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**A SYSTEMATIC STUDY TO REDUCE TRIHALOMETHANE  
PRECURSORS IN LITTLE ROCK DRINKING WATER BY  
COMBINED ALUM COAGULATION—POWDERED  
ACTIVATED CARBON TREATMENT**

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**Chemistry Department  
University of Arkansas-Little Rock**

Publication No. 101

June, 1983

Research Project Technical Completion Report A-057-ARK

Arkansas Water Resources Research Center  
University of Arkansas  
Fayetteville, Arkansas 72701



**Arkansas Water Resources Research Center**

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Project A-057-ARK

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Arkansas Water Resources Research Center  
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## ABSTRACT

### A SYSTEMATIC STUDY TO REDUCE TRIHALOMETHANE PRECURSORS IN LITTLE ROCK DRINKING WATER BY COMBINED ALUM COAGULATION - POWDERED ACTIVATED CARBON TREATMENT

Studies have been conducted to evaluate powdered activated carbon (PAC) as an agent for controlling trihalomethanes in drinking water. Laboratory studies indicate that PAC is highly efficient in removing free trihalomethanes in water within a few hours. The removal efficiency of humic acid, a known THM precursor, by PAC is considerably less. However, longer treatment time can remove the precursors quite significantly. Humic substances in surface water samples can also be removed by PAC.

KEYWORDS - \*Powdered Activated Carbon, \*Trihalomethanes, chloroform, bromoform, bromodichloromethane Dibromochloromethane, \*THM Precursors, Humic Acid, \*Direct Aqueous Injection, Solvent Extraction, \*Gas Chromatography

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## I. INTRODUCTION

Organics in drinking water are of major concern to the United States Environmental Protection Agency (EPA). Both the Safe Drinking Water Act (PL 93-523) and court-orders have directed EPA to control organic materials of synthetic origin, as well as those of natural origin that are transformed by chlorination. A number of these compounds are proven or potential toxins and/or carcinogens. To date, EPA has recognized 129 of these substances as priority pollutants which, above a certain concentration level in water, represent a chronic health hazard to humans through food-chain concentration, bioaccumulation, or molecular genetic damage. Among these pollutants, 14 are metals and the remaining 115 are organic compounds. Among organics, there are two classes - volatiles and extractables. Volatiles are low molecular weight pollutants which can be easily volatilized (for example, using the purge-and-trap method) and are almost exclusively composed of halomethanes, commonly called Trihalomethanes (THM).

In 1974-75, EPA sponsored an 80-city National Organic Reconnaissance Survey (NORS). THMs were found to be the most widespread organic pollutants and they also occurred at the highest concentrations. These compounds were produced by the reaction of chlorine, the most widely used disinfectant in the United States, with naturally occurring compounds such as humic acid, fulvic acid, humin, algae and some other chemicals. Season, temperature, disinfectant residual and other factors contribute to the variation of

THM levels. The Federal Register of February 9, 1978 established a maximum contaminant level (MCL) of 100 parts per billion (ppb) of THM for water purification systems serving a population of 75,000 or more. The water supply system for the municipality of Little Rock, Arkansas, currently meets this standard. A yearly average of 60 ppb of THM are detected in "finished water". At the present state of available analytical techniques and instrumentation, however, it is conceivable that many THM and other organic compounds of potential toxicity and/or carcinogenicity remain undetected due to their lower levels. It appears that more compounds are going to be added to the EPA list of pollutants in water as research efforts continue for improved analytical methodology, and further progress is made towards the evaluation of toxicity and/or carcinogenicity of these compounds.

The major types of organic compounds found in natural water are humic substances, tannins and sulfonated lignins, phenolics, amino acids, hydrocarbons and fatty acids. Laboratory studies on low molecular weight hydrocarbons and fatty acids show that these compounds do not produce significant amounts of THM during chlorination. Since the amount of phenolics and amino acids are usually small, their contribution towards THM formation is insignificant. Where streams run through forested areas, levels of tannin will be higher and THM coming from this source will be significant. Otherwise, the major source of THM after chlorination are humic substances.

The most widespread THM in natural waters are chloroform ( $\text{CHCl}_3$ ), bromodichloromethane ( $\text{CHCl}_2\text{Br}$ ) dibromochloromethane ( $\text{CHClBr}_2$ ),

and bromoform (CHBr<sub>3</sub>). Although the amount of chloroform is the highest among these, sometimes as much as 95% of the total THM, the others are formed due to reaction between dissolved bromide in raw water and the humic substances.

A. Research Objectives

The most logical approach to reduce the amount of THM in drinking water is to remove humic acid, fulvic acid and some other specific organic compounds, generally known as THM precursors, prior to chlorination. The initial objectives of this project therefore, were:

- 1) to evaluate the adsorption capability of powdered activated carbon (PAC) and a commercially available coagulant with respect to the removal of selected halomethanes in water.
- 2) to evaluate the adsorption capability of PAC and the coagulant to remove THM precursors (e.g., humic acid) in laboratory made water samples, as well as in natural water collected from Little Rock water supply reservoirs. The experimental model was to be set up to simulate the existing conditions (e.g., treatment time, etc.) at Little Rock water treatment facility.

Severe budget cutback, combined with the fact that the funding was approved for one year instead of two years as originally proposed, resulted in revision of project objectives. It was decided therefore to evaluate the performance of PAC only. The removal efficiency was

determined in terms of THM levels before and after PAC treatment. Total organic carbon (TOC) measurement, a very important parameter for the indication of precursor removal, had to be omitted due to lack of proper facilities.

#### B. Related Research

Review of the literature indicates that a tremendous amount of research has been performed worldwide to develop analytical techniques for detection and estimation of organic compounds commonly found in water. Much of the attention has been focused on THMs because of their common occurrence and relative abundance.

Absolute chemical verification of a volatile organic pollutant generally requires the use of a precision gas chromatograph, selective detectors, and mass spectrometry. Selective detectors and mass spectrometers normally cut significantly into personnel and regular laboratory budgets. Since the water quality laboratory's performance is measured for both analytical quality and daily sample volume, the cost per test can be significantly affected by down time, repair and long set-up procedures. To counter these difficulties, several advances in the area of automation and high resolution gas chromatography have become available in recent years. These advances offer an alternative approach while maintaining high sample volumes with expanded and more precise identification of a particular compound. Automation permits the laboratory to establish an analytical method to carry out both analysis as well as data processing.

A detailed review of recent development in the determination

of priority pollutants is given by Fishman and Erdmann(1). For THMs and other small and volatile compounds, gas chromatography is used almost exclusively as a method of detection and estimation (2-4). For better sensitivity, THMs in samples are generally preconcentrated by either the purge-and-trap method or by the liquid-liquid extraction method(5). The purge-and-trap technique involves extracting THMs from water by purging with an inert gas and then absorbing on a porous polymer trap. THMs are then normally desorbed from the trap onto a GC column for separation and detection. In the liquid-liquid extraction method, THMs are extracted from water into a hydrocarbon solvent such as hexane by liquid-liquid extraction. The sample is then injected into a GC column. Comparative purge-and-trap and liquid-liquid extraction data agree to within 20 percent(6), both with detection limits for individual THMs to about 0.5  $\mu\text{g}/\text{l}$ . Nicholson, Meresz, and Lemyk(3) developed a direct aqueous injection (DAI) method, thus avoiding lengthy sample preparation time, with a detection limit of less than or equal to 1  $\mu\text{g}/\text{l}$  for haloforms, and quantitates THMs that can form after chlorination of natural water. Kuo, Chiau, and DeWalle(4) concentrated low molecular weight (less than 85) volatile polar organic compounds by distillation. By directly injecting the distillate into a GC column, compounds were measured in  $\mu\text{g}/\text{l}$  level with a relative standard deviation of 5 percent. Schultz(5) used a GC column in conjunction with a tripping chamber and cold trap apparatus to measure  $\mu\text{g}/\text{l}$  quantities of THMs in water samples. Formalin was added to stop bacterial activity and to preserve

samples, with no measurable loss for as many as seven days. Kissinger and Fritz(6) found that residual chlorine in drinking water reacts with organics to increase THMs on storage. The addition of ascorbic acid stabilized the samples. Analytical methods are also described.

Application of computer-based chromatograph for automated monitoring of low molecular weight organics in drinking water, especially THMs, is discussed by Dowty, Green, and Laseter(7). Some techniques for analysis of trace quantities of volatile organics in water by GC combined with mass spectrometry and a computerized data system are discussed by Lingg, et.al.(8). Pereira and Hughes(9) have determined nineteen selected volatiles, purgable priority pollutants, in water by using GC coupled with a quadruple mass spectrometer with a detection limit of 1  $\mu\text{g/l}$  or less.

A review of the literature suggests that for precise, sensitive, and fast analysis of THMs in water, the state-of-the-art is an automated GC coupled with a mass spectrometer-computer system. Unfortunately, such an instrument is economically well beyond most of the municipal water supply systems. For the purpose of our investigation, where the number of samples to be analyzed are only a few and the number of THMs to be identified are not excessive, a high resolution gas chromatograph may be adequate to perform the task even if it is to be done on a routine basis. Larger numbers of samples can be analyzed by a GC-MS-computer system if accessible. UALR has a high-resolution GC available for this type of determination. Because it is well-documented and recommended by EPA, liquid-liquid extraction

of THMs into hydrocarbon solvents as preconcentration step seems to be the best choice. For samples containing higher THM levels, direct aqueous injection into GC can be performed to avoid time-consuming sample preparation.

#### REMOVAL OF THMs FROM WATER

Much attention has been focused on the removal of THMs from drinking water. Should chlorination be retained as a water disinfectant, the removal of THM precursors prior to chlorination is an obvious treatment strategy, now used by several utilities and likely to be used more extensively in the future.

Reduction of the amount of particulate and dissolved organic matter in natural waters may be achieved through improved coagulation (10), by adsorption onto suitable materials such as Granulated Activated Carbon (GAC) or polymeric resins(11,12), by membrane processes such as ultrafiltration(13) or reverse osmosis(14), and by chemical oxidation(15). Membrane processes and chemical oxidation are unlikely to be cost effective as compared with coagulation and GAC. Use of a GAC bed is gaining almost universal popularity both nationally and internationally(16). The GAC bed removes THM precursors such as humic acid, fulmic acid, and humin(17) as well as algae(18). Algae are also known to be THM precursors. GAC has been used to treat surface water, ground water, and waste water both on the pilot plant scale as well as full scale(9,11,12) with great success. As an alternative to GAC, some polymeric resins were found to be equally effective(19,20). The mechanism of adsorption of these precursors

on GAC and resin were also investigated by the authors. The cost of the addition of a GAC bed to an existing facility and its maintenance appears to be high(20,21) and hence may not be affordable for small municipal water utilities. Coagulation, on the other hand, is quite effective in precursor removal and requires much less capital investment(10). Its effectiveness, however, is not as universal as GAC. For example, it is difficult to remove fulvic acid by coagulation(10).

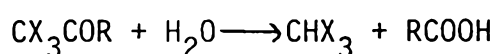
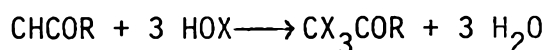
The use of powdered, activated carbon (PAC) has been quite extensive for removal of odor and taste. And there is a wealth of practical experience available for this type of treatment(15). It is widely used in France for odor and taste removal from water containing a low concentration of organic substances and ammonia. It is also particularly well adapted to meet organic matter peaks of short duration without heavy capital costs. In such cases, the treatment consists of injecting large doses of carbon, up to 100 mg/l, for a short period. Anderson, Butler, Holdren and Kornegay(22) have conducted a plant-scale study to evaluate the feasibility of THM precursor removal using PAC. Results of their study indicate that a powdered carbon, especially formulated for a specific removal, can be successful in reducing THM formation levels up to 56% at carbon dosages considerably less than previously reported. The study demonstrates that the right powdered carbon can remove THM precursors efficiently.

While the effectiveness of PAC in eliminating organic sub-



stances is somewhat limited economically (due to the need for relatively large doses), substantial removal can be achieved. Combined with a well-designed and well-operated flocculation-sedimentation process, a dosage of 30 mg/l can reduce the total dissolved organic matter by 60 percent. This efficiency can be improved further by longer contact time between PAC and water as it occurs in the Little Rock Water Supply system. A larger ammonia content in the raw water, however, would reduce this efficiency because a larger chlorine dose would be needed to neutralize the ammonia which, in turn, could produce larger quantities of THMs. A review of the overall situation at the Little Rock facility indicates that a combined PAC-alum treatment is an excellent alternative to the GAC-bed treatment for THM precursor removal. Moreover, the availability of a fluidized-bed technique for the regeneration of PAC, with an efficiency of 90 percent recovery, makes it an even more attractive alternative(23).

The mechanism of THM formation in aqueous solution has been studied quite extensively. Morris(24) described the chlorination reaction in alkaline aqueous solution as follows:



Where hypochlorous acid (HOCl) is present,  $\text{CHCl}_3$  is produced. If bromide is also present, hypobromous acid (HOBr) is formed first which, in turn, produces brominated THM compounds. Trussel and Umphres(25) presented a summary of functional groups on humic acid, such as  $-\text{COCH}_2\text{C}^{\ominus}$ ,  $-\text{OCOCOCH}_3$ ,  $-\text{COCH}_3$  etc., which have been shown to

form THM. Arguello et.al.(26), Norwood et.al.(27) and Boyd et.al. (28) have described the reaction pathways of THM formation from the halogenation of model compounds for humic acid. Minear(29) studied in detail the effect of bromide ion on the formation of THM. It was observed that bromine is more reactive than chlorine in forming THM. However, the amount of chloroform formation can be reduced significantly by increasing the amount of bromide ions, although the concentrations of brominated species increase concomitantly.

## II. EXPERIMENTAL DESIGN

### A. Analytical Methods for THM Analysis

Due to its high sensitivity, rapidity and the relative ease of operation, the Direct Aqueous Injection (DAI) method developed by Nicholson, Meresz and Lemyk(3) was adopted as the principle analytical procedure for this study. All experiments were performed using pyrex glasswares cleaned properly with soap solution, distilled water and deionized water, in that order. Solutions were prepared and kept at room temperature ( 20°C) during all experiments.

A Hewlitt-Packard Model 5750 gas chromatograph equipped with a Nickel-63 electron capture detector was used. For DAI method, a 6 ft. x 1/4 inch (2 mm i.d.) glass column packed with chromosorb 101 (80/100 mesh) was employed. The column oven was operated isothermally at 150°C, whereas the temperatures of the injection port and the detector were 170°C and 250°C respectively. The flow-rate of the argon-methane (5% methane) carrier gas was maintained at 60 mL per minute. The sample injection volume was generally between one and five microliters.

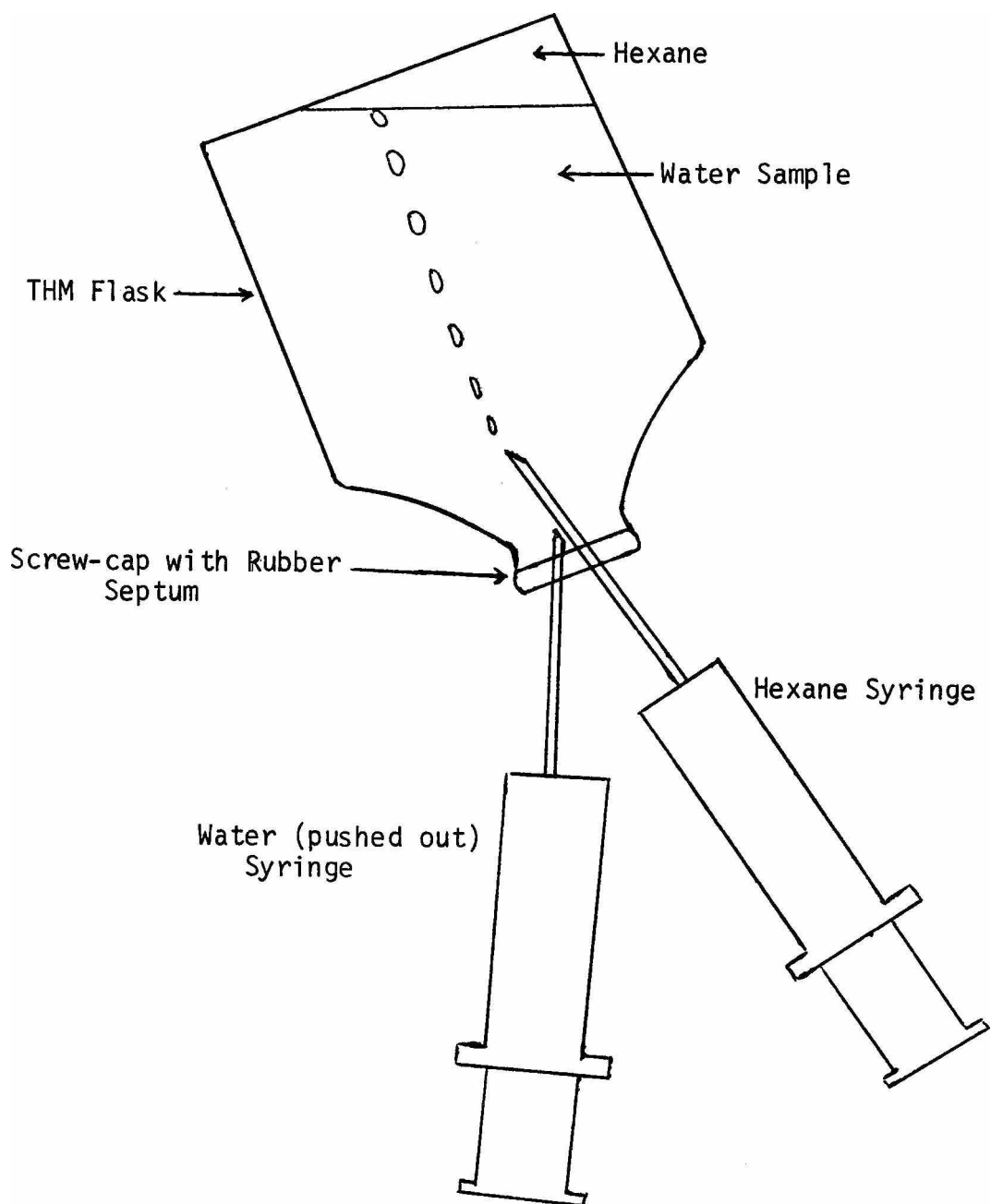
In preparing the standard curves, a standard solution of THMs listed in table 1 was obtained from Supelco Inc. (Houston, TX). Standard solutions of various lower concentrations were prepared by dilution in methanol. The final experimental solutions, to be injected into GC, were prepared by adding appropriate volumes of the standard solutions in deionized water contained in 300 mL BOD bottles. The bottles were completely filled, then tightly sealed with glass

stoppers and stirred on a magnetic stirrer using teflon coated stirrer bars. At least 24 hours was allowed for complete dissolution of THMs in aqueous solution.

Although not described in the literature, attempts were made to use the same Chromosorb 101 column for analyzing THMs in organic solvents such as hexane. When the GC separation was found to be as good as by DAI method, a solvent extraction (SE) procedure was also developed in order to carry out comparative study. Nanograde quality hexane was obtained from Burdick and Jackson (Muskegon, MI). Solvent extraction was performed by filling up 25 mL THM flasks (with screw top and rubber septum; Supelco Inc.) with aqueous standard solutions. 5.0 mL hexane was then injected into the flask, held inverted as shown in Figure 1, while an equal volume of aqueous layer was drawn out under pressure. The flasks were then hand-shaken vigorously for half-an-hour to ensure complete extraction of THMs in hexane. After settling for five minutes, 5.0  $\mu$ L of the hexane (the upper) layer was drawn and injected into GC for analysis.

Preliminary studies were also conducted to develop Purge-and-Trap method. The method generally involves removal of trihalomethanes in aqueous solution by purging with an inert gas (e.g., nitrogen) and collected on a tenax trap. The halomethanes are then desorbed from the trap by heating up to about 180°C followed by carrying them directly into GC. Initial attempts were made to develop a purge-and-trap device which can be easily mounted on a Finnigan model 1015 GC-MS-Computer. Due to lack of time,

Figure 1: Apparatus for the Liquid-Liquid Extraction with Hexane



further studies on this method were discontinued and the method development was excluded from this project.

B. Removal of Trihalomethanes and Their Precursors by Powdered Activated Carbon (PAC)

Only one brand of PAC (Huskey, obtained through Little Rock Water Supply Division) was used for this study. Humic acid standard was obtained from Aldrich Chemicals. (Milwaukee, WI). Sodium hypochloride solution (Fisher Scientific) was used for chlorination of humic acid standards as well as natural water. The following experiments were performed:

1. The effect of PAC on trihalomethanes in aqueous solution was tested by taking 0.00, 0.05, 0.30 and 0.45 g. PAC in 300 mL BOD bottles and then adding standard solution of THM, followed by filling up with deionized water, to make 1.0 ppm in each of the halomethanes. Assuming complete miscibility, these solutions correspond to 166.7, 1000 and 1200 ppm of PAC. The bottles were tightly sealed and stirred well, using magnetic stirrer bars, for a certain period of time. 1.0 mL portion of the solution was then filtered and analyzed immediately by DAI method using 5.0  $\mu$ L injection volume. For further time-dependent study, the 1.0 mL volume (withdrawn earlier) was made up with de-ionized water (the bottles must be completely filled) and the stirring was continued.
2. The effect of PAC on humic acid in standard solutions

was tested by adding varying amounts of PAC to a certain amount of humic acid solution. Twelve 300 mL BOD bottles were prepared as described below:

<u>Bottle #</u>	<u>Humic acid (ppm)</u>	<u>PAC (ppm)</u>
1	0	0
2	1.00	0
3	1.67	0
4	2.34	0
5	0	533
6	1.00	533
7	1.67	533
8	2.34	533
9	0	1667
10	1.00	1667
11	1.67	1667
12	2.34	1667

Each solution was stirred for 24 hours using stirrer bars. A 50 mL portion of the solutions was filtered through 0.4 micron filter paper under suction. In 25 mL THM flasks, 1.0 mL sodium hypochlorite solution (~4% by weight) was taken and the flasks were then filled up with the filtered PAC-treated humic acid solutions. The flasks were tightly stoppered and were allowed to sit for 24 hours for the generation of THM due to chlorination. The 24-hour PAC treatment and an equal length of

chlorination time was chosen to simulate the existing conditions at Little Rock Water treatment facility. After chlorination, the reaction was quenched by adding 0.20 g. sodium thiosulfate to destroy excess chlorine. The solutions were then analyzed by DAI method first and then by solvent extraction.

3. The effect of PAC on THM precursors in Lake Maumelle water was tested by adding varying amounts of PAC to the same amount of water. Four 300 mL BOD bottles were prepared in which 0.00, 0.10, 0.30 and 0.50 g PAC were taken. The bottles were then filled up with lake water and stirred as before. The solutions correspond to 330, 1000 and 1650 ppm of PAC. After 24-hour PAC treatment, a portion of the solutions was filtered and chlorinated for another 24 hours as described earlier. The PAC-treatment was continued for longer than 24 hours in order to observe better removal of the precursors.



### III. RESULTS AND DISCUSSION

#### A. Analytical Methods

According to Anderson, Meresz and Lemyk(3), the direct aqueous injection method using a Chromosorb 101 column provides excellent separation of all four trihalomethanes, listed in Table 1, with a detection limit around one ppb when an injection volume of 9  $\mu\text{L}$  is used. A typical chromatograph obtained by this method for the halomethanes are shown in Figure 2. This chromatogram represents a 5.0  $\mu\text{L}$  injection of 1.0 ppm solution of each compound. The standard curves are shown in Figure 3. The relative detector response of various halomethanes agree quite well with that obtained by Anderson et.al.(3), with bromodichloromethane being the most sensitive and bromoform the least. However, the detection limit for each compound was found to be much higher than the literature value (3), namely  $\sim 50$  ppb for chloroform,  $\sim 20$  ppb for bromodichloromethane,  $\sim 30$  ppb for Dibromochloromethane and  $\sim 100$  ppb for bromoform. The significant difference in detection limits could be due to (a) the instrument sensitivity: a Nickel-63 electron capture detector on a Hewlett-Packard model 5750 GC was used in our laboratory as opposed to a scandium titride detector on a Varian model 2400 GC used by Anderson et.al.(3), and (b) the loss of trihalomethanes from standards, possibly through evaporation, during dissolution in aqueous solution. Original THM standards of various concentrations were prepared in methanol. The final aqueous solution was prepared

Table 1: List of Trihalomethanes Used for Generating Standard Curves

CHLOROFORM ( $\text{CHCl}_3$ )

BROMOFORM ( $\text{CHBr}_3$ )

BROMODICHLOROMETHANE ( $\text{CHBrCl}_2$ )

DIBROMOCHLOROMETHANE ( $\text{CHBr}_2\text{Cl}$ )

Figure 2: Sample Chromatogram of Standards by Direct Aqueous Injection

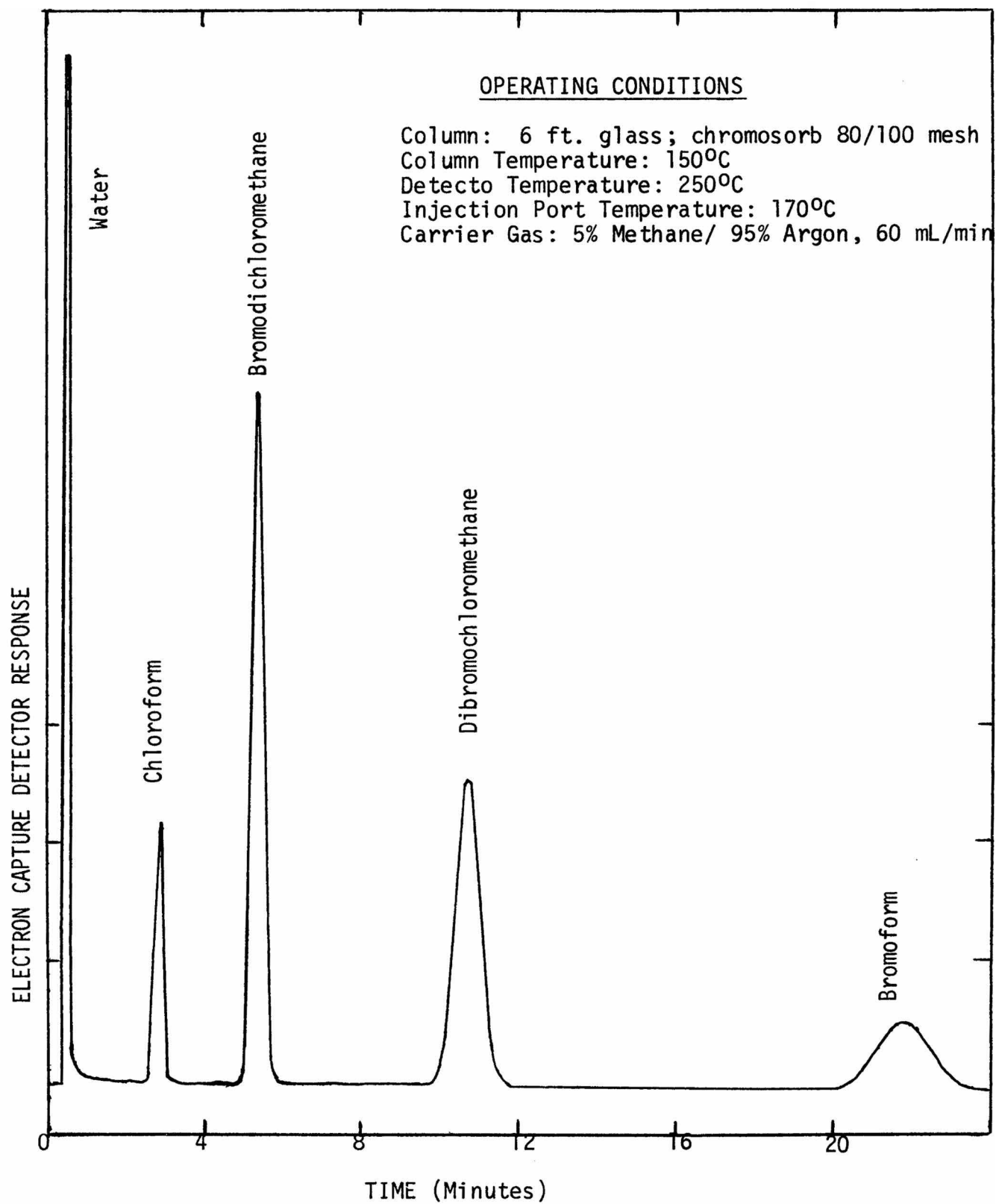
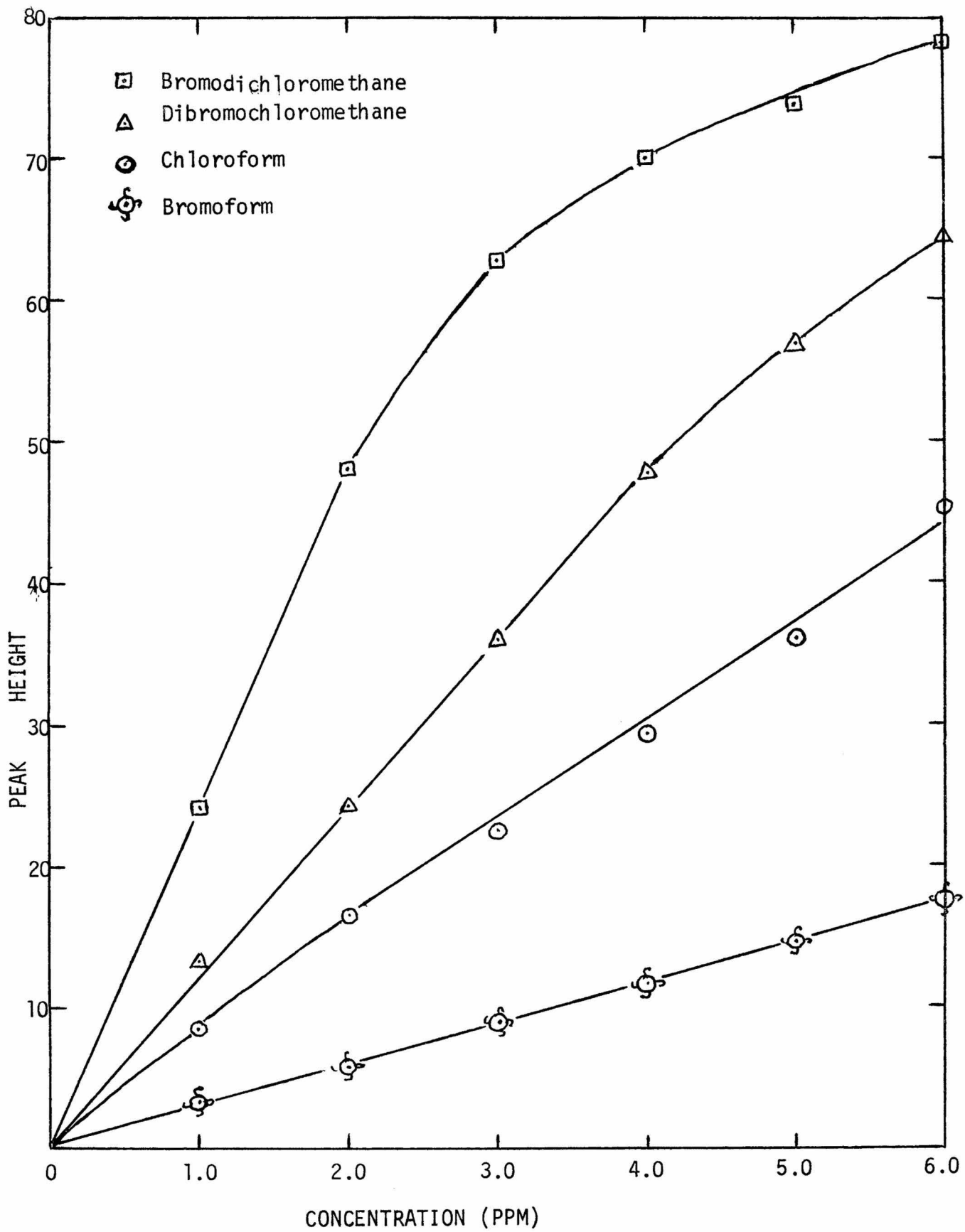


Figure 3: Standard Curves for Trihalomethanes by Direct Aqueous Injection



by mixing appropriate amounts of standard into 300 mL BOD bottles, filled completely with deionized water, sealed tightly and allowed to stir vigorously (using magnetic stirrer bar) for 24 hours. This procedure ought to produce homogeneous mixture with maximum solubility. Repeated attempts to improve the detection limit proved futile. Since a lower detection limit seemed essential, especially for the analysis of natural water, it was decided to preconcentrate using solvent-extraction technique. Liquid-Liquid solvent extraction technique described by Henderson et.al(30) requires a column (Supelcoport, obtained from Supelco Inc.) on which direct aqueous injection could not be performed with high sensitivity. However, chromosorb 101 can be used for trihalomethane analysis using hexane as a solvent. This is demonstrated in the chromatogram shown in Figure 4. It is evident that hexane gives a negative peak on this column. However, excellent separation of all four halomethanes was achieved with retention times quite comparable to those obtained by direct aqueous injection. Using the same column, one can perform analysis by direct aqueous injection or by solvent extraction as necessary. The standard curves in hexane solution are shown in Figure 5. An improvement in detection limit by a factor between 5 and 10 was obtained, principally due to preconcentration procedure where the halomethanes from a 25 mL aqueous solution were extracted into 5 mL hexane. It was found that a preconcentration by a factor of 25 can be achieved without any apparent loss in sensitivity, provided the extraction procedure was performed in a completely-

Figure 4: Sample Chromatogram of Standards by Solvent Extraction into Hexane from Aqueous Solution

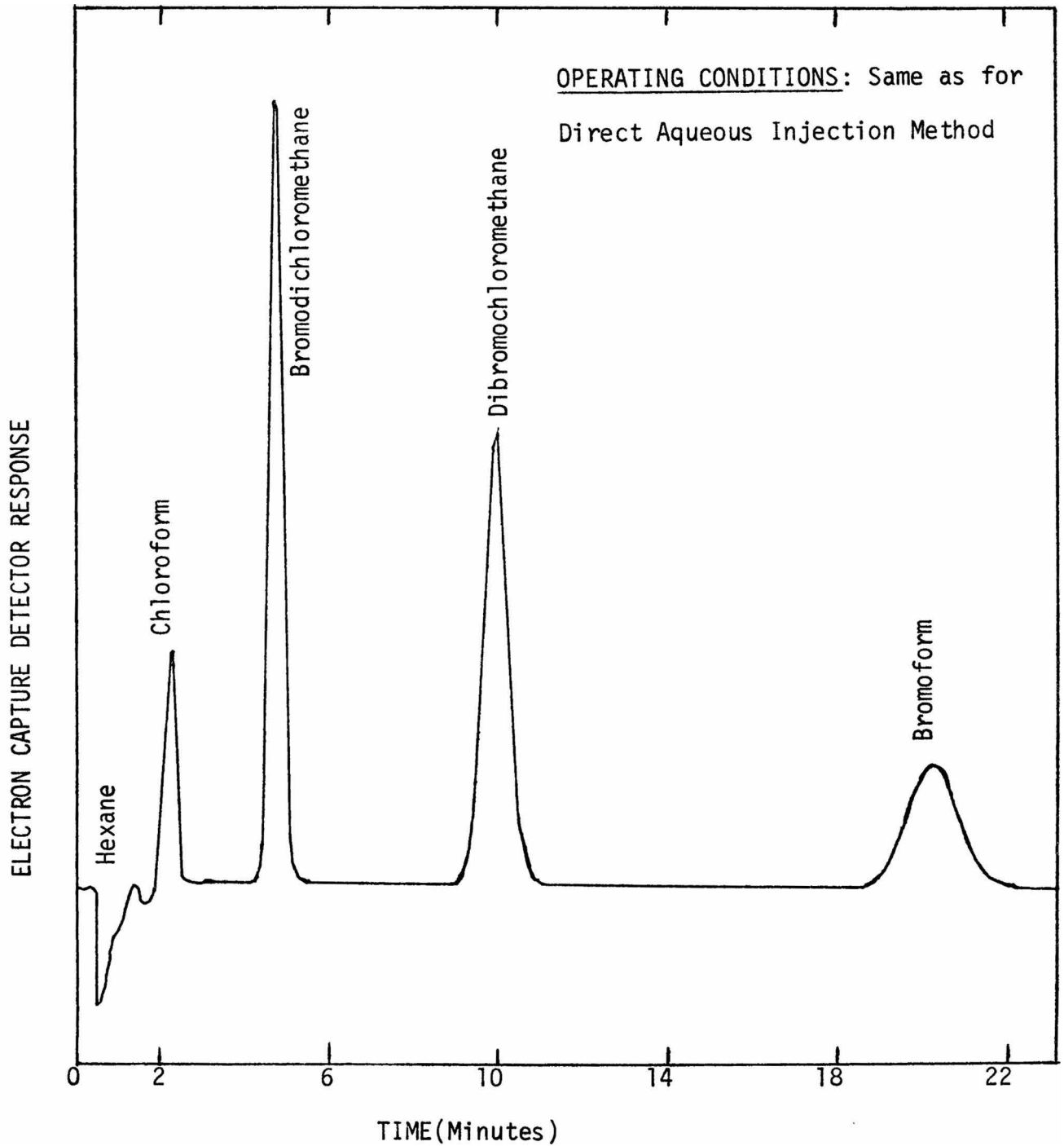
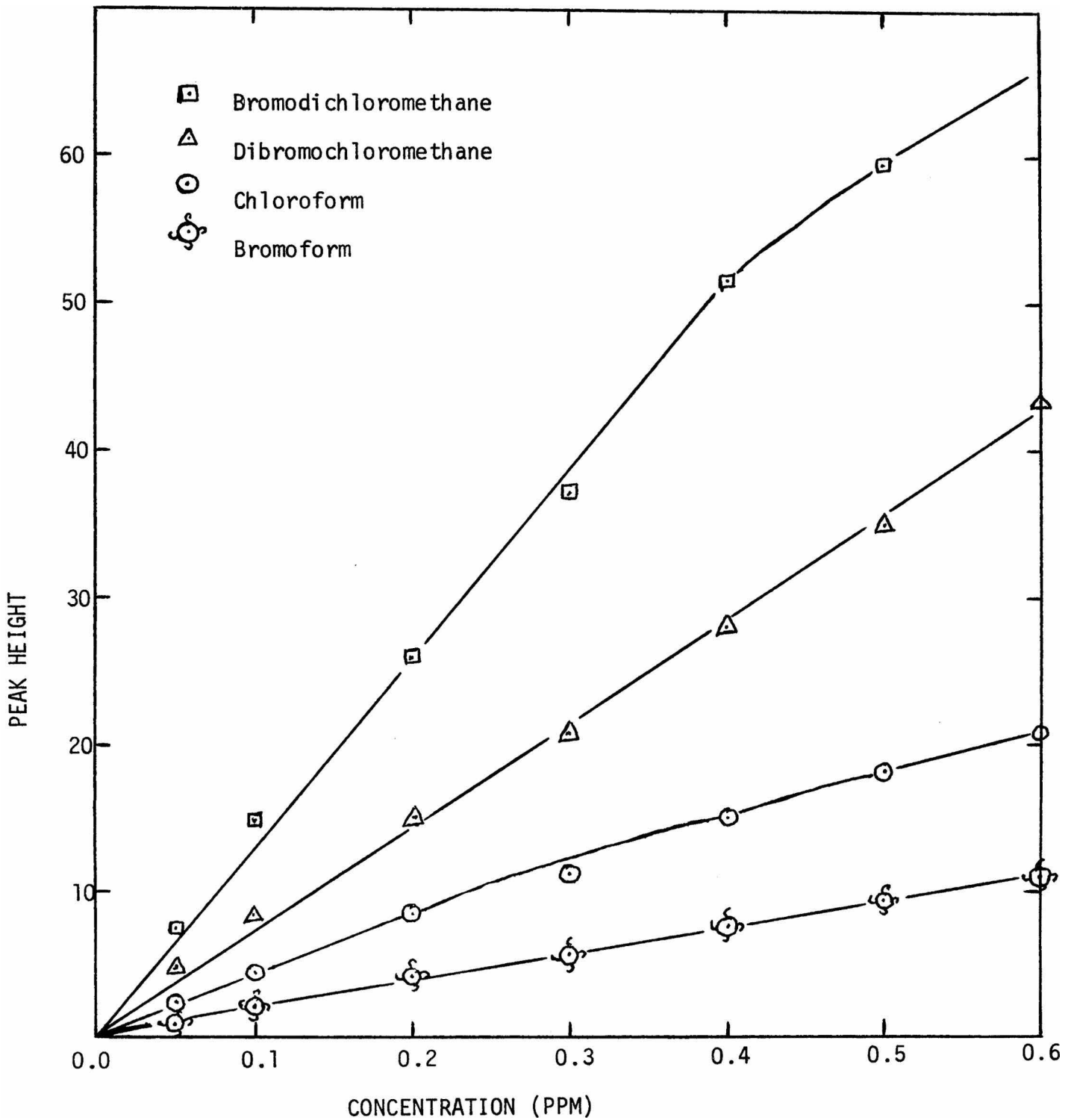


Figure 5: Standard Curves for Trihalomethanes by Solvent Extraction into Hexane from Aqueous Solution



filled and tightly sealed container under vigorously-stirred condition for half-an-hour or longer.

b. Removal of Trihalomethanes and Their Precursors by Powdered Activated Carbon (PAC)

The laboratory experiments were designed to simulate the existing conditions at the Little Rock Water treatment facility, with the intention of eventually applying the results to plant-scale evaluation. At the treatment plant here, the treatment time with PAC occasionally employed to lower the total trihalomethane level in finished water, is approximately 24 hours. PAC is applied at the reservoir and is filtered at the treatment plant which is about 25 miles away. Water is chlorinated twice -- once at the reservoir site and the other at the plant. It appears, therefore, that significant amounts of trihalomethanes can be formed during this period. Should PAC be used during the same phase, it is conceivable that both free trihalomethanes as well as the precursors could react. It was, therefore, decided to evaluate the adsorption of both on PAC. Figure 6 shows the adsorption of trihalomethanes after 24-hour PAC treatment. One sees that all four trihalomethanes are adsorbed significantly. A quantitative estimate of the removal is given in Table 2. Using PAC concentration of 1200 ppm or more, complete removal of all trihalomethanes can be achieved even though they are present at 1 ppm level each. It is interesting to notice that longer PAC-treatment does not seem to remove trihalomethanes significantly. The same solutions analyzed after 72-hour PAC treatment did not



Figure 6: Adsorption of Trihalomethanes on Powdered Activated Carbon

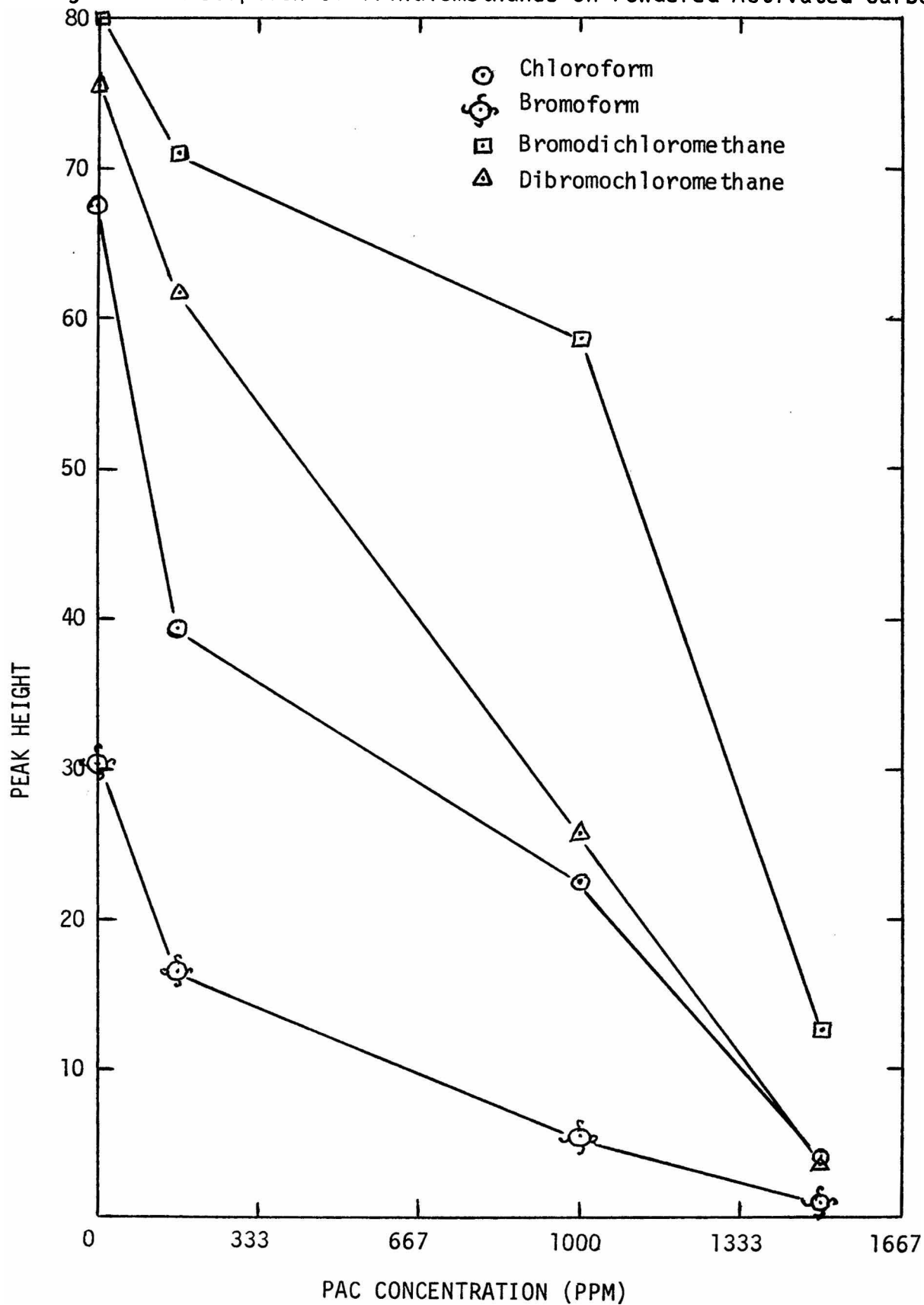


Table 2: Removal Efficiency of Powdered Activated Carbon on Trihalomethanes after 24-Hour Treatment

SOLUTION #	PAC CONC.(PPM)	PERCENT REMOVAL OF CHCl <sub>3</sub>	PERCENT REMOVAL OF CHBrCl <sub>2</sub>	PERCENT REMOVAL OF CHBr <sub>2</sub> Cl	PERCENT REMOVAL OF CHBr <sub>3</sub>
1	166.7	41.5	11.2	18.1	45.9
2	1000	66.7	26.6	65.7	82.0
3	1200	94.1	84.4	95.4	96.7

remove trihalomethane to a great extent. However, when another 1000 ppm of PAC was added to each of solutions #1 and #2 (Table 2), and stirred for two hours, complete removal of all trihalomethanes was achieved. It appears from the later experiment that the adsorption process is quite rapid. This was further verified by studying the adsorption kinetics of chloroform on PAC. Figure 7 shows the results of 1000 ppm PAC treatment on an 1 ppm chloroform solution. The kinetic follows a typical first order reaction, and chloroform was completely adsorbed on PAC within one hours.

The removal efficiency of PAC on THM-precursors (e.g. humic acid) was also evaluated. The results of the effect of PAC on humic acid after 24-hour treatment are shown in Figure 8. As expected, chloroform was the only halomethane formed. Due to lack of a proper facility, the non-volatile total organic carbon (NVTOC) could not be measured to estimate the extent of removal of humic substances. An estimate of the remaining amount of humic substances was obtained, indirectly, by measuring the amount of chloroform produced after chlorination. This method of evaluation, however, cannot be quantitative, since the relationship between humic acid content and chloroform formation was not established by another experiment in our laboratory. However, a linear relationship is expected. Table 3 shows the percent removal of chloroform produced from humic acid as a result of PAC treatment. One sees that the humic acid concentration of up to 2.34 ppm can be removed almost quantitatively by 1667 ppm PAC within 24 hours. However, 533 ppm PAC could not remove

Figure 7: Adsorption Kinetics of Chloroform on Powdered Activated Carbon

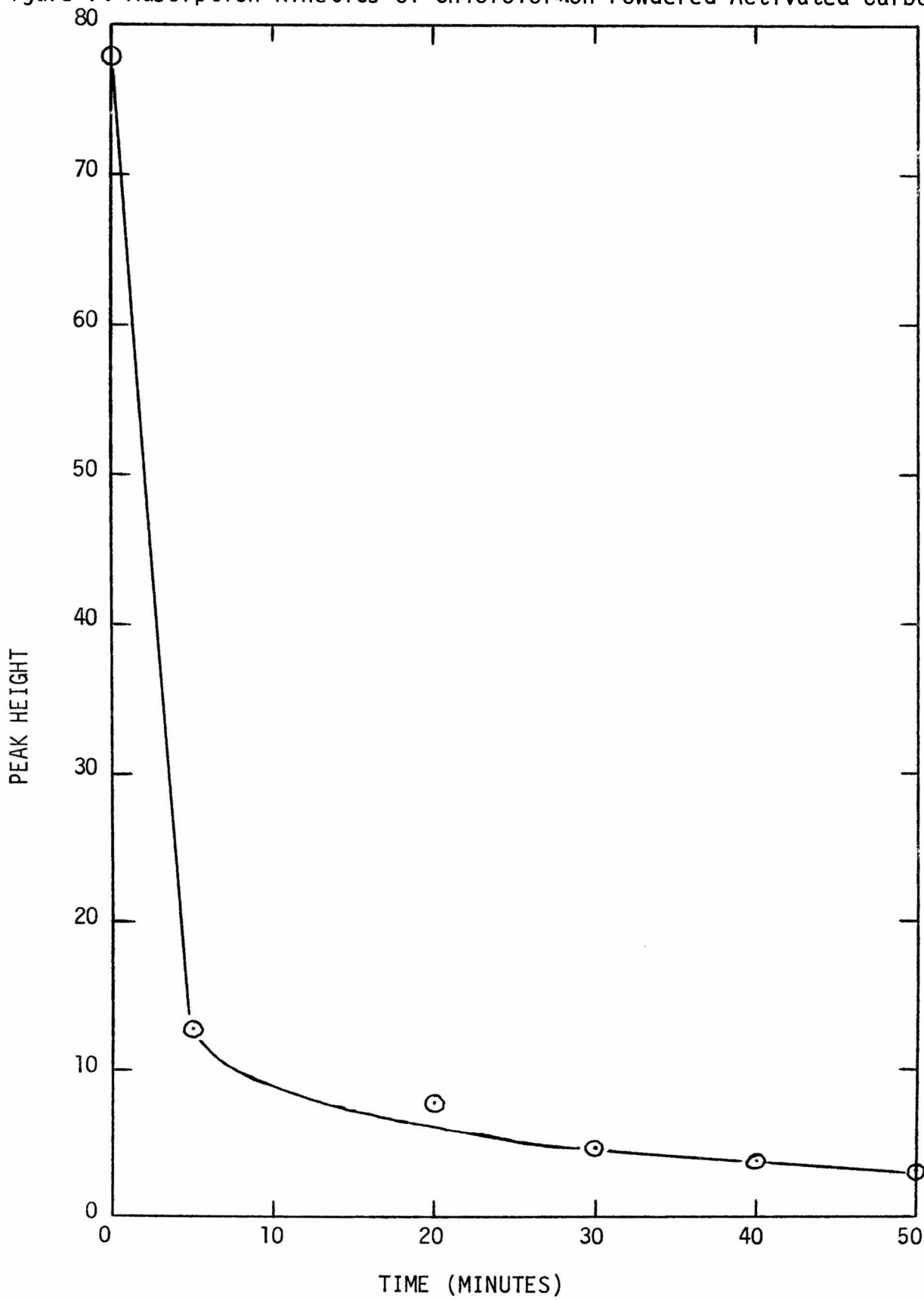
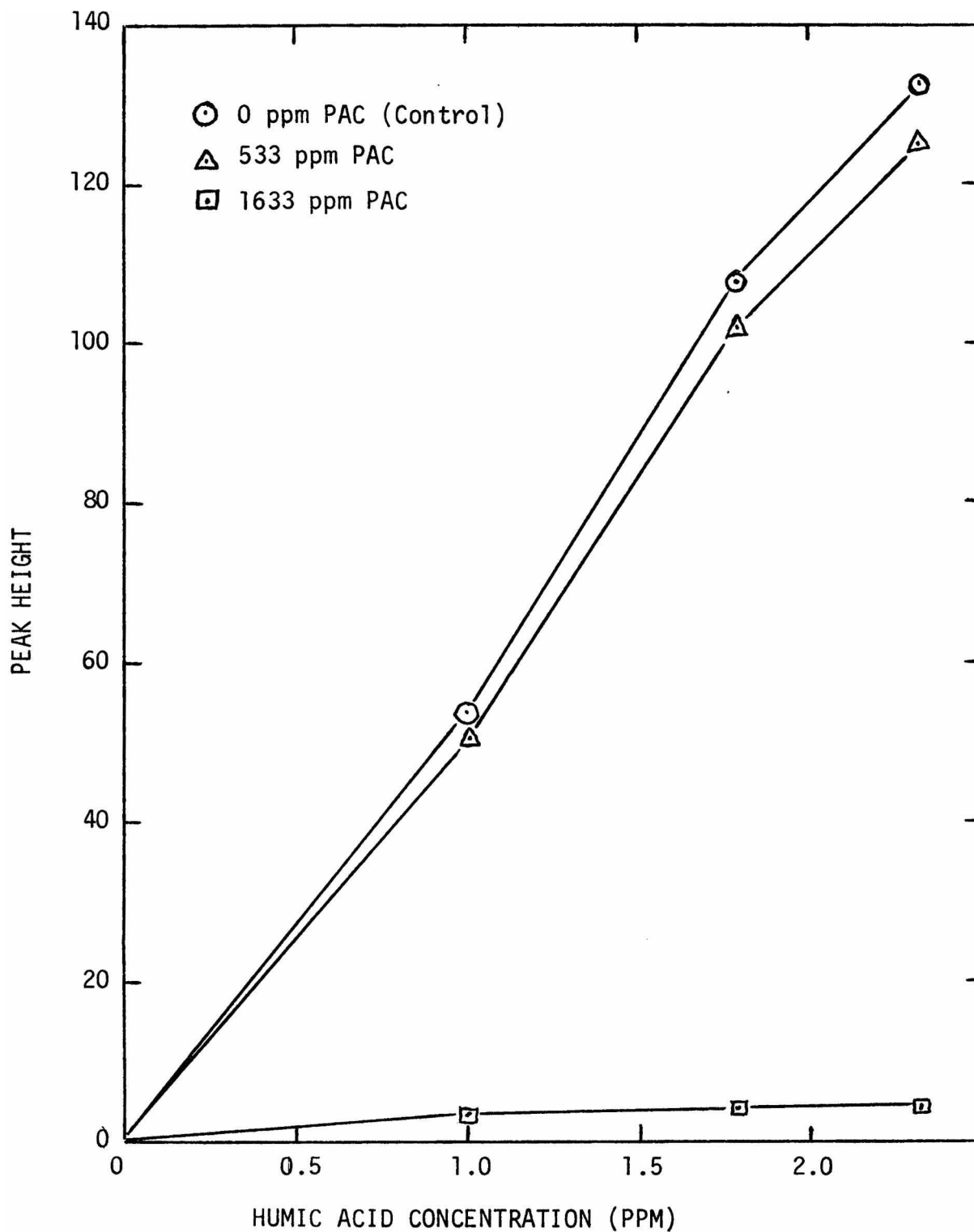


Figure 8: Removal Efficiency of Powdered Activated Carbon on Humic Acid Solution (Twenty Four Hour Treatment)



the precursors significantly within the same time period. PAC-treatment for a longer period of time (e.g. 7 days) can remove humic acid to a great extent, as illustrated in Figure 9.

Studies were also conducted to evaluate the removal of humic substances from lake water by PAC-treatment. The results are shown in Figure 10. Chloroform was found to be the major THM formed (>95%), with a small amount of bromodichloromethane. Using chloroform formation as an indicator of humic acid removal, it was observed that 1665 ppm PAC was sufficient to remove THM precursors almost completely from lake water after 24-hour treatment. Because of the low level of chloroform formation from lake water, solvent extraction was performed to preconcentrate trihalomethanes by a factor of ten. A rough estimate of about 85 ppb of chloroform formation was obtained for lake water sample not treated with PAC. This agrees quite well with data obtained at the water treatment plant, where an annual average of 60 ppb chloroform was found in finished water.

Table 3: Removal Efficiency of Powdered Activated Carbon on Humic Acid Standards and Natural Water after 24-Hour Treatment

<u>SAMPLE TYPE</u>	<u>SAMPLE CONC. (PPM)</u>	<u>PAC CONC. (PPM)</u>	<u>Percent Removal of CHCl<sub>3</sub> Produced</u>
Humic Acid	1.00	533 1667	6.54 93.5
Humic Acid	1.67	533 1667	5.82 96.8
Humic Acid	2.34	533 1667	5.60 97.0
Lake Water	----	333 1000 1650	36.0 80.0 95.0

Figure 9: Removal Efficiency of Powdered Activated Carbon on Humic Acid Solution (Twenty Four Hour and Longer Treatment)

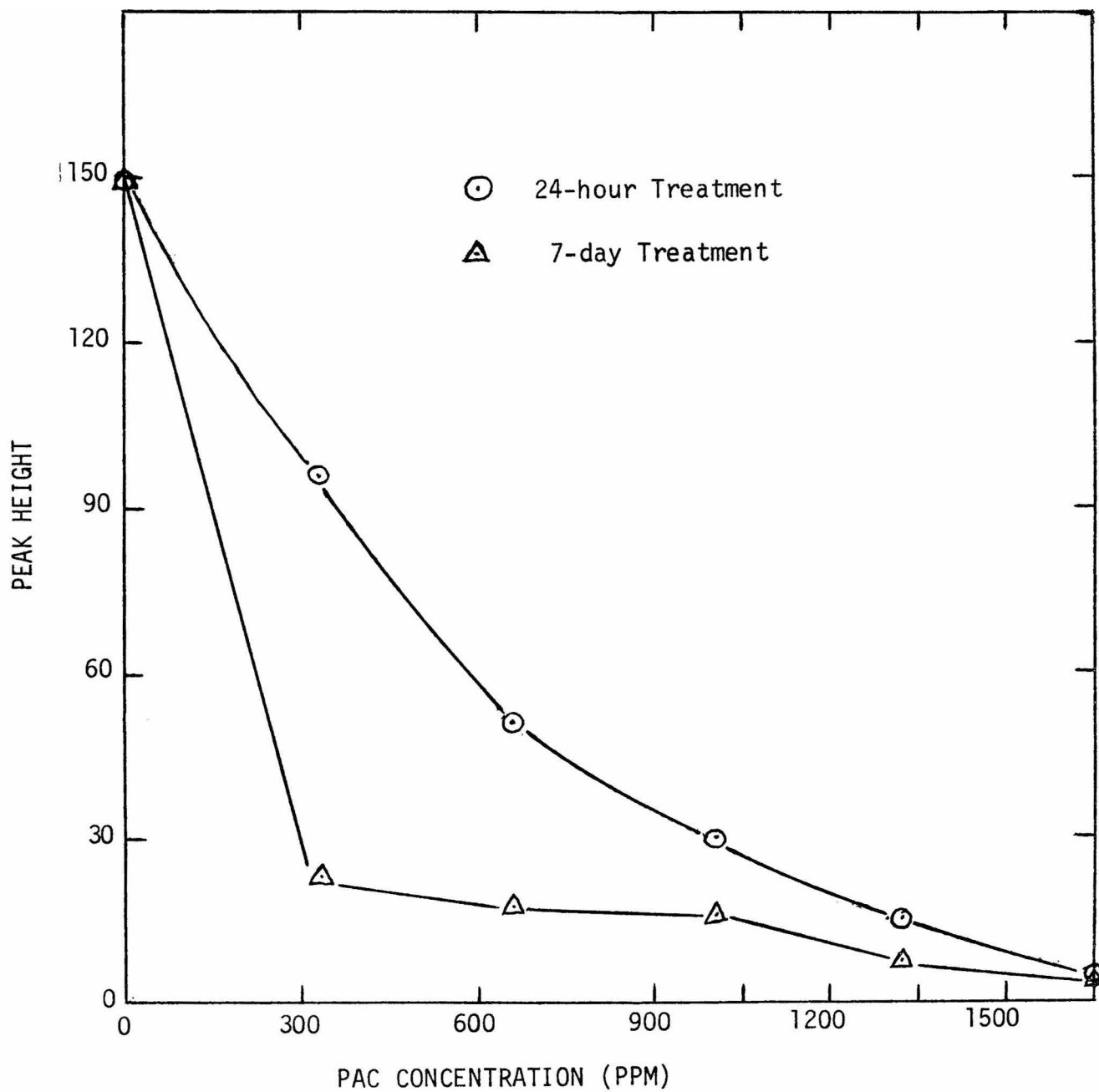
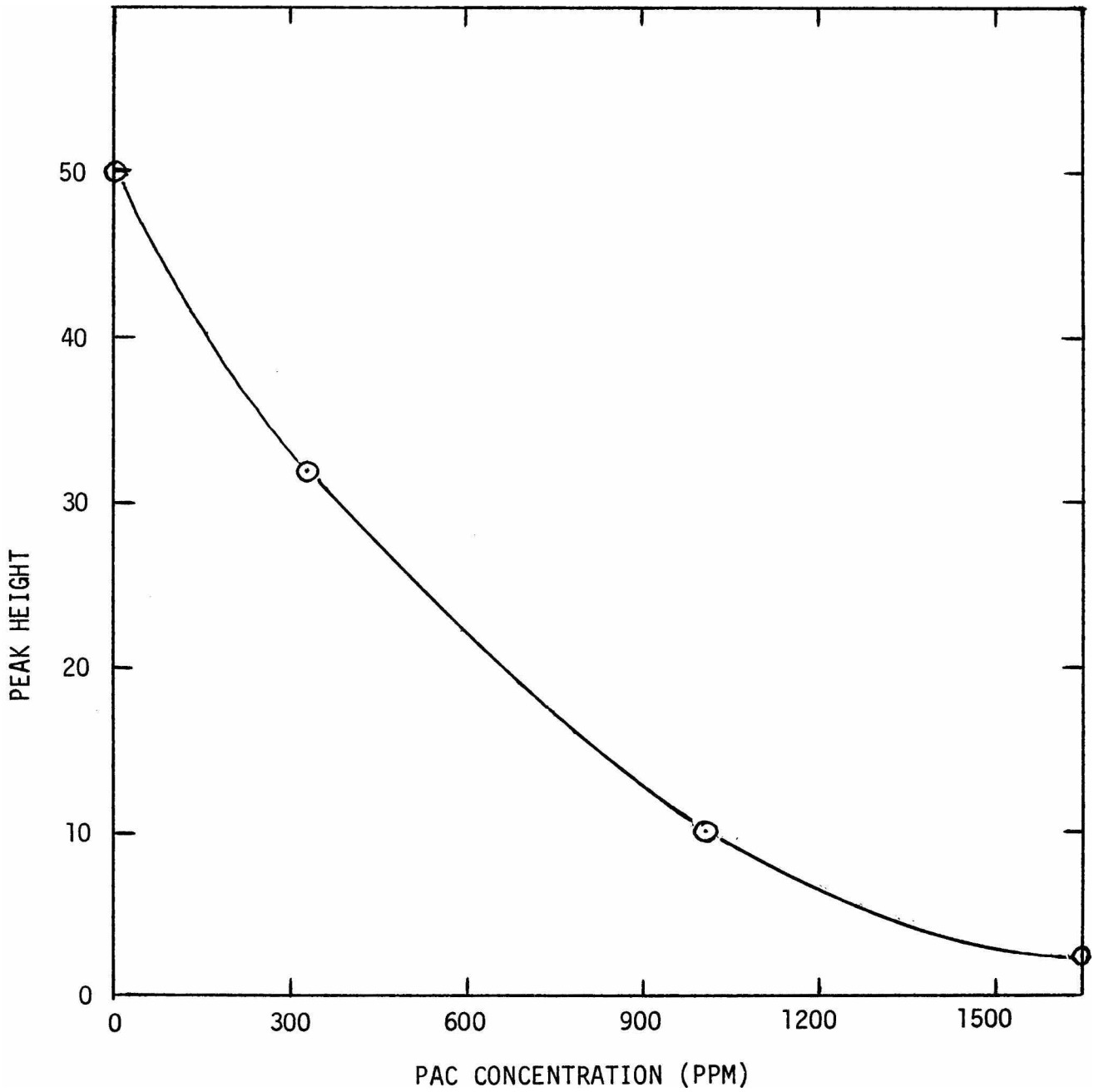




Figure 10: Removal Efficiency of Powdered Activated Carbon on Lake Maumelle Water



#### IV. CONCLUSION

It has been well-documented in the literature that the formation of trihalomethanes as a result of chlorination of natural water is affected by (a) the level of humic substances, (b) the pH of water, (c) the temperature of water, and (d) the concentration of dissolved salts, especially bromide. Extensive research has been conducted to understand the mechanism of THM formation, as well as to develop methods for controlling them. The most common approach to control the amount of trihalomethanes in "finished" drinking water has been the removal of THM precursors by using granulated activated carbon or coagulants. The initial goal of this project, therefore, was to develop a combined powdered activated carbon/coagulant method for efficient removal of the precursors by first, a systematic laboratory study to evaluate their effect and second, to apply the results to a plant-scale study at the Little Rock water treatment facility. Due to severe cutback in funding and shorter project duration, the goal has been revised extensively. The studies conducted under this project, though very positive and quite significant, ought to be considered preliminary results toward achieving an efficient and cost-effective method for controlling trihalomethanes.

The significance of results obtained in this study is two-fold:

1. Powdered activated carbon can remove free trihalomethanes in aqueous solution very rapidly with high efficiency. A part per million level of all four commonly found

trihalomethanes can be removed almost quantitatively within an hour or two using 1200 ppm level of PAC.

2. PAC can also remove THM precursors, such as humic acid. However, the removal efficiency is much lower than that of halomethanes. Long treatment time is required for efficient removal.

Due to lack of high sensitivity of the analytical methods used for the present study, the level of THMs used for laboratory studies was much higher than normally found in water. Consequently, larger dosages of PAC were used to cause significant removal. Although it is reported in the literature that relatively large PAC dosages are necessary for removal of THMs from surface waters, the present study reveals that much smaller amounts of PAC may suffice in controlling trihalomethanes in water. Further studies are being conducted to develop more sensitive analytical methods so that studies using smaller concentrations of trihalomethanes, their precursors and PAC can be conducted with better precision and accuracy.

Until now, most workers have attempted to control THM precursors in water. Since the overall goal for water utilities is to minimize trihalomethane level in "finished" water, an idea generated by the results of this research can be employed easily to plant-scale study. Since PAC can remove trihalomethanes more efficiently than its precursors, it would be practical to add a treatment chamber where high dosages of PAC will be in contact with water under vigorously stirring condition for two or three hours. The chamber may be

located just before the final water filtration bed prior to the consumer tap. Most of THMs can be removed by this procedure. Referring to Little Rock water treatment facility, it may not be necessary to conduct PAC-treatment for 24 hours. Two-point chlorination may still be continued for better disinfection. However, residual chlorine in "finished" water must be reduced in order to minimize THM formation at a later stage.

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