihalomethanes.

Because the identities of these organic compounds are not known precisely at this time, total THM precursor concentration also could be expressed as concentrations of THM or concentration of TTHM obtained from that reaction. No standardized procedure for measuring this parameter exists, however, and considerable research will be required to establish the optimum conditions to insure the complete reaction of all precursors to yield maximum trihalomethane concentrations.

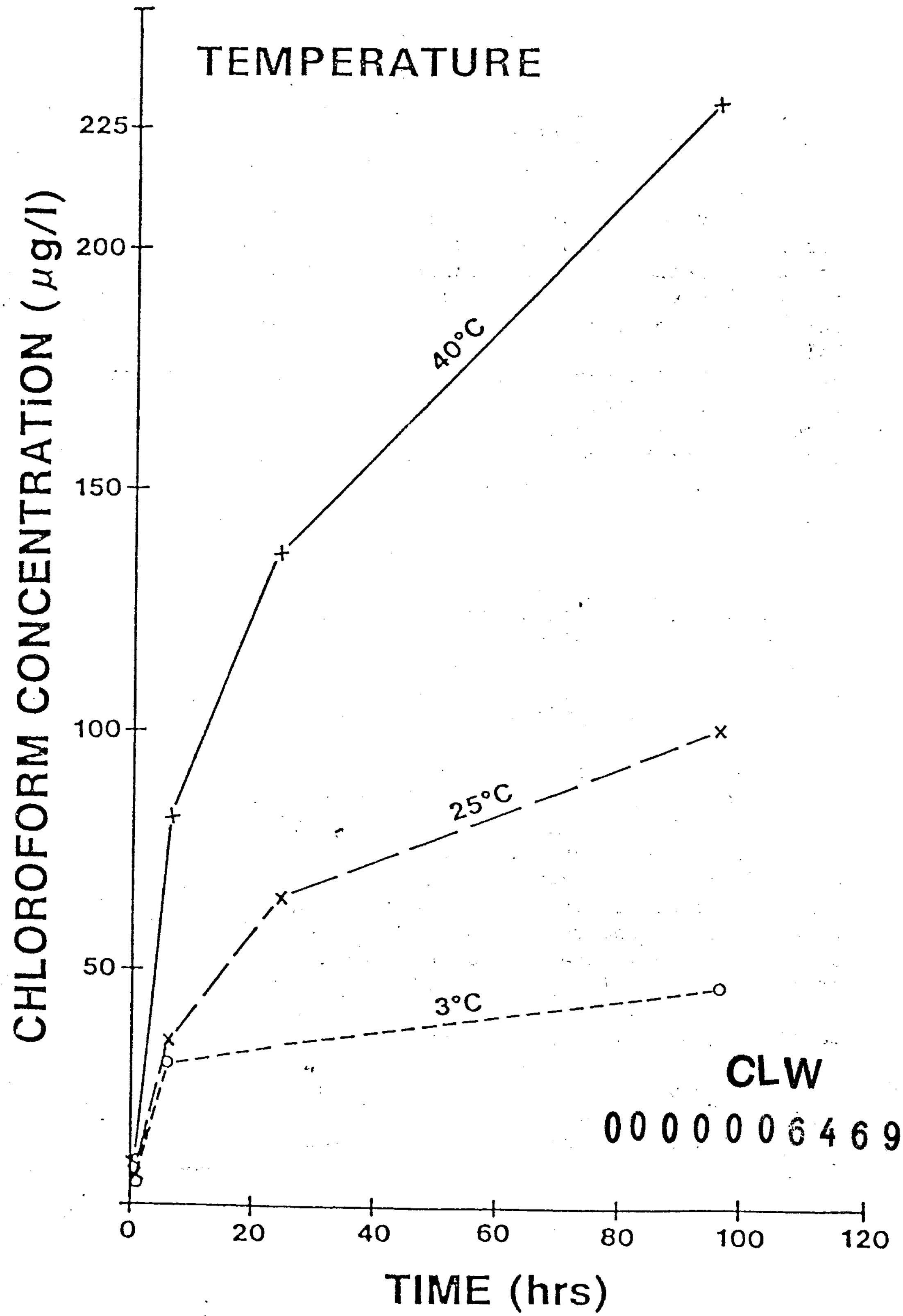

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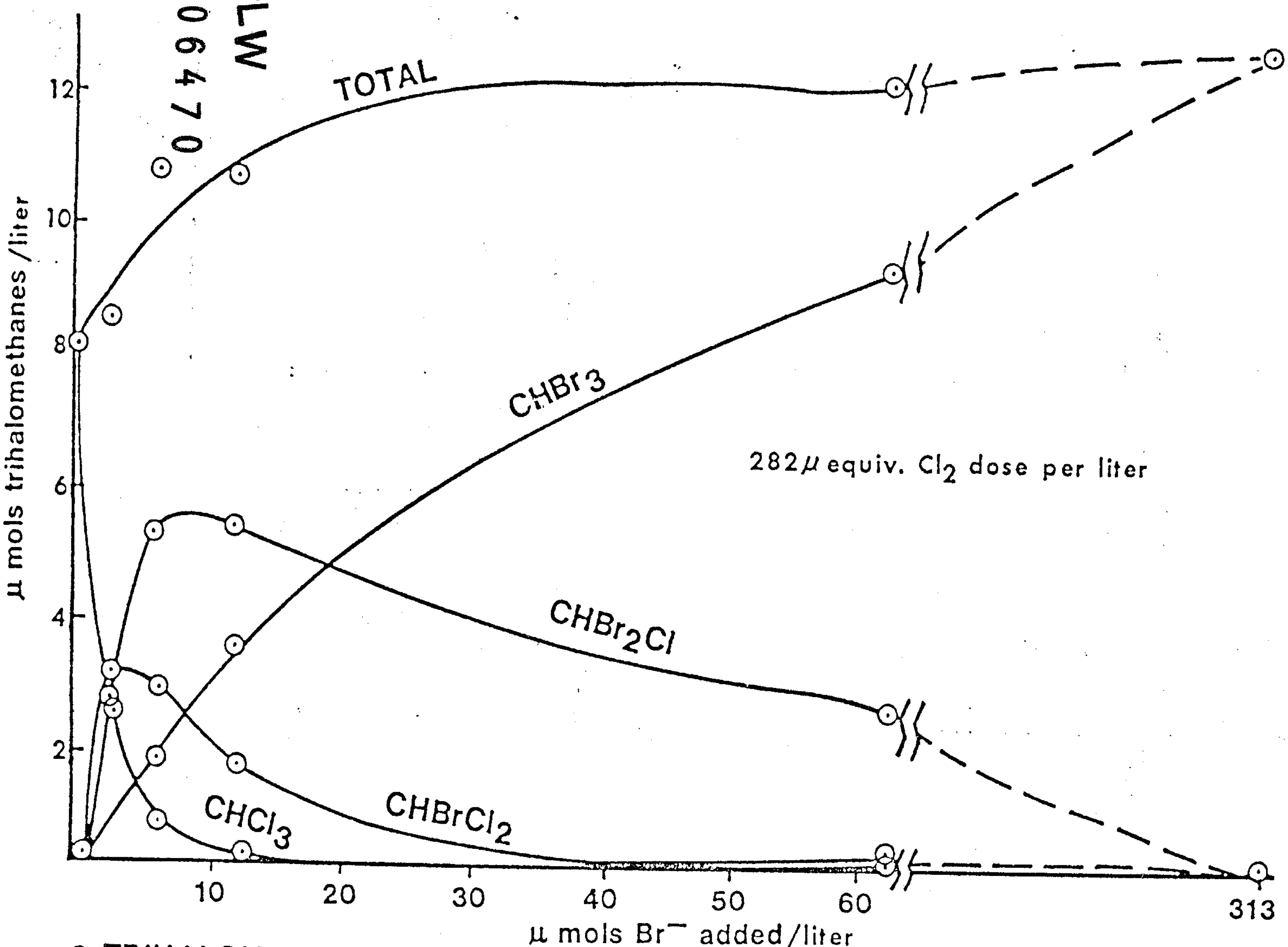
FIG.1 EFFECT OF TEMPERATURE ON CHLOROFORM FORMATION



gure 2 TRIHALOMETHANES FORMED BY REACTION OF HUMIC ACID WITH AQUEOUS CHLORINE IN THE PRESENCE OF VARYING BROMIDE ION

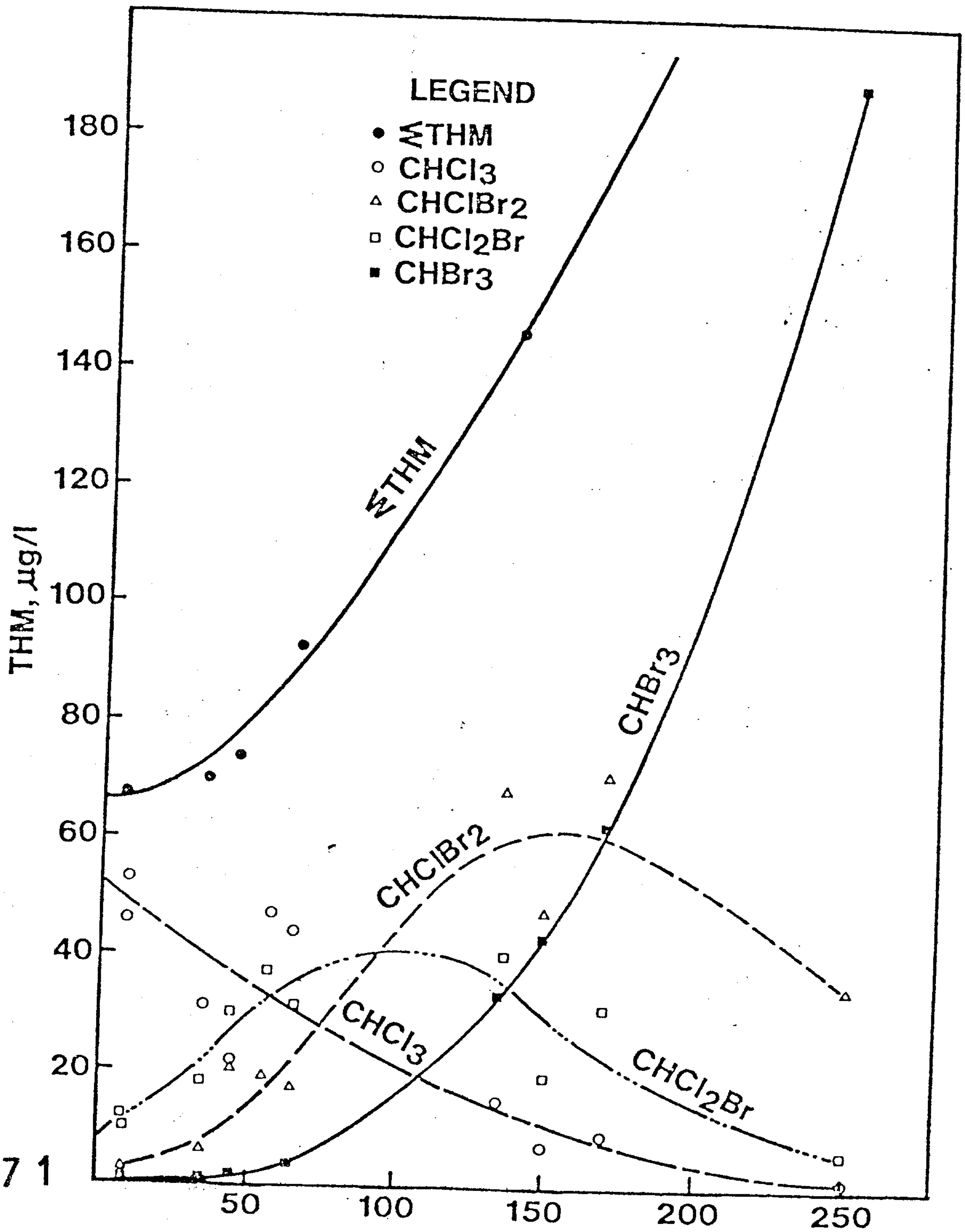


Figure 3 EFFECT OF SALT WATER INTRUSION ON THM FORMATION POTENTIAL (FROM LANGE, 1978)

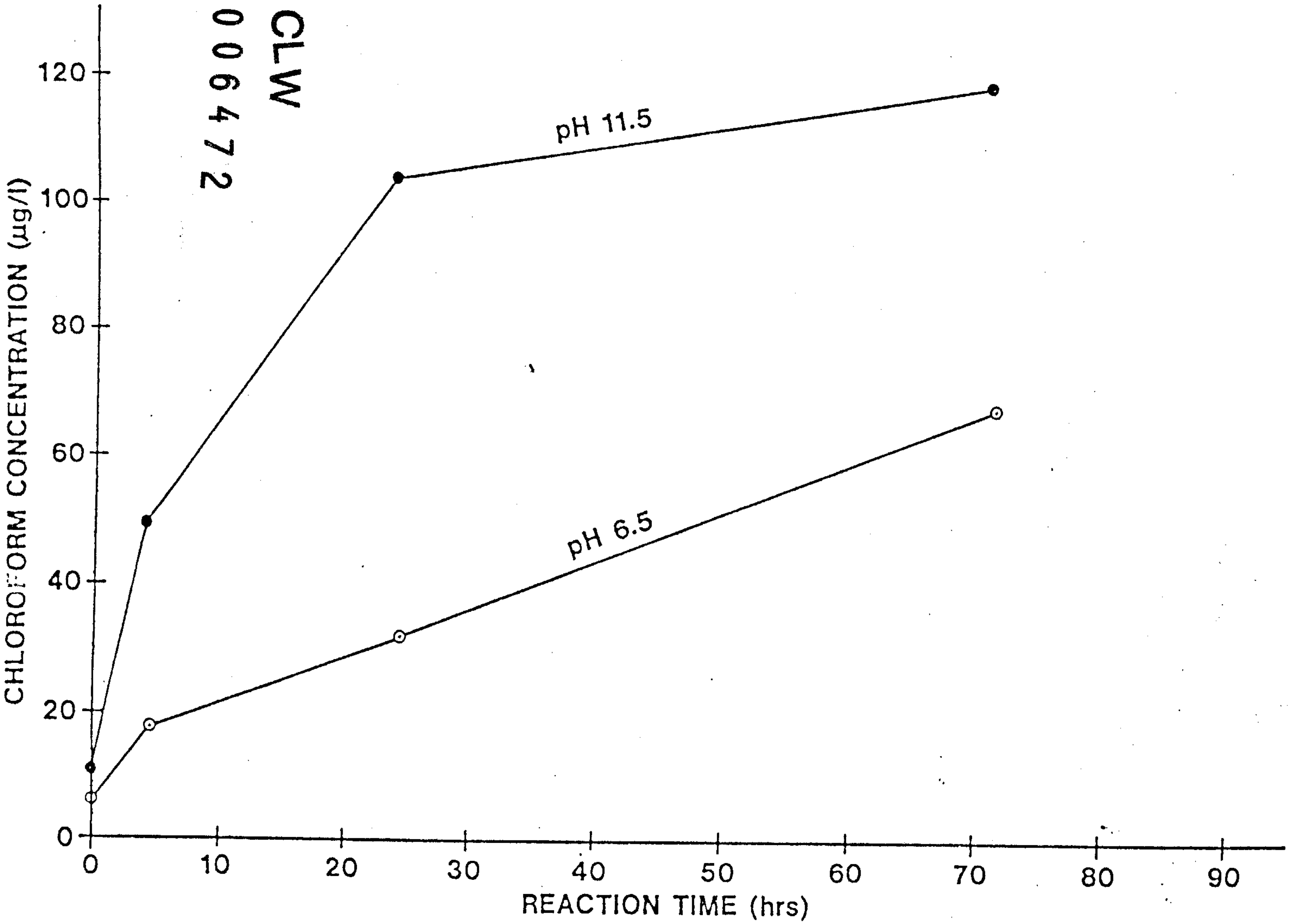


Figure 4 EFFECT OF pH ON CHLOROFORM PRODUCTION, SETTLED WATER 25°C, 10mg/l CHLORINE DOSE

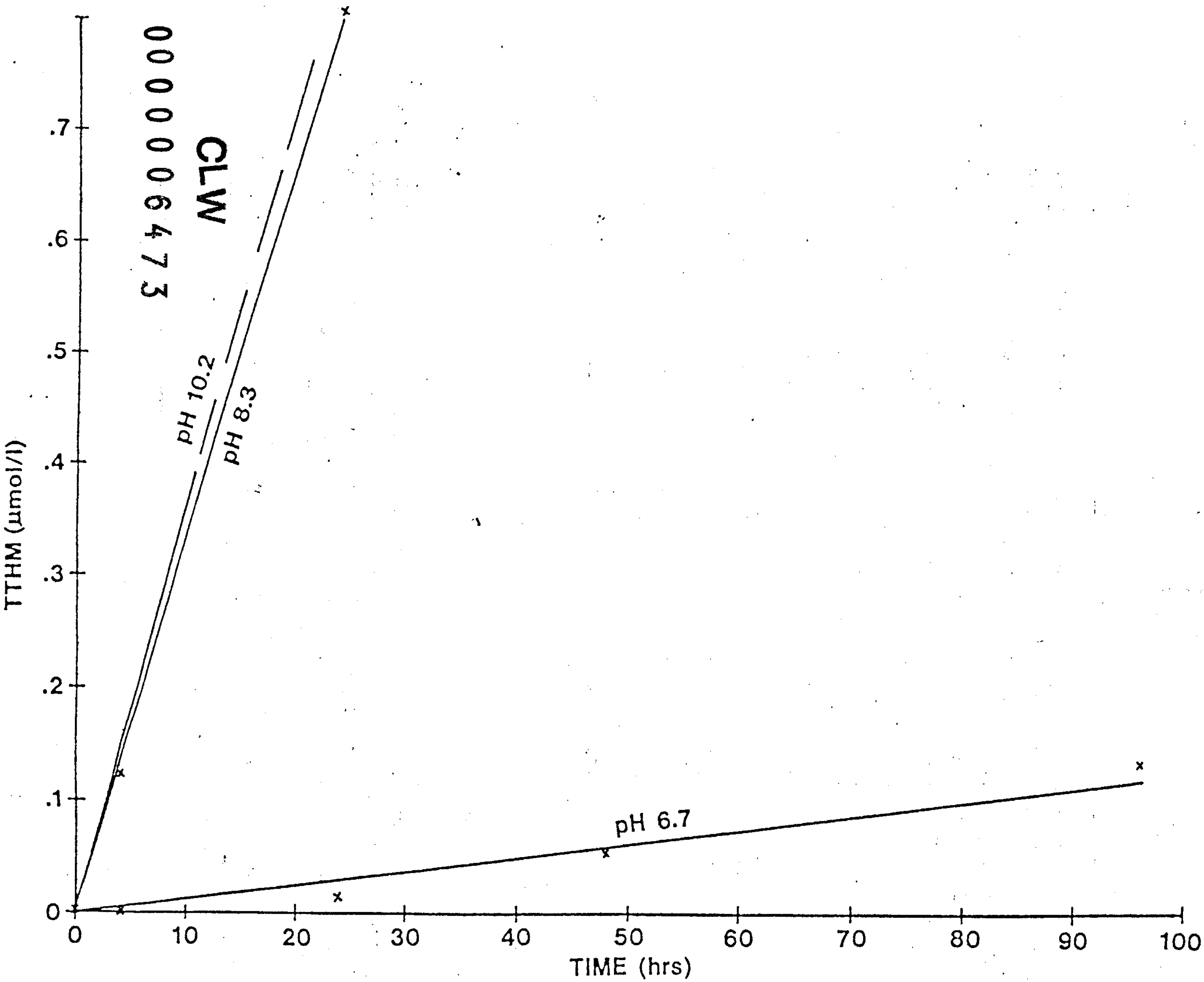


FIG. 5 EFFECT OF pH ON TRIHALOMETHANE PRODUCTION FROM ACETONE, 1mg/l, 25°C, CHLORINE DOSE 10mg/l

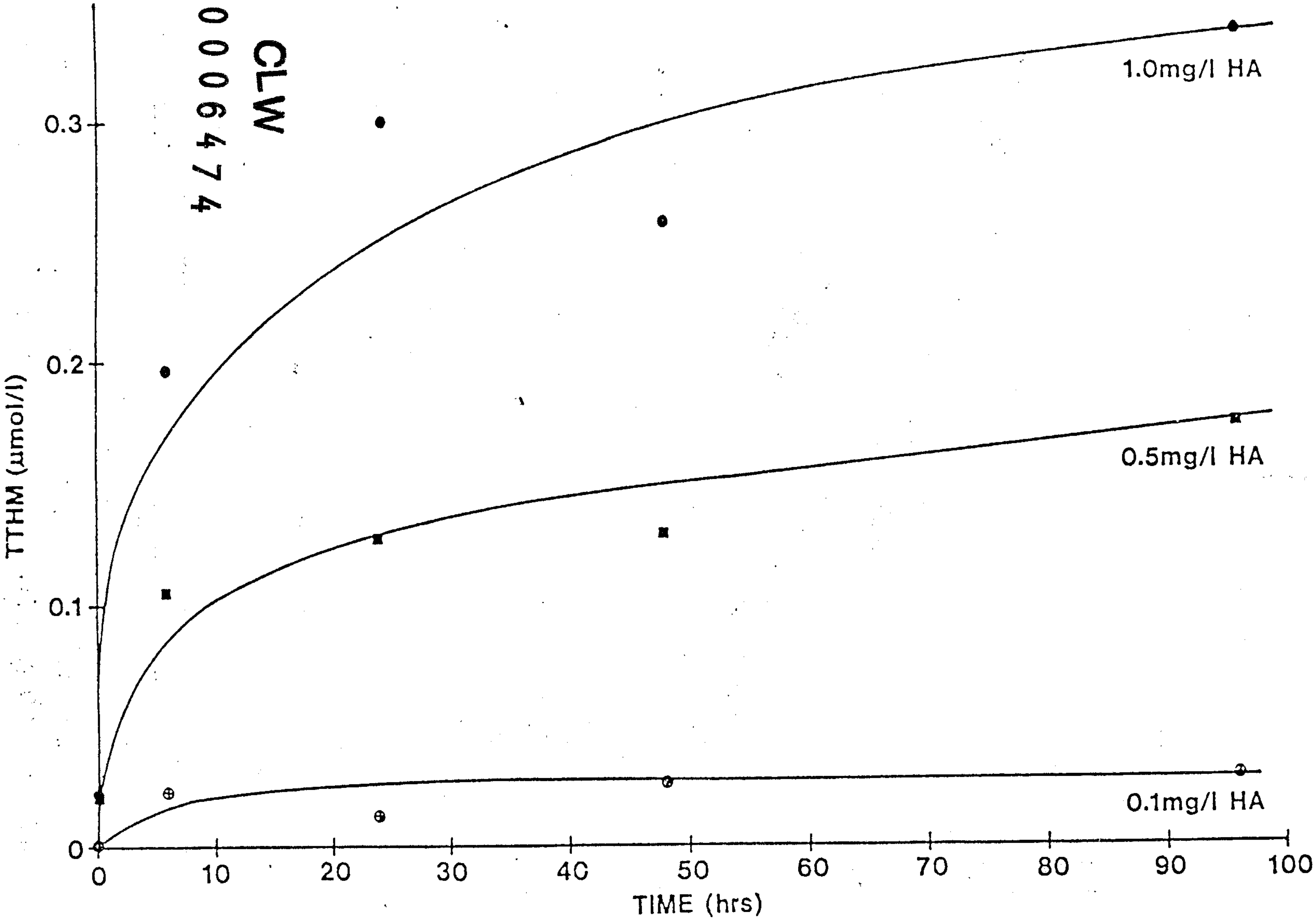


Figure 6 EFFECT OF HUMIC ACID CONCENTRATION ON TRIHALOMETHANE PRODUCTION, pH 6.7, 25°C, 10mg/l CHLORINE DOSE

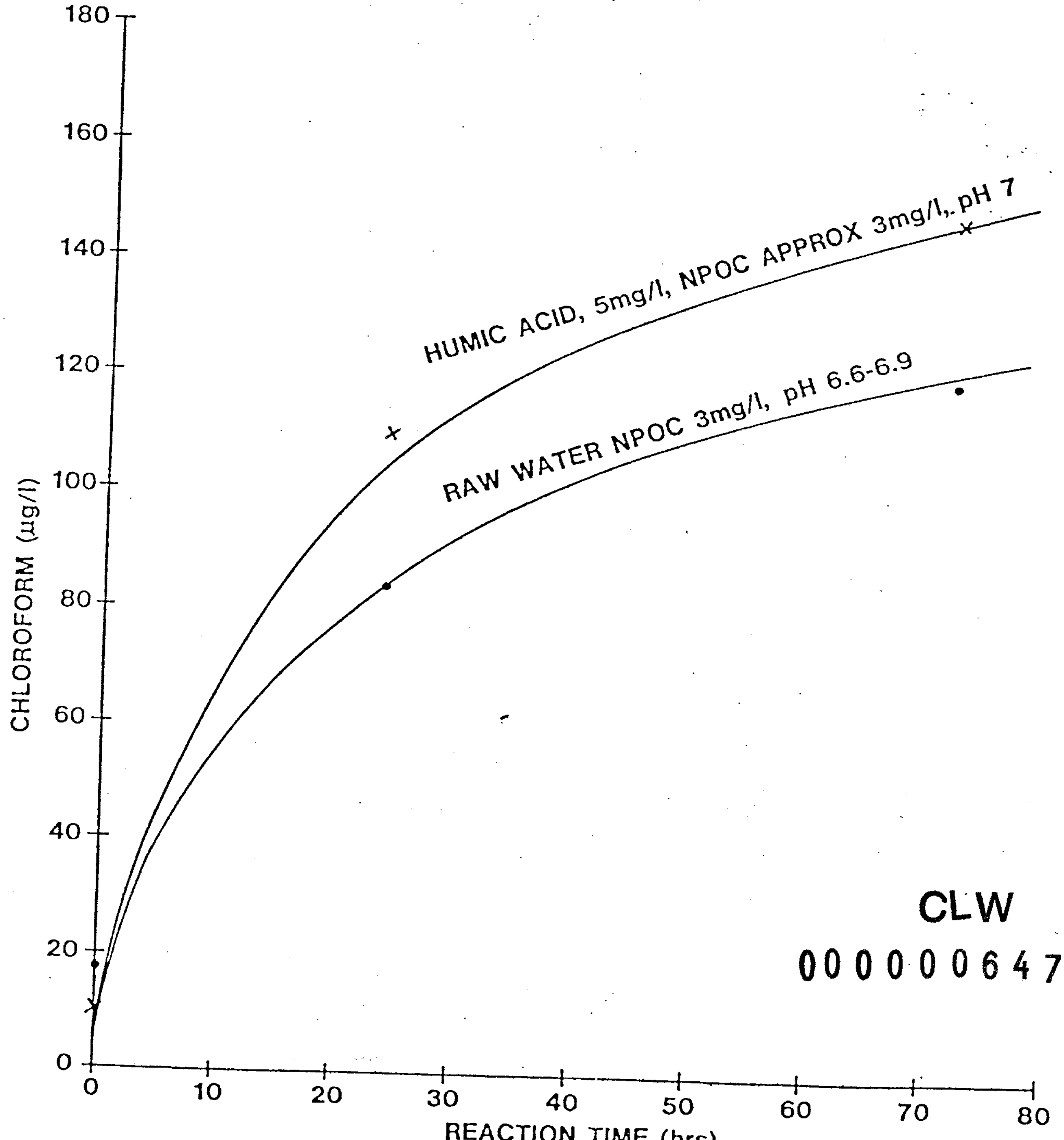


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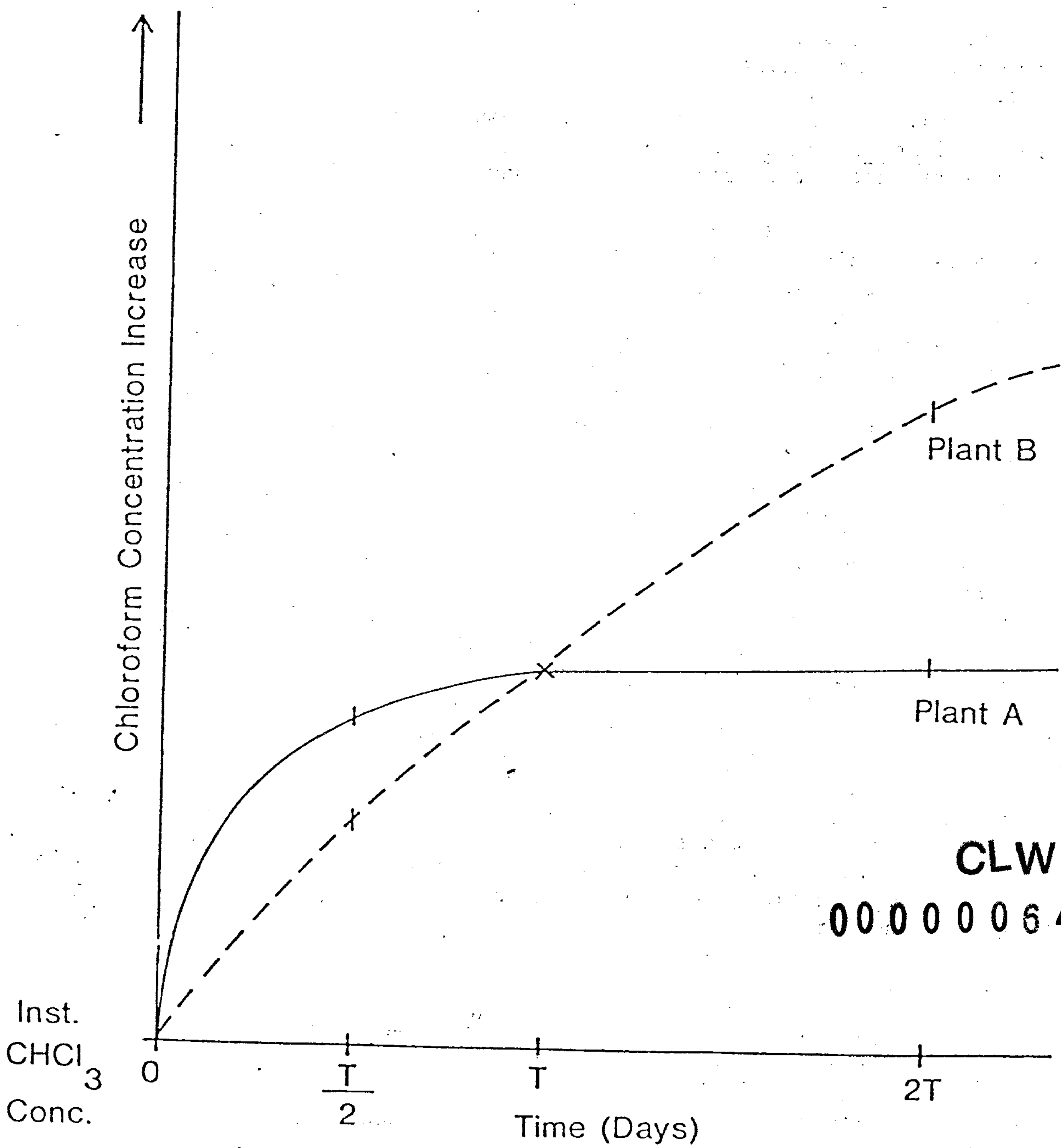
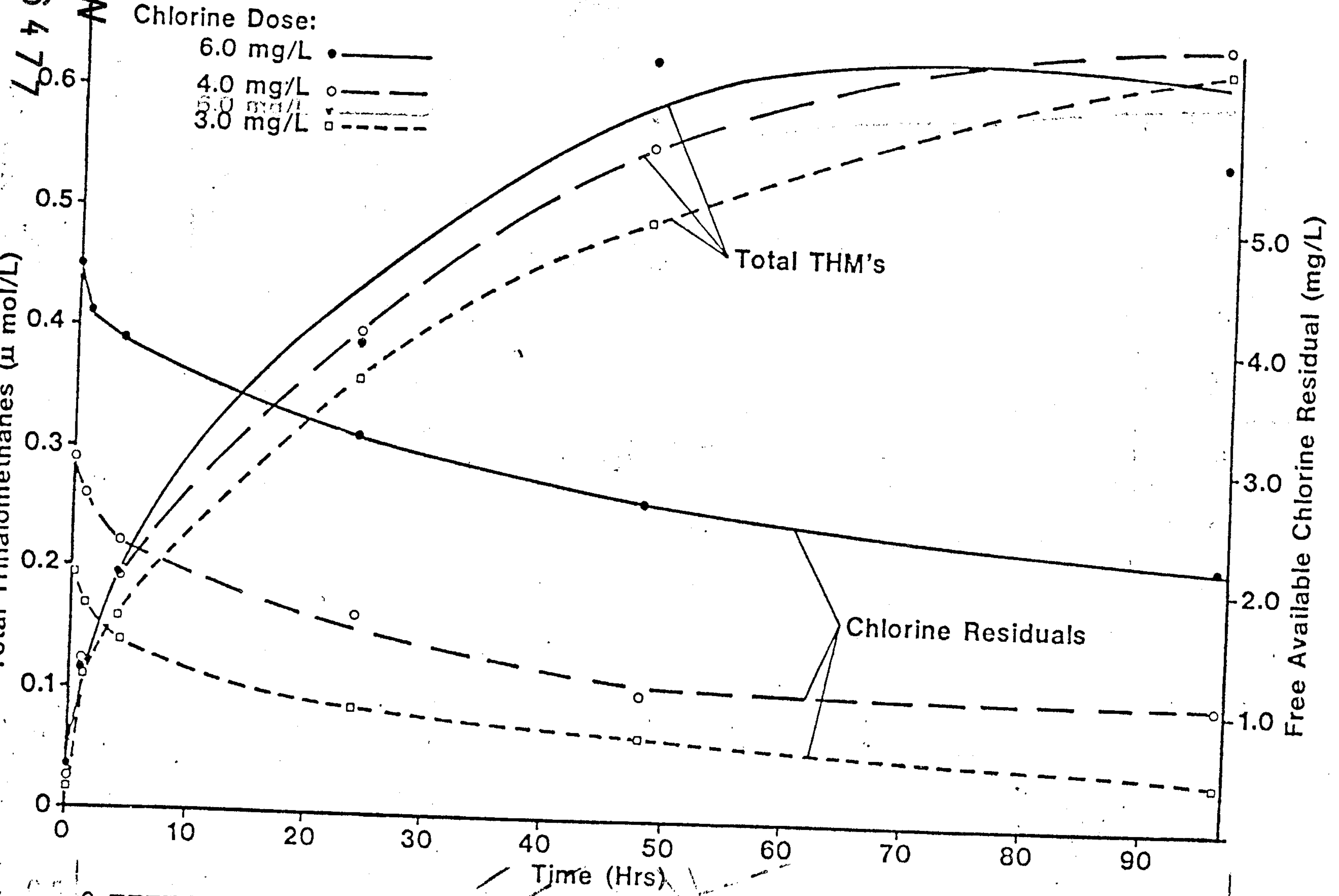
Figure 7 COMPARISON OF HUMIC ACID, RAW WATER REACTION RATES AT SIMILAR NPTOC CONCENTRATIONS, 10 mg/l CHLORINE DOSE



Formation of Chloroform Under Widely Different Treatment Plant Conditions

FIG. 8



gure 9 EFFECT OF CHLORINE DOSE ON TRIHALOMETHANE FORMATION

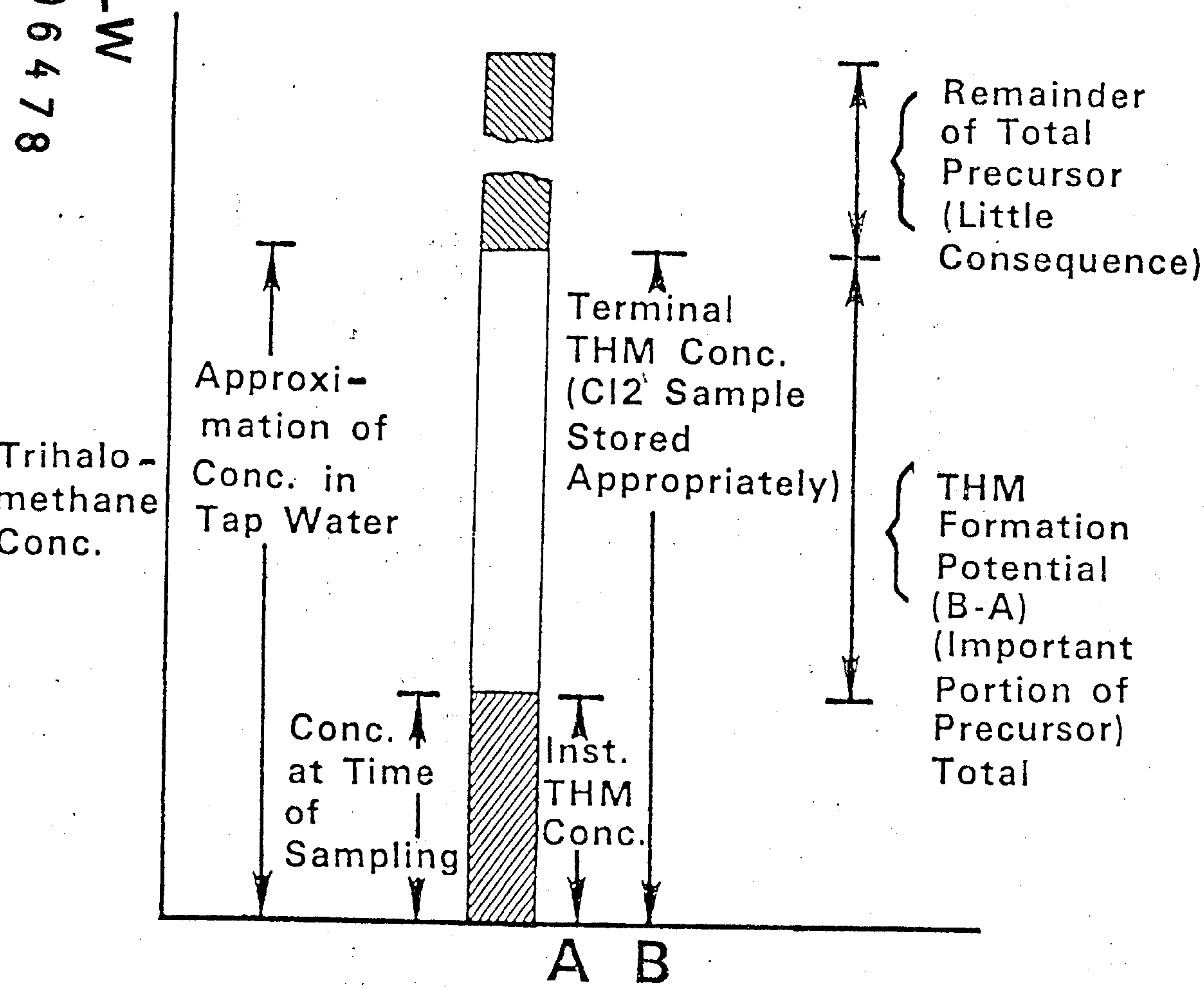


FIG. 10 FOUR TRIHALOMETHANE MEASUREMENT PARAMETERS

The preceding outline was taken from this paper

(DWRD0002)

FORMATION AND MEASUREMENT OF TRIHALOMETHANES IN DRINKING WATER

by

Alan A. Stevens and James M. Symons

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