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TECHNICAL COMPLETION REPORT

Project Number A-048-NH

Water Resource Research Center
University of New Hampshire
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ABSTRACT

The formation of halogenated organic compounds in drinking waters is a potentially serious environmental problem. This study examined the production of trihalomethanes by the chlorination of drinking waters containing fulvic acid and the effects of conventional water treatment processes on this phenomenon. Fulvic acid is defined as the acid and base soluble fraction of soil humic matter and is an important precursor to trihalomethane formation. The purpose of this investigation was to relate chemical characteristics of fulvic acid to trihalomethane formation potential and to provide an understanding of the removal of this potential by treatment processes such as coagulation. Initially, fulvic acid was further fractionated into four subfractions by column chromatograph techniques. Chemical analysis via C-H-N-O elemental analysis, infrared spectroscopy, and nuclear magnetic resonance spectroscopy was employed to gain information on functional group content and distribution. The chlorination of fulvic acid fractions confirmed that fulvic acid compounds are significant precursors to trihalomethane formation and indicated that a number of chemical structures and functional groups is involved in the haloform reaction. Chloroform yields, on a carbon basis, of .28-.45% were observed. The removal of fulvic acid in coagulation processes and its relationship to trihalomethane formation upon subsequent chlorination were studied in controlled experiments. Coagulation is the principal treatment process for removal of trihalomethane precursors in most treatment plants. Results indicated that coagulation does not uniformly remove all fulvic acid compounds. Evidence suggests that low molecular weight aromatic compounds are poorly removed by coagulation processes. In addition, studies demonstrated that the trihalomethane yield of fulvic acid compounds decreased significantly following coagulation.

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Finally, this report contains the significant contributions of the graduate students involved in the project whose ideas and laboratory efforts were substantial. These students, Richard L. Bixby, Marc A. Jewett, and Kenneth M. Stewart made the work embodied in this report a stimulating and enjoyable experience.

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INTRODUCTION

In recent years, concern has been mounting over the occurrence of organic contaminants in drinking water and their effect on human health. Existing analytical technology has revealed the presence of over 700 organic compounds in various water supplies across the nation (1). A total of 298 volatile organic compounds were considered by the National Research Council as having reportedly high concentrations in drinking water and for which data suggest toxicity to man (2).

One class of compounds, the trihalomethanes, are of particular concern as they are known to be byproducts of the water chlorination process. Chlorine, when applied at normal disinfection levels, can react with naturally occurring organic matter present in the raw water to form the trihalomethanes. Trihalomethane formation during chlorination presents a potentially serious health problem as chloroform, the primary trihalomethane species formed in the process, has been implicated in several types of cancers in laboratory animals.

The production of trihalomethanes is unavoidable in those water treatment plants which employ chlorination as a disinfection process. The recent water supply surveys conducted by the Environmental Protection Agency (EPA) found that 95 to 100% of the finished chlorinated drinking waters surveyed contained chloroform in concentrations ranging from .1-311 μg/ℓ (3). Although the chloroform concentrations in drinking water may be small relative to the total human exposure from all possible sources, the fact that a suspected carcinogen can be distributed through public water supplies justifies further research as to the extent, formation, and control of halogenated organics in finished water.

The specific organic compounds identified in U.S. drinking waters can be divided into two major classes: (1) Those of natural origin and (2) Those of synthetic origin.

The natural substances represent by far the greatest portion by

weight and consist primarily of humic and fulvic material produced by the decomposition of organic matter. These compounds, which may number one thousand or more, are not considered to be harmful.

The synthetic organic compounds can be further subdivided into two groups:

1. Those chemicals, such as carbon tetrachloride and pesticides, which are introduced to the water source as a result of point and non-point source pollution from industrial and municipal discharges as well as from land surface runoff.
2. Those chemicals that result from water chlorination practices, such as the trihalomethanes.

It is this latter group of the synthetic organic compounds that is of concern in this study.

Ten distinct trihalomethane compounds can be formed upon chlorination but national surveys have identified only four in finished drinking waters. These are:

$CHCl_3$	chloroform (trichloromethane)
$CHBrCl_2$	bromodichloromethane
$CHBr_2Cl$	dibromochloromethane
$CHBr_3$	bromoform (tribromomethane)

The concentrations of these compounds in raw and finished waters, as measured in a national EPA survey (3), are presented in Table 1. Chloroform is almost universally found in the highest concentration, often representing greater than 90% of the total trihalomethane concentration.

The trihalomethane production reaction can be basically stated as follows:

$$HOCl + \text{Organic Precursor} \rightarrow \text{trihalomethanes} + \text{other degradation products} \quad (1)$$

Hypochlorous acid (pKa = 7.5) is the aqueous form of molecular

Table 1

Results of National Organics Reconnaissance Survey
Afer Symons et al. (3)

	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$
Raw Water	nf-0.9	nf-0.8	nf	nf
Finished Water	0.1-311	nf-116	nf-100	nf-92
Median Finished Water	21	6	1.2	below detection limit

nf indicates none found

chlorine and is a strong chemical oxidant. The organic reactant in this overall equation is given the nondescriptive appellation, "organic precursor", to indicate two points. First, it is generally felt that a wide variety of organic compounds from diverse sources (humic matter, algal debris, agricultural runoff) can serve as precursors. Secondly, the exact chemical identity of the organic precursor compounds in most instances has yet to be discovered. This is especially true of naturally occurring humic compounds. The precursor compounds to be studied in this investigation will be limited to the fulvic acid fraction of soil-derived humic material.

Nature of Fulvic Acid

Fulvic acid is a generic term for the acid and base soluble fraction of humic material found in nature as a result of the decomposition of plant and animal matter. The humic compounds are darkly colored, aromatic, acid complexes, with molecular weight ranging from a few hundred to many thousand molecular weight units (4). The humics form the bulk of the organic load of natural waters, are extremely resistant to microbial attack, and exhibit long residence times in the aquatic environment.

Humic substances are catagorized on the basis of solubility criteria. The classification scheme developed by Oden (5), still in use today, acknowledges three major fractions. Under this scheme, humic acid is soluble in base, but not acid; fulvic acid is soluble in both acid and base; and the humin fraction is that material not soluble in water. A fourth and lesser component is recognized as hymatomelanic acid, which is that portion of humic acid soluble in alcohol.

The three major fractions are structurally similar but differ in molecular wieght and functional group content, with the fulvic acid fraction having a lower molecular weight than the humic acid and humin fractions, and a higher proportion of oxygen containing functional groups (4).

It is important to note that this classification scheme is somewhat arbitrary and not always satisfactory, as the fractions are considered molecularly heterogeneous with the resultant composition more dependent on the nature of the source material and its state of degradation.

A number of researchers have investigated the distribution of humic materials in naturally colored waters. Black and Christman (6) found the fulvic acid fraction accounted for 83 - 90% of the total organic residues isolated from ten different water bodies. Humic and hymatomelanic acids comprised the remaining weight of the isolates. Bordelon (7) in a study of freshwater habitats in Louisiana found a distribution of 83% fulvic acid, 13% hymatomelanic acid, and 4% humic acid. The ratio was quite consistent throughout the aquatic systems investigated.

Humic material consists of polymeric units whose basic structure is aromatic rings which are bridged by -O-, -NH-, CH_2-, or -S- linkages (4). Attached hydroxy groups provide acidity, hydrophilic properties, and cation exchange capacity. Fulvic acid is considered to be the least polymerized of the fractions.

Wershaw and Pinckney (9) have conducted extensive investigations into the nature and properties of aquatic humus. Based on their findings, they conclude that fulvic acids are complex mixtures of molecular aggregates with different chemical and physical properties. In theory, a whole host of structurally different compounds could exist within the fulvic acid fraction, provided they had similar solution properties. In order to obtain detailed structural information about these materials, it was first necessary to fractionate the chemically similar components found within the fulvic acid mixture.

Since the conclusions by Dubach and Meta (10) that no two molecules of fulvic acid may be exactly identical, a number of researchers have attempted to isolate the chemically similar molecular species which comprise a complex mixture such as fulvic acid. The most common approach is to attempt a molecular weight

fractionation by gel-permeation chromatography (11, 12, 13).

However, with complex unknown mixtures such as fulvic acids, one cannot be sure that the mixture consists of uniform materials which will behave ideally on the gel. In this case the fractionation is more dependent upon chemical interactions, such as adsorption and electrostatic attraction. As a result, chemical separation is possible based on the functional group composition of the molecule (9). Hence chemically homogeneous fractions can be isolated with this technique.

Although the occurrence of fulvic acid in natural waters does not in itself constitute a known health hazard, there exist a number of reasons for concern over the reactive properties of this material.

Fulvic acid has been shown to be a complexing agent for di- and tri-valent metal ions in aqueous solutions (4). As a result, toxic metal ions can be held in solution at greater concentrations than would normally occur without the presence of the organic matter.

Similarly, Poirrier, et al. (14) demonstrated that DDT was adsorbed by aquatic humus and concentrated over 15,000 times its ambient concentrations in the water phase.

Color in water is undesirable for asthetic reasons, and as a result the current drinking water standards limit the color of filtered water to 15 platinum-cobalt units. High concentrations of color can also limit the productivity of natural waters through the capacity to absorb photosynthetically active light (7).

And lastly, fulvic acid has been implicated as a precursor in the haloform reaction during the chlorination process. Rook (15) presented experimental evidence for the formation of trihalomethanes as byproducts of the chlorination of naturally colored waters containing fulvic acid. He tested the assumption that aromatic rings with metapositioned hydroxyl groups may be the active site for haloform formation, and used model substances known to contain these structures. His results indicate that metahydroxylated

benzenes can undergo the haloform reaction when treated with chlorine. Since these structures are possible within the fulvic acid molecule, Rook speculates this site may be responsible for the observed levels of chloroform during the chlorination of naturally colored waters.

Trihalomethane Formation in Water Treatment Plants

Referring to the overall trihalomethane reaction, equation 1, several obvious approaches to the control of trihalomethanes in water treatment plants become evident. These can be summarized as follows:

1) Discontinue the use of chlorine as a disinfectant.
2) Remove trihalomethanes after formation by existing or new treatment processes.
3) Reduce or eliminate the precursor concentration before contact with chlorine.

In recent years, extensive research has been conducted in areas pertinent to each of the above strategies. The study of alternative disinfectants such as ozone, chlorine dioxide, and chloramines, all of which do not result in trihalomethane formation, has accelerated. Much interest has been generated in the use of synthetic resin and activated carbon adsorption processes for removal of organic compounds, including trihalomethanes. However, a more economical approach, especially for the small plants typically found in New England, is embodied in the third alternative: modification and optimization of existing treatment processes to maximize precursor removal. This may involve many different and independent actions such as changing the point of application of chlorine from the raw water intake to points nearer the filtration process. Reductions in trihalomethane levels by this single process change have been well documented (16, 17) and have been extensively adopted where appropriate.

In water treatment plnats, the principal processes designed for removal of soluble humic compounds are coagulation-flocculation, sedimentation, and filtration. Of these, the most important is the

coagulation-flocculation process (hereafter coagulation) by which the humic compounds are chemically destabilized and aggregated for subsequent removal in the sedimentation and filtration steps. Several laboratory studies have attempted to relate removal of humic substances and trihalomethane formation potential (defined as maximum yield of trihalomethanes obtainable, under conditions of excess time and chlorine). Babcock and Singer (18), as well as Oliver and Lawrence (19), determined chloroform yields of humic solutions before and after coagulation under laboratory conditions and concluded that a selective removal of trihalomethane precursors had taken place. However comforting this result may be, this finding needs further scrutiny and research to determine the causes of this phenomenon. Additional fundamental knowledge of the chemical behavior of humic compounds during coagulation and the impact upon trihalomethane production is needed to determine the extent that process modifications can and should be employed to control chlorinated organics in drinking water treatment plants. This was a major goal of this research.

Research Objectives

The specific objectives of this study were:

1) Characterization of fulvic acid. Fractionation techniques, based upon the principle of adsorption chromatography, were employed to obtain more chemically homogeneous fractions of fulvic acid. Attempts were made to identify structural components and functional groups by spectral methods (IR and NMR). The purpose of these and other chemical analyses was to relate chemical properties of fulvic acid to its behavior in treatment processes.

2) Chlorination of Fulvic Acid. Yields of trihalomethanes were determined as a function of time, chlorine dose, and fulvic acid concentration.

3) Effect of Coagulation on Trihalomethane Production. Utilization of the aforementioned fractionation techniques allowed study of the ability of alum coagulation to remove

trihalomethane precursor compounds.

4) Effect of Treatment Plant Practices on Trihalomethane Production. The effects of time, temperature, and point of application of chlorine were studied at the Durham-UNH Water Treatment Plant at Durham, New Hampshire, which treats a moderately colored surface water.

EXPERIMENTAL

Analytical Methods

Water free of interfering organics was obtained by passing deionized water through a Barnstead "Nanopure" treatment system. This system consistently produced water with a chloroform concentration of less than 1 $\mu g/\ell$ and was found acceptable for preparation of gas chromatography (GC) standards and other reagents. As will be discussed later, contamination of glassware by adsorbed organic compounds caused problems in the analysis of trihalomethanes. A rigorous glassware washing procedure was followed for all glassware (described later) and all pipettes, beakers, and other glassware was stored after washing in an oven at a temperature above $150^{o}C$.

Isolation of Fulvic Acid

The fulvic acid used in this study was isolated from an organic-rich B_2 horizon podzol soil donated by Dr. J.H. Weber of the University of New Hampshire Chemistry Department. The fulvic acid was extracted by the use of a modification of the method of Schnitzer and Skinner (20) developed by Weber. Distilled water (16 l) was placed in a five gallon carboy and purged of air with nitrogen gas. Then 2.5 kilograms of soil and sufficient sodium hydroxide to make the solution 0.5M were added. The solution was allowed to stand for 24 hours with an occasional vigorous shake. Basic solutions were kept under a nitrogen atmosphere at all times.

The solution was decanted from the residue and centrifuged for thirty minutes at 10,000 G to remove any traces of colloidal impurities. The centrifuged solution was passed through a column which contained the hydrogen ion form of rexyn 101H strong acid cation exchange resin. The pH of the effluent was monitored closely and when it began to rise the resin was regenerated. This process exchanges H^+ for Na^+ which lowers the pH and the humic acid precipitates in the column.

The acidified fulvic acid solution was evaporated to a very concentrated state under reduced pressure at 40°C. The concentrate was freeze dried to produce powdered fulvic acid and stored in a dessicator under P_2O_5.

Fractionation of Fulvic Acid

The fractionation of fulvic acid was accomplished by Sephadex gels under conditions designed to promote gel-solute interactions. Under normal operation, Sephadex chromatography is based upon the principle of size exclusion from the porous gel beads. However, in this study the sample was added to the chromatographic column at pH 11 and eluted with neutral pH eluant (organic free water). A pH gradient is set up within the column and ion exchange and adsorptive processes may influence the separation. Hence, the separation is not strictly due to molecular weight differences in a heterogeneous mixture of compounds. Wenshaw and Puckney have discussed the nature of Sephadex separations under varying solution conditions (9).

The purpose of this fractionation procedure was to obtain a chemical separation of fulvic acid compounds. Because of the fractionation techniques used in this study, it would be difficult to assign molecular weights to the fractions by calibration of the column with known molecules because of shape and orientation differences between the standards and the unknown fulvic acid molecules. Determination of molecular weights by other traditional techniques were not possible due to the very limited amounts of the fractions that were available. Therefore, in this investigation no attempt will be made to correlate chemical properties of the fulvic acid fractions to molecular weight except where evidence from other studies can be used.

Separation was accomplished using three grades of Sephadex gels, packed into individual 5 cm diameter prep-scale chromatography columns. Initial separation was accomplished on Sephadex G-50, packed to a height of 52 cm. A 1% fulvic acid solution was prepared

and the pH adjusted to 11 with sodium hydroxide, to enhance gel interactions (9). 13 ml of the fulvic acid solution was carefully applied to the G-50 column and eluted with organic-free water at a flow rate of 127 to 173 ml per hour. 9 ml portions of eluate were collected automatically with a Gilson fraction collector. Following collection, the absorbance of the eluate was measured at 435 nm with a Bausch and Lomb Spectronic 70 spectrophotometer. The results of the separation were plotted and the cutoff points between fractions determined graphically. Following intitial fractionation on Sephadex G-50, the three major fractions were each concentrated to 50 ml using the technique described below, and refractionated on either a 26 cm G-25 column or a 68 cm G-100 column. The absorbance of the eluates was measured at 500 nm.

Since heat-induced concentration methods are thought to denature fulvic acid, a rotary freezing technique was used to reconcentrate the fractions in this study. A 500 ml round bottom flask half filled with eluate was immersed in a mixture of crushed ice and salt (about $-12^{\circ}C$). Seeding of flasks with a small layer of ice prevented flash freezing. The flask was attached to the rotor of a Buchler flash evaporator and rotated until a predetermined volume of pure water had been frozen, usually concentrating the diluted fractions by a factor of about 10.

Following completion of the refractionation process, the eluates were again freeze concentrated, and then freeze dried for 48 hours on a freeze drying apparatus. The solid fractions were placed in individual glass vials, sealed, and stored in a dessicator under P_2O_5.

Analysis of Trihalomethanes and Other Chlorinated Organics

A Barber-Colman Series 5000 gas chromatograph equipped with a ^{63}Ni electron captive detector (ABC Labs, Columbia, MO) was used for all GC analyses. Operating conditions were: carrier gas, N_2 at 60 mls/min; column temperature, $75^{\circ}C$; injector temperature, $120^{\circ}C$; detector temperature, $280^{\circ}C$. The columns were glass, 6' x ¼",

packed with either 6.9% Carbowax 20M on 60-80 mesh Chromosorb G or 0.2% Carbowax 1500 on 60-80 mesh Carbopak.

Analyses of volatile organic compounds at the parts per billion (ppb) level is subject to several types of errors. Extensive investigation of analytical GC laboratory procedures demonstrated that volatilization of chloroform and other compounds from organic solvents was a significant problem. This was handled by using 40 ml screw cap vials with teflon faced septa (Pierce Chemical Co.) for storage of GC standards under headspace free conditions. The septum allowed withdrawal of sample without opening the vial. Standards stored in this manner were found to remain unchanged for 3 months.

A second source of error was adsorption and desorption of organic compounds on glassware. For instance, chloroform could adsorb onto glass surfaces from high strength solutions and subsequently desorb in more dilute solutions. This was controlled by the following glassware washing procedure which was used for all pipettes, beakers, flasks, and sampling vials used in GC analyses. Glassware was soaked overnight in chromic acid cleaning solution, rinsed thoroughly with organic free water, dried in an oven at 125°C, rinsed with isooctane, baked for 2 hours at 125°C, and stored in an oven at 125°C until just prior to use. Tests showed that these procedures prevented glassware contamination problems.

Liquid-Liquid Extraction Method for Trihalomethanes

Analysis of trihalomethanes in water was performed by a liquid extraction method similar to that described by Richard and Junk (21). Initially, pentane was used as the solvent with a sample/pentane ratio of 5 ml/1 ml. After vigorous shaking for approximately one minute in glass stoppered 15 ml centrifuge tube, 3 ml aliquots of the pentane layer were injected for quantitative analyses. Due to the high volatility of pentane, a switch was made to isooctane as the solvent. Using isooctane, a 1:1 isooctane/sample ratio

(3 ml each) was utilized. Replicate injections were made for all standards and samples. Reproducibility was very good; peak areas of replicate injections always agreed within ± 5%. The lower limit of detection of chloroform by this method was determined to be 1 µg/ℓ.

GC standards for trihalomethane analysis must be prepared with care. The following procedure was followed to minimize problems due to volatilization. 40.0 ml of isooctane was pipetted into 40 ml screw cap vials. 10 µl of the particular trihalomethane (reagent grade) was injected via GC syringe through the septum into the vial to obtain a stock solution. Dilution from the stock solution into 40 ml vials filled with isooctane by the same technique yielded standards in 9-400 µg/ℓ range.

For quantitative analysis of trihalomethanes in aqueous solution by the liquid-liquid extraction method the extraction efficiency must be known. Aqueous standards of trihalomethanes were prepared by a procedure similar to the above. The initial stock solution was prepared by delivering an aliquot of the trihalomethane via microsyringe into a 40 ml screw-cap vial filled with spectroquality methanol. Dilution of this stock solution into organic free water produced concentrations in the range 9.3 to 232.7 µg/ℓ. The initial dissolution in methanol was necessary because of the low aqueous solubility of the trihalomethane compounds. These aqueous standards then were extracted in the usual manner and quantified by comparison to standards of the compound in isooctane. Calculated extraction efficiencies in this concentration range were 100 ± 5% for chloroform. An extraction efficiency of 100% was used in all calculations of chloroform concentrations.

Purge and Trap Analyses of Volatile Organic Compounds

A method for GC analysis of volatile halogenated organic compounds in water at sub-ppb levels in the purge and trap method. In this procedure, volatile compounds are stripped from solution and adsorbed on a suitable sorbent at room temperature. Subsequently,

the compounds are desorbed at elevated temperature onto a GC column at room temperature with no carrier gas flow. When desorption is essentially complete, the carrier gas flow is commenced and routine GC analysis is performed. The apparatus for this method was constructed exactly according to specifications of Bellar and Lichtenberg (22) (Desorber #2 was used with Tenax GC as the trapping material). Operating parameters were essentially the same as those of Bellar and Lichtenberg (22). In this investigation, the purge and trap method was used for the qualitative identification of chlorinated products of the fulvic acid-chlorine reaction.

Characterization of Fulvic Acid

Fulvic acid and its composite fractions were subjected to a variety of analyses. Carbon, hydrogen, and nitrogen elemental analyses were performed by personnel of the University Instrumentation Center, University of New Hampshire, with an F & M Model 185 C-H-N Analyzer. This analysis is accurate to within 0.5%. Water content was determined on a Perkin-Elmer Thermogravimetric Analyzer (TGA) with an accuracy of 0.1%. The TGA measures weight change with temperature change utilizing a microbalance. The upper temperature limit of the TGA was 500°C. Normally, the ash content of the sample would be determined from the residue after evaporation and combustion in the TGA. However, the fulvic acid fractions would not combust at 500°C and, therefore, were ashed in a muffle furnace at 650°C. Initial and final weights were taken on the TGA microbalance, and the fractions were transported to and from the furnace in a dessicator containing P_2O_5. The precision of these determinations was within 10%, based upon two replicate analyses of each of the four fractions.

Infrared spectra were obtained on a Perkin-Elmer 337 grating spectrophotometer over two frequency ranges. Each fraction was dissolved in a halocarbon mull and scanned over the 4000 cm^{-1} to 1300 cm^{-1} range. Then the fractions were dissolved in a Nujol

mull and scanned over the 1300 cm^{-1} to 600 cm^{-1} frequency range.

Aqueous, equimolar (as carbon) samples of the fractions were analyzed in the ultraviolet wavelength region of 200 nm to 350 nm on a Cary 14 Spectrophotometer.

NMR spectra were run on a JEOL FX 90 Q instrument operated in the Fourier transform mode locked on D_2O. Samples were deuterated by successive D_2O washes and freeze drying, dissolved in D_2O, and read in 5 mm tubes. Concentrations of the samples ranged from 23.7 to 78.7 mg/ml D_2O. Both proton and ^{13}C NMR spectra were acquired under frequency domain accumulation with the internal standard allowed to overflow. Full proton decoupling was utilized for ^{13}C NMR spectra. NMR parameters are presented in Table 2.

Miscellaneous Analytical Methods

Fulvic acid concentrations were determined spectrophotometrically at 350 nm in 1 cm cells with a Bausch and Lamb Model 710 spectrophotometer. Equal volumes of sample and a potassium phosphate buffer (76.0 g/ℓ K_2HPO_4) were mixed prior to spectrophotometric analysis. For samples containing turbidity, centrifugation for 15 minutes at 20,000 rpm in an IEC B-20A centrifuge prior to the absorbance measurement removed this interference.

Free residual chlorine was measured by the Stabilized Neutral Orthotdidne (SNORT) method (23). A calibration curve was developed over the range .1 - 2.5 mg Cl/ℓ. Stock chlorine solutions were prepared from a commercial bleach solution and standardized iodometrically (24). In the chlorination yield experiments conducted in phosphate buffer at pH 7.0, it was found that the buffer exerted a significant chlorine demand. Chlorine demand free buffer solutions were prepared by adding 2 - 5 mg/ℓ of chlorine to the buffer solution, allowing reaction to occur over several days in the dark until the chlorine concentration was stable, and discharging the residual chlorine with ultraviolet light.

Total organic carbon (TOC) data were obtained with a Model 524 Total Organic Carbon Analyzer (Oceanography International).

Table 2

^{1}H and ^{13}C NMR Parameters

Parameter	^{1}H	^{13}C
Solvent	D_2O	D_2O
Reference	H_2O	Dioxane
Pulse Interval	1.00ms	1.00ms
Pulse Delay	100ms	0.45s
Frequency	1000Hz	5000Hz
Irradiation Set	54.00KHz	54.00KHz
Acquisition Time	4.09s	0.0190s
Observation Set	44.70KH z	32.700KHz
Observation Frequency	22.5MHz	22.5MHz
Pulse Width 1	5.00us	5.00us
Pulse Width 2	20.00us	20.00us
Dead Time	50.00us	50.00us

Standards were prepared from reagent grade potassium acid phthalate. Appropriate blanks were prepared for all fulvic acid and fulvic acid fraction samples.

Experimental Procedures

Chlorination Yield Experiments

These experiments were conducted in 40 ml screw cap vials with teflon-faced septa. The reaction was initiated by the addition of a stock chlorine solution to a stock solution containing the fulvic acid fraction. In some experiments the pH was maintained at 7.0 with a phosphate buffer (.061 M K_2HPO_4, .039 M KH_2PO_4), in which case the fulvic acid stock solution was prepared in a solution of buffer and added to the stock chlorine solution to start the reaction. Stock chlorine solutions were standardized iodometrically (24). For any given experiment replicate vials were prepared; one was analyzed at each reaction time. Reaction blanks consisting of the reaction solution minus the fulvic acid fraction were also prepared and monitored for residual chlorine and trihalomethane production. Blanks for TOC determinations contained the fulvic acid fraction in the reaction solution with no chlorine added.

Fulvic Acid Coagulation Experiments

These experiments were designed to study the effect of coagulation with aluminum sulfate ($AL_2(SO)_4)_3 \cdot 18\ H_2O$) on the distribution of fulvic acid fractions. Aluminum sulfate was added to a 150 mg/ℓ fulvic acid solution at pH 6 until visible flocculation occurred. The pH was maintained at pH 6 during aluminum sulfate addition by titration with NaOH. The solution was allowed to settle overnight and the overall removal of fulvic acid was determined by spectrophotometric analysis of the residual fulvic acid. The clarified supernatant was decanted and freeze concentrated, freeze dried, and resuspended in 14 ml of organic free water at pH 11.5. (In some experiments, the freeze drying step was omitted and the freeze concentrated solution was adjusted to pH 11.5 with NaOH pellets.) This solution was applied

to a 1.5 cm I.D. column packed to a depth of 61 cm with Sephadex G-50. The fulvic acid was eluted with organic free water at pH 11.5 at a rate of 15 ml/hr. The high pH eluant was necessary to prevent aluminum hydroxide precipitation in the column. Since this fractionation scheme differed somewhat from the original fractionation, retention volumes of each fraction were determined by applying each fulvic acid fraction separately to the column at eluting with pH 11.5 organic free water.

Aluminum-Fulvic Acid Complexation Study

In this experiment, individual fulvic acid fractions were titrated with aluminum sulfate until visible flocculation occurred. Initial fraction concentrations of 20 - 60 mg/ℓ were titrated with a 5000 mg/ℓ stock aluminum sulfate solution at pH 6 maintained with .2 N NaOH. The volume of fraction was 100 ml and after each incremental addition of aluminum, the solution was slowly stirred for two minutes and observed for evidence of floc formation.

RESULTS AND DISCUSSION

Chemical Analyses of Fulvic Acid

The purpose of a further separation of humic matter into discrete fulvic acid fractions was to aid interpretation of experiments designed to study the behavior of fulvic acid in water treatment processes. Sephadex gels were employed for the fractionation with experimental conditions adjusted to enhance solute-gel interactions and hopefully to produce fractions of some chemical homogeneity.

Fractionation of Fulvic Acid

The results of the fractionation of the parent fulvic acid on Sephadex G-50 is presented in Figure 1. The fractionation proved to be very consistent and reproducible. Many column runs were needed to obtain sufficient masses of the fractions for further experiments. Three fractions can be identified and are labeled FA 1, FA 2, and FA 3 in the order of their elution from the column. Each of these fractions was further fractionated on Sephadex G-25 or G-100 columns as described in the Experimental section of this report. These elution curves are shown in Figures 2-4. Several subfractions resulted from the refractionation, but most were minor in terms of their weight percentage of the parent fulvic acid. A fraction was deemed significant if it represented at least 5% of the mass of the parent fulvic acid (percentages were determined by measurement of the appropriate areas under the elution curves). Using this guideline only refractionation of FA 2 produced further usable fractions, labeled FA 2A and FA 2B, again in order of elution from the Sephadex G-25 column. Thus, the fractionation of fulvic acid produced a total of four fractions identified as FA 1, FA 2A, FA 2B, and FA 3. Some experiments reported herein were conducted with just three fractions: FA 1, FA 2, and FA 3. The relative distribution of the fractions, as a percentage of the parent fulvic acid, is presented in Table 3.

Fractionation of the parent fulvic acid, Figure 1, was not

FIGURE 1
FRACTIONATION OF FULVIC ACID ON SEPHADEX G-50

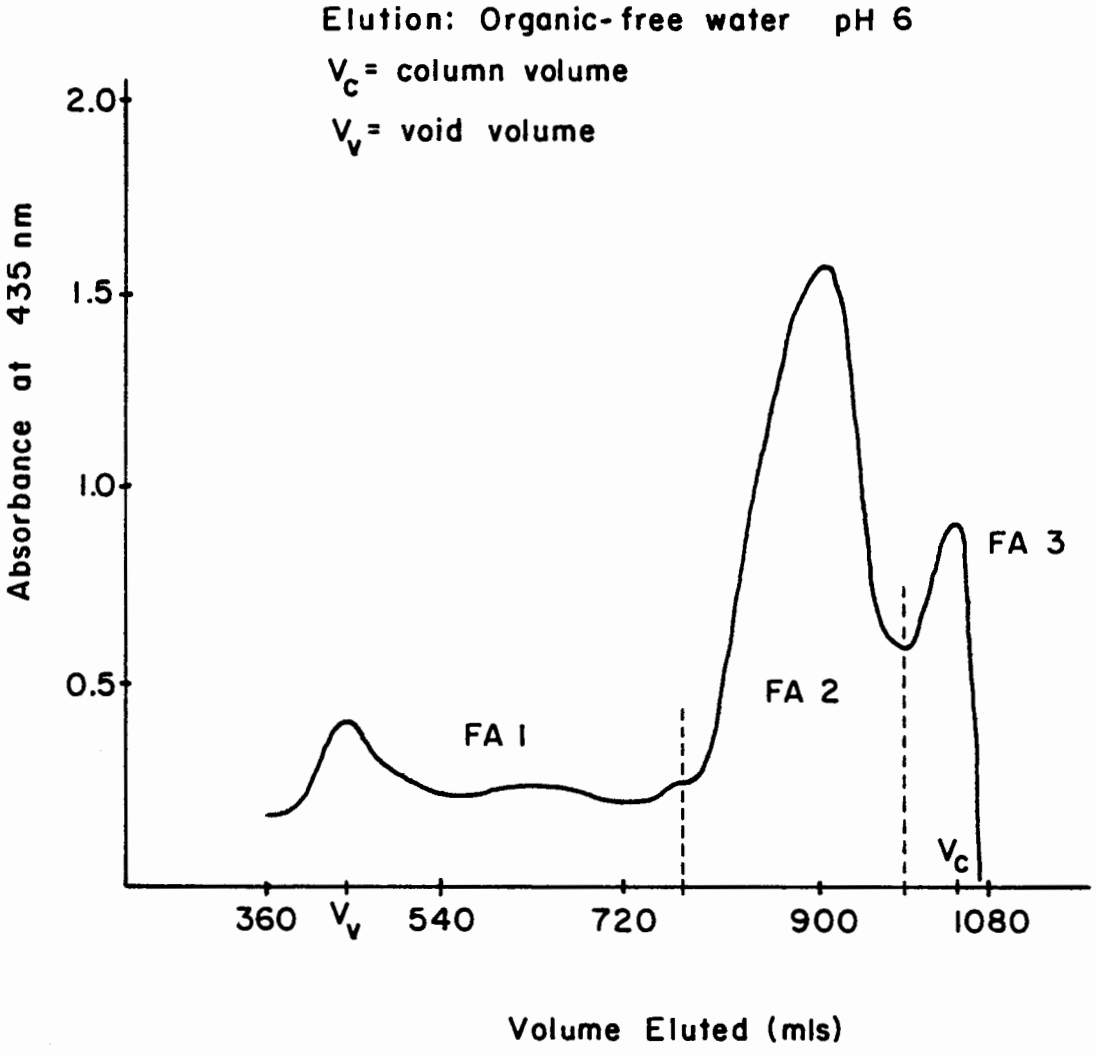


FIGURE 2
FRACTIONATION OF FULVIC ACID FRACTION I
ON SEPHADEX G-100

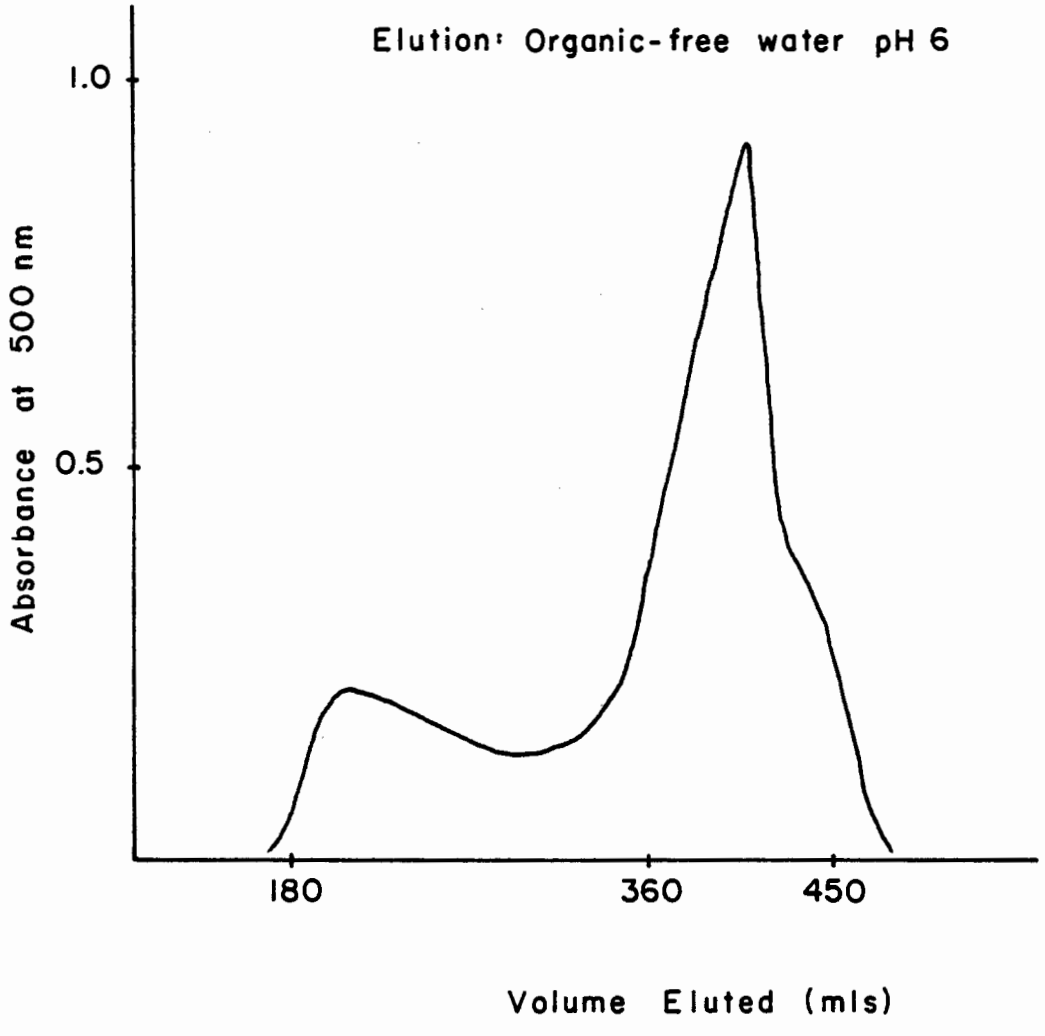


FIGURE 3
FRACTIONATION OF FULVIC ACID FRACTION 2
ON SEPHADEX G-25

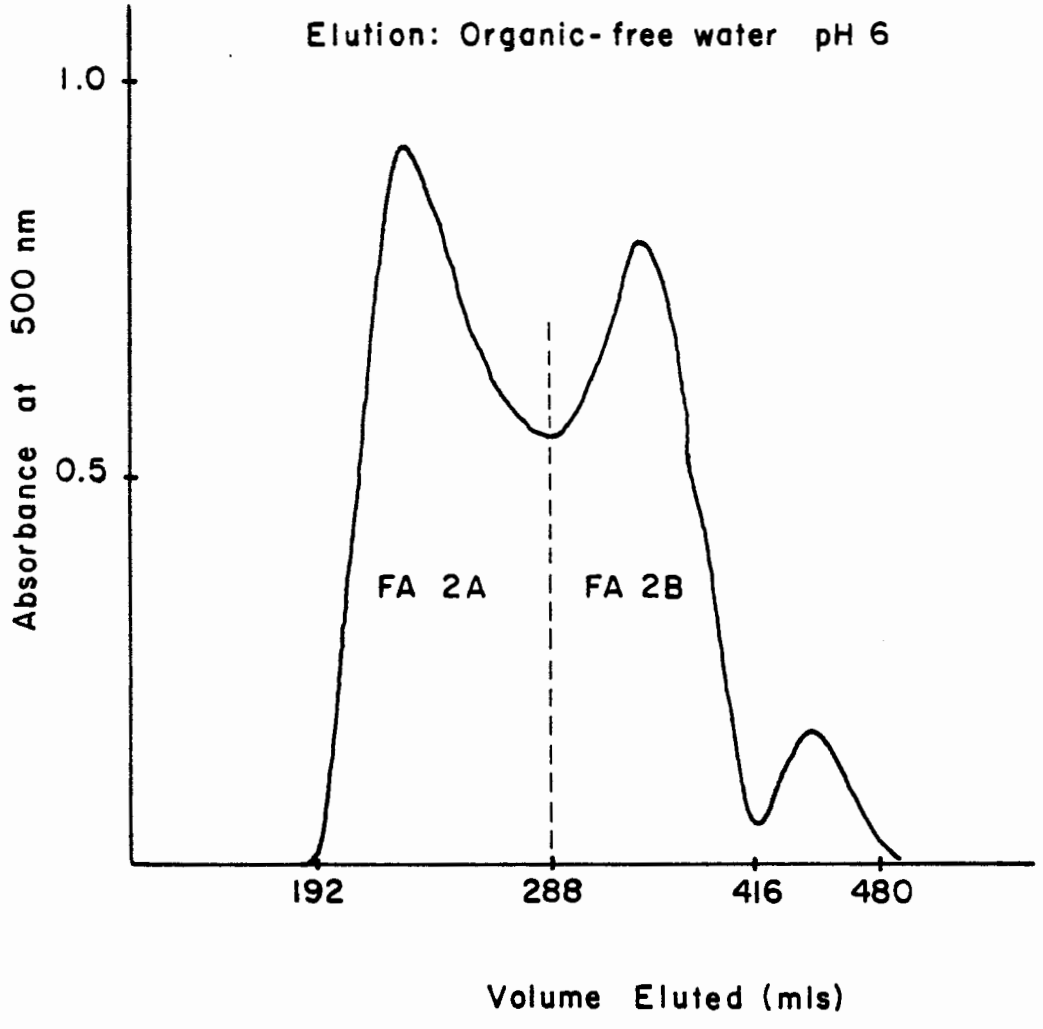


FIGURE 4
FRACTIONATION OF FULVIC ACID FRACTION 3
ON SEPHADEX G-25

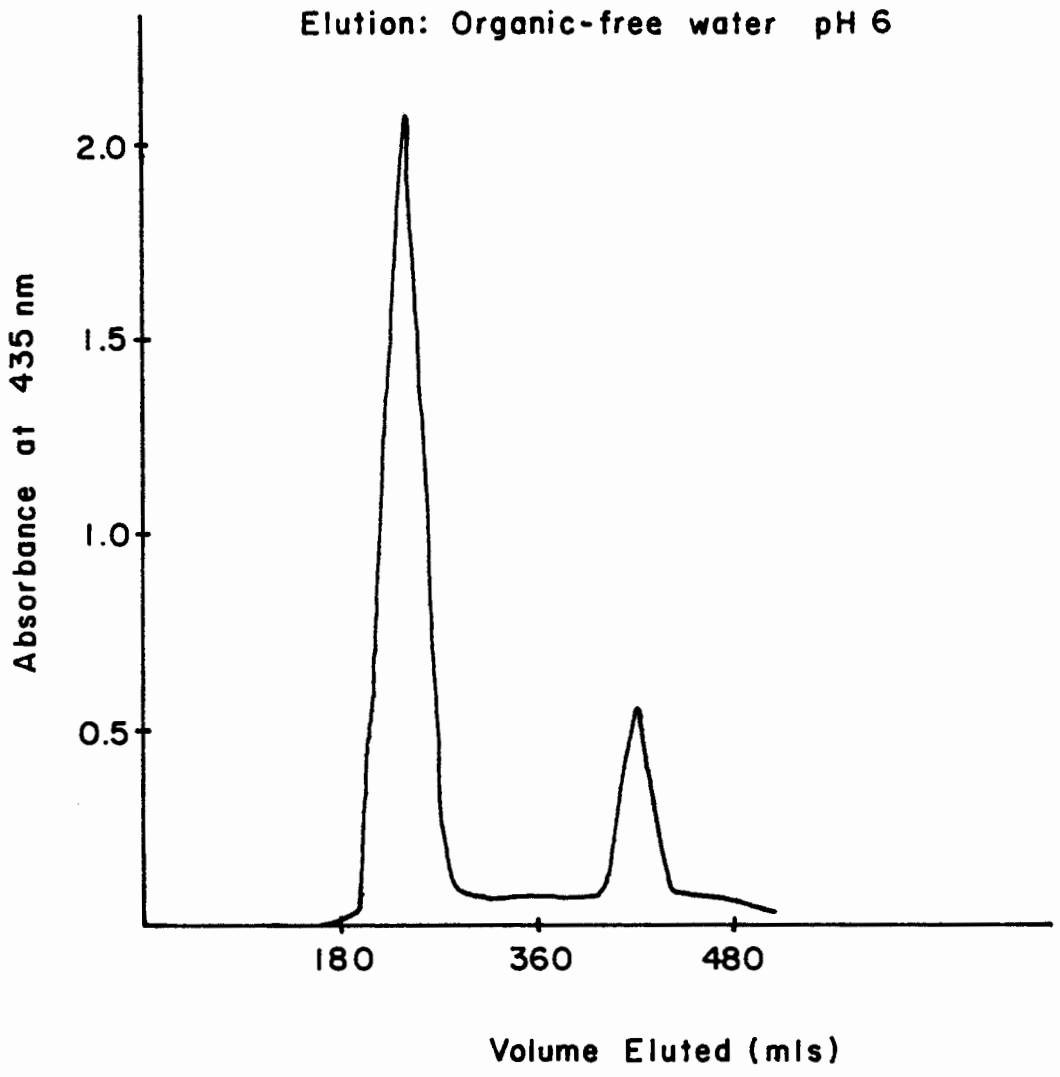


Table 3

Relative Distribution of Fulvic Acid Fractions

Fraction	Percent of Parent Fulvic Acid
FA 1	33.2
FA 2A	30.0
FA 2B	27.1
FA 3	9.7

simply as a result of molecular sieving since a fraction eluted at an elution volume intermediate between the void volume (V_v) and total column volume (V_c). Chemical phenomena, such as adsorption, are presumed to occur in the column as discussed by Wershaw and Pinckney (9). Following these authors' terminology, the fractionation of fulvic acid under these conditions was due to adsorption chromatography. No further efforts were made to determine the nature of the separation so that no conclusions may be drawn concerning chemical differences between fractions based on these results alone. As mentioned previously, it would be especially dangerous to draw inferences concerning molecular weights of the fractions.

Elemental Composition of Fulvic Acid

The parent fulvic acid and each fraction were subjected to elemental C-H-N analysis. Results are presented in Table 4. Ash and water contents were also determined in order to calculate the chemical composition of each fraction. Water and ash results are shown in Table 5 and the calculated chemical compositions are reported in Table 6.

Several points can be made about these results. The fulvic acid fractions are higher in ash content than the parent fulvic acid due to the experimental conditions employed in their fractionation (i.e., the fractionation at pH 11, adjusted with NaOH). Emission spectrographic analysis of the fractions confirmed this fact in that sodium was found to be the predominant metal in the freeze dried fractions. Although the ash content of FA 3 seems rather high, this may be due to free inorganic ions and molecules in the fulvic acid which would elute from the Sephadex column at the column volume, concurrently with fraction FA 3. However, Ishiwateri (25), has reported a low molecular humic acid fraction with 70% carbon and 30% oxygen. It should be noted that there was some variability in the ash content of the fractions and especially for FA 3, a slight change in the ash content could significantly change the chemical composition results. The results are reasonable and in agreement with other investigators (26, 27) who have reported carbon and oxygen contents of

Table 4

Elemental Composition of Fulvic Acid and Fractions

Sample	Percent of Element* C	H	N
Parent FA	44.8	3.33	.95
FA 1	34.8	4.01	0.63
FA 2A	27.3	2.00	0.55
FA 2B	29.6	2.92	0.50
FA 3	22.1	1.93	0.55

*Average of two analyses

Table 5

Water and Ash Contents of Fulvic Acid and Fractions*

Sample	% Ash	% Water
Parent FA	5	9.8
FA 1	26	4.0
FA 2A	43	3.5
FA 2B	43	0.9
FA 3	68	5.5

*by Thermogravimetric Analysis

Table 6

Chemical Composition of Fulvic Acid and Fractions-Water and Ash-free Basis

Sample	Percent* C	H	N	O**
Percent FA	53	1	4	42
FA 1	50	1	6	43
FA 2A	52	1	4	44
FA 2B	53	1	5	41
FA 3	84	2	7	6

*Total may not equal 100 due to rounding off

**by difference

approximately 50% and 40%, respectively. In conclusion, it appears that, except for fraction FA 3, the fractionation scheme employed in this study has produced fractions with similar chemical composition.

Spectral Analysis of Fulvic Acid

Infrared analysis of fulvic acid and the four fractions is presented in Figure 5. Fractions FA 1, FA 2A, and FA 2B are nearly identical to the parent fulvic acid. Lack of absorbance intensity by FA 3 may be due to the low percent of organic mass which makes up the fraction. The infrared band frequencies noted in the fraction spectra and the tentative structures assigned to them are listed in Table 7. The loss of bands by the fractions in the carboxylate region (1720 cm^{-1}) is probably due to the high pH of the fractions (pH 7 - 8).

The ultraviolet spectra (Figure 6) were not structurally informative as the fractions only showed one broad shoulder in the 270 nm region. The shoulder does not show up well due to the highly reduced nature of Figure 6. However, the analyses were performed such that the aqueous fraction concentrations were equal in carbon content, and the spectra indicate that UV absorbance is proportional to the mass of the fraction rather than carbon concentration. Here, molar absorptivity is assumed to be constant for all the fractions.

Proton NMR (Figure 7) was a useful tool for comparing the abundance of functional groups within each fraction, while carbon-13 (^{13}C) NMR (Figure 8) was only adequate in interpreting the functional group structure. The tentative assignment of chemical shifts for the proton spectra are presented in Table 8, while those for ^{13}C spectra are in Table 9. The ^{13}C spectra for FA 2A and FA 2B showed no resonances. The relative amounts of functional groups within any one fraction, obtained from the proton NMR data, are indicated in Table 10.

Functional groups associated with fraction FA 1 are primarily sterically strained methyl groups. Fraction FA 1 contains small amounts each of carboxylates, alcohols, and has some aromatic features,

FIGURE 5
INFRARED SPECTRA OF FULVIC ACID FRACTIONS

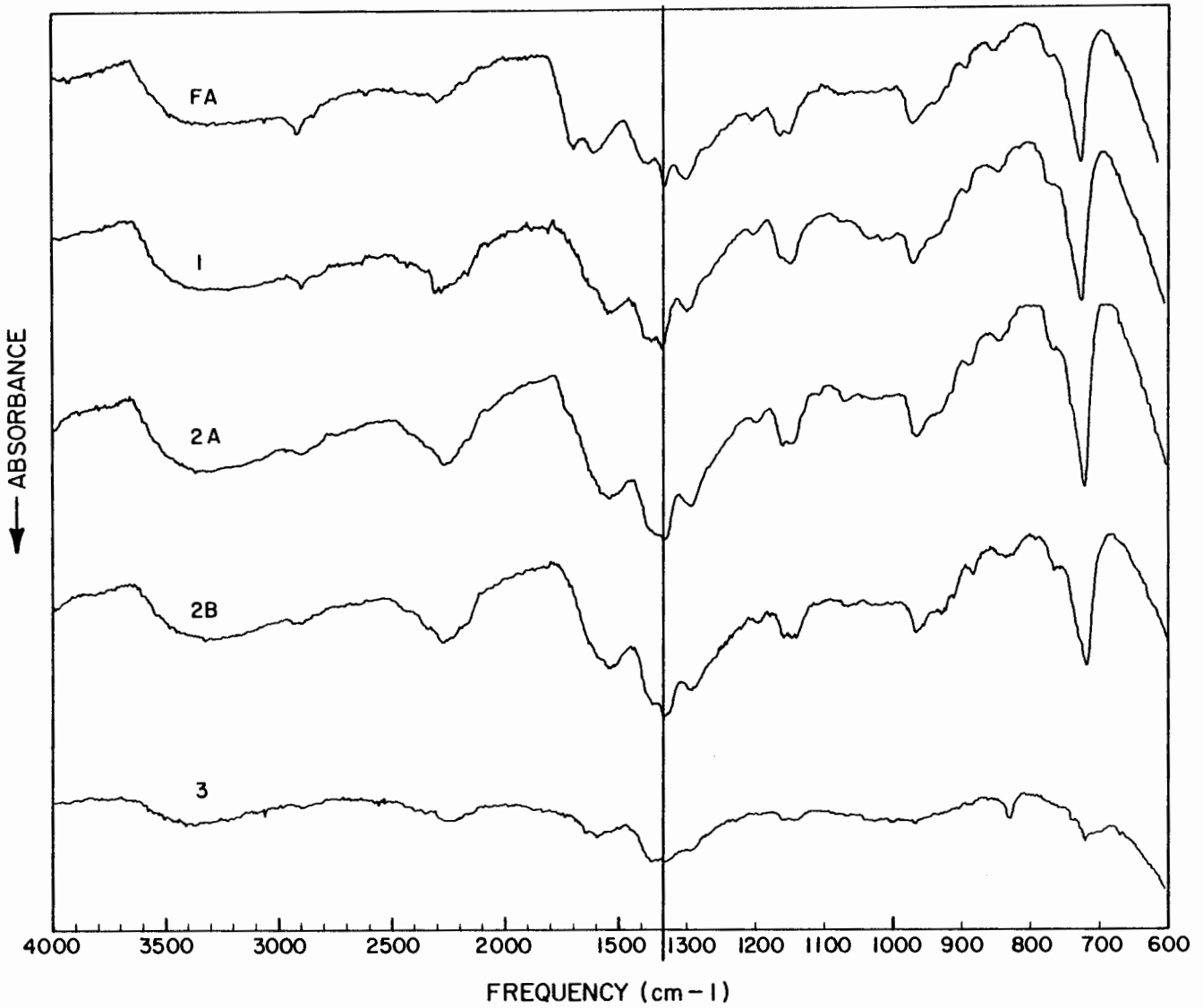


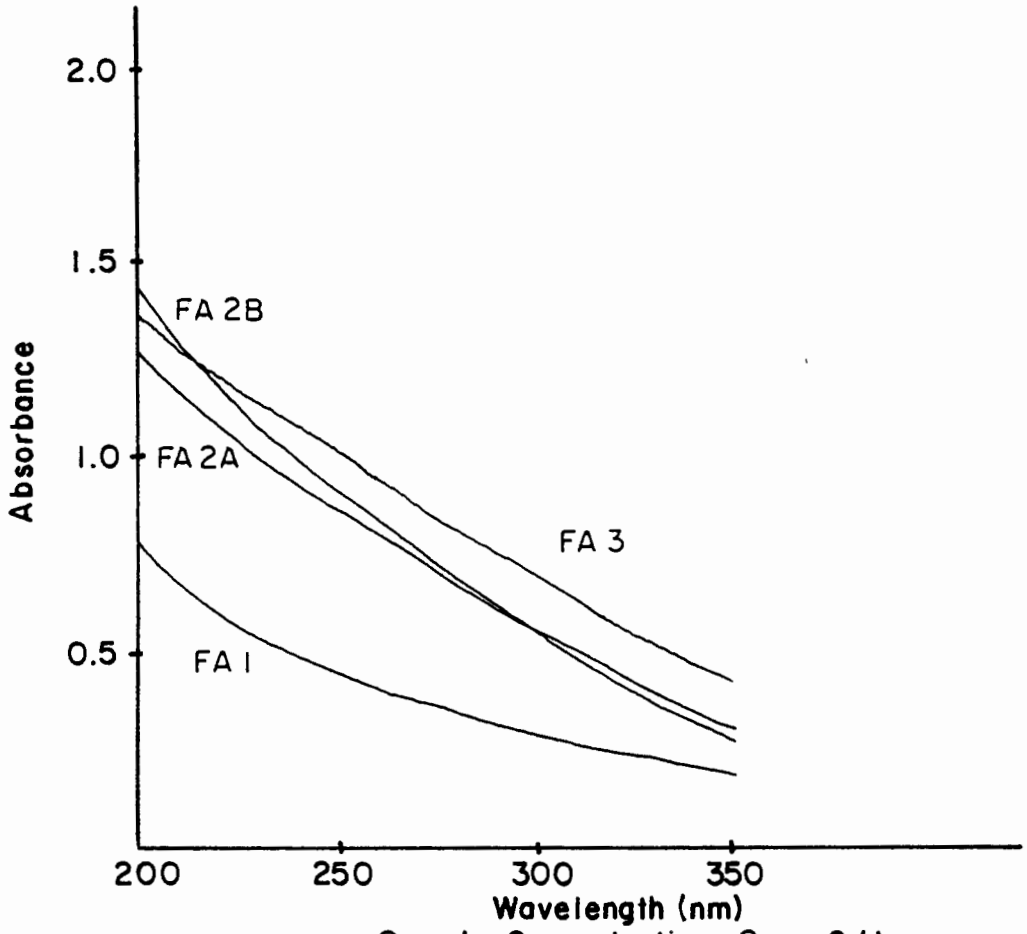
Table 7

IR Band Frequencies vs Structure

Frequency (cm^{-1})	Type of Vibration	Structure
3400	stretch	hydrogen-bonded OH
2910 and 2840	stretch	aliphatic C-H
1700	stretch	carbonyl of un-ionized carboxyl
1600	stretch	aromatic C=C
1380	bend	aliphatic C-H
1160	stretch	C-O-C
970	bend	alkene
730 and 850	bend	aromatic

FIGURE 6

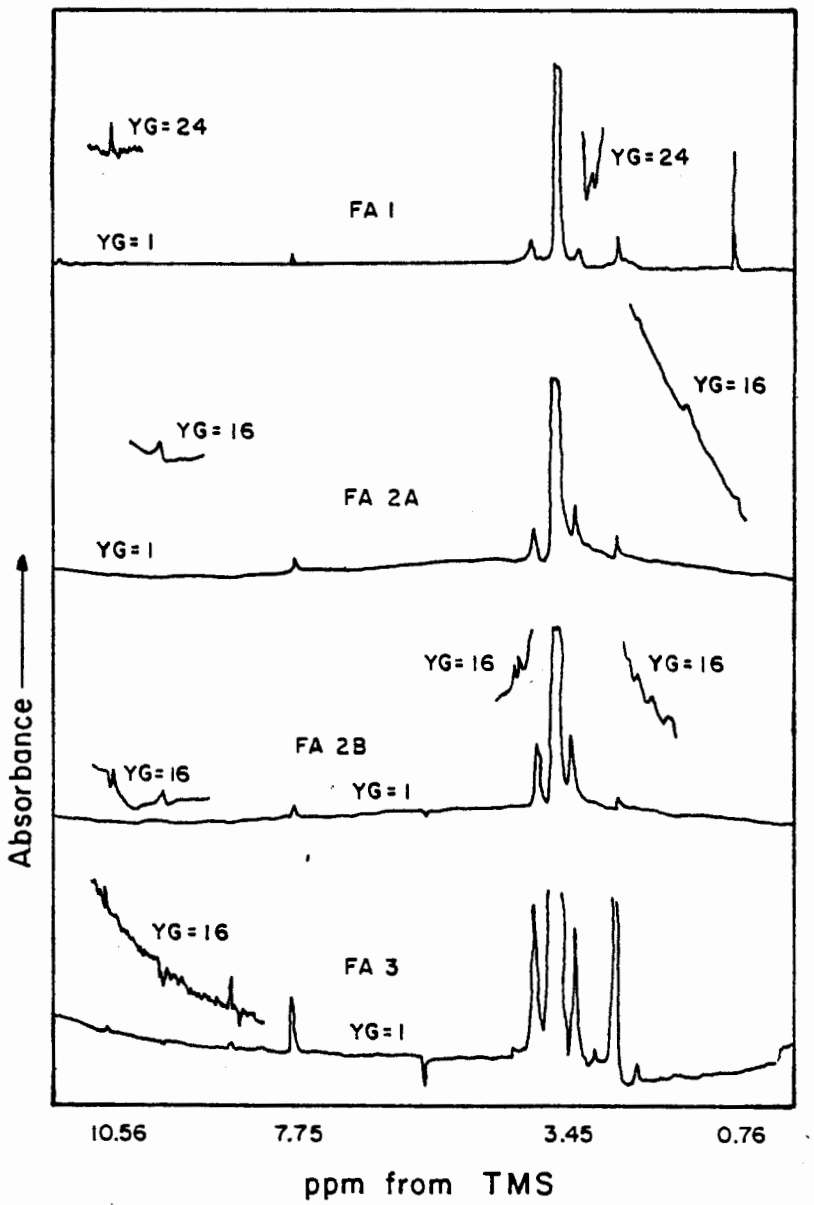
ULTRA VIOLET SPECTRA OF FULVIC ACID FRACTIONS



Sample Concentration: 8 mg C/l

Solvent: Organic-free water

FIGURE 7
PROTON NMR SPECTRA OF FULVIC ACID FRACTIONS



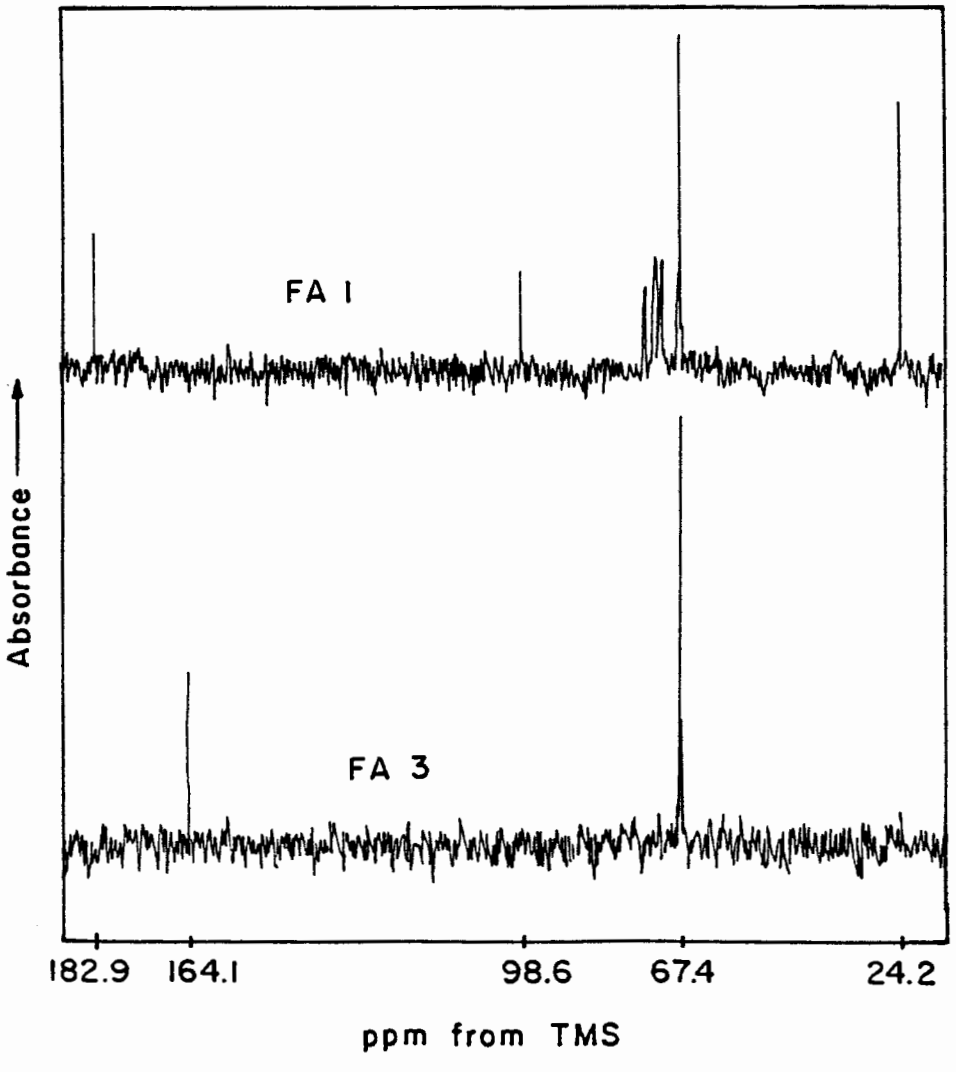
Solvent: D_2O

Reference: H_2O

YG = Gain Factor

FIGURE 8

CARBON[13] NMR SPECTRA OF FULVIC ACID FRACTIONS



Solvent: D_2O

Reference: Dioxane

Table 8

Tentative Assignment of Proton NMR

Chemical Shifts of Fulvic Acid Fractions*

Functional Group	PPM From TMS* FA 1	FA 2A	FA 2B	FA 3
phenolic carbonyl		9.64	9.67	
carboxyl	10.38		10.43	10.46
alcohol			3.65	
sterically strained methyl	.6	.56		
aromatic	7.57	7.53	7.58	7.60
aromatic carboxylate				8.55
methyl	2.825	2.18	2.89	

*Corrected from ppm relative to H_2O

Table 9

Tentative Assignment of ^{13}C Chemical Shifts of Fulvic Acid Fractions*

Functional Group	PPM from TMS* FA 1	FA 3
aromatic carboxylate		164.804
carboxylate	182.9	
methylene	99.305	
alcohol	74.745 72.53 71.644 70.758 67.22	
sterically strained methyl	24.87	

*corrected from ppm relative to dioxane

Table 10

Relative Amounts of Proton

NMR Chemical Shifts for Fulvic Acid Fractions

Functional Group	Relative Peak Area FA 1[a]	FA 2A[b]	FA 2B[c]	FA 3[d]
phenolic carbonyl		0.5	0.5	
carboxylate	0.5		0.4	1.5
methyl	0.3	0.25	0.5	
alcohol	1		1	
sterically strained methyl	60	0.25		
aromatic	1.5	7	6.5	27.5
aromatic carboxylate				2.5

a 290 scans

b 220 scans

c 500 scans

d 252 scans

but its overall structure is considered to be aliphatic. Fraction FA 2A also contains aliphatic groups but has significant amounts of aromatic groups including phenolics. Fraction FA 2B is similar to fraction FA 2A except that it has some carboxylates and alcohols associated with it. Fraction FA 3 seems to be composed of one structure, an aromatic carboxylate. It appears then, that as the fractions elute from the Sephadex G-50 column they become increasingly aromatic and contain a higher proportion of carboxylates.

It is interesting to note that although the chemical composition, IR, and UV results for the fulvic acid fractions indicated that, except for fraction FA 3 in some instances, there were no significant differences among fractions, the NMR data clearly show that some chemical separation occurred during the fractionation. The IR results are in good agreement with previously reported spectra (28-30). A review of the literature for NMR spectra of fulvic and humic acids found few spectra with good resolution and most spectra (26, 31, 32) contained only broad resonances. The ^{13}C NMR spectra reported herein, along with those in a recent work (33) which were obtained concurrently, represent possibly the most definitive NMR spectra of humic matter at this time. Interpretation of ^{13}C NMR shifts in heterogeneous samples such as fulvic acid fractions is difficult and any functional group assignments of such shifts on this basis alone must be considered tentative until further studies are completed.

Reactions of Fulvic Acid in Water Treatment Processes

Chlorination of Fulvic Acid

Several approaches were undertaken in the study of the chlorination reactions of fulvic acid. The reactivities of the carbon atoms in the fulvic acid fractions were investigated in experiments conducted on an equivalent carbon basis. TOC data were also used in this regard in some experiments. The effect of the initial chlorine concentration on haloform production was studied. All experiments were carried out to a minimum reaction time of 48 hours to determine the

maximum yield of trihalomethanes in a time period corresponding to a reasonable maximum detention time in a water treatment plant and distribution system. In all experiments, chloroform was the only trihalomethane detectable. Evidently, the extracted fulvic acid contained little bromide which could act as a source of bromine atoms for brominated halomethanes. The temperature in all studies was room temperature, 21 - 24°C.

A first set of experiments examined the yield of chloroform from fulvic acid fractions FA 1, FA 2A, FA 2B, and FA 3 at chlorine doses of 3 mg/ℓ (as Cl) and 10 mg/ℓ. In these studies, the fraction concentrations were equivalent on a carbon basis which was 8 mg C/ℓ, which would represent a reasonable maximum for colored surface waters in the northeastern U.S. Furthermore, no pH control was practiced; the pH values of the reaction solutions were 7.5, 6.7, 7.2, and 6.7 for FA 1, FA 2A, FA 2B, and FA 3, respectively. The chloroform yields as a function of time are presented in Figures 9 and 10 and residual chlorine concentrations are plotted in Figures 11 and 12. The chloroform yields for the 3 mg/ℓ chlorine dose are not meaningful except to illustrate the strong chlorine demand of the reaction solution. These chloroform yields were obviously limited by the lack of chlorine in all fraction runs at 12 hours. At the 10 mg/ℓ chlorine dose residual chlorine was present for all fractions at 24 hours and some insights can be gained concerning relative reactivity of fulvic acid fractions. Forty-eight hour chloroform yields ranged from 222-359 mg/ℓ which agrees well with the highest yields observed by EPA in a national survey (3). Interestingly, the order of yields from lowest to highest was FA 1, FA 2A, FA 2B, FA 3. Molar yields of chloroform were calculated and are presented in Table 11. These results demonstrate that all fulvic acid fractions produce significant yields of chloroform with differences in yield observed among fractions. Reasons for this variation could be several. pH is known to affect the haloform reaction (34) and the differences in pH in the fraction solutions in these experiments could account for this effect. Based upon reactions of chlorine with molecular weight fractions of humic material, Oliver and Visser

FIGURE 9

CHLOROFORM PRODUCTION FROM CHLORINATION OF FULVIC ACID FRACTIONS

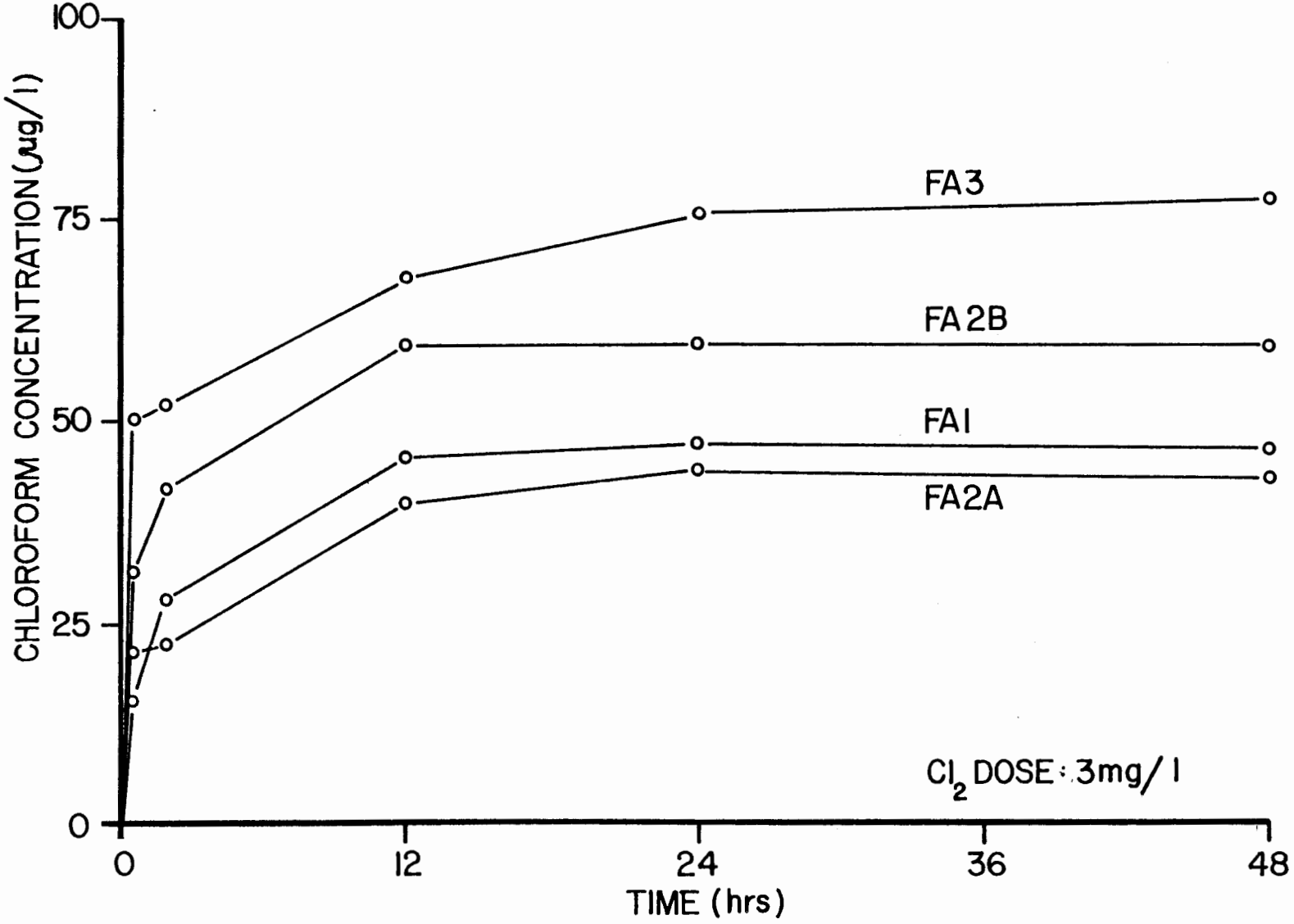


FIGURE 10
CHLOROFORM PRODUCTION FROM CHLORINATION OF FULVIC ACID FRACTIONS

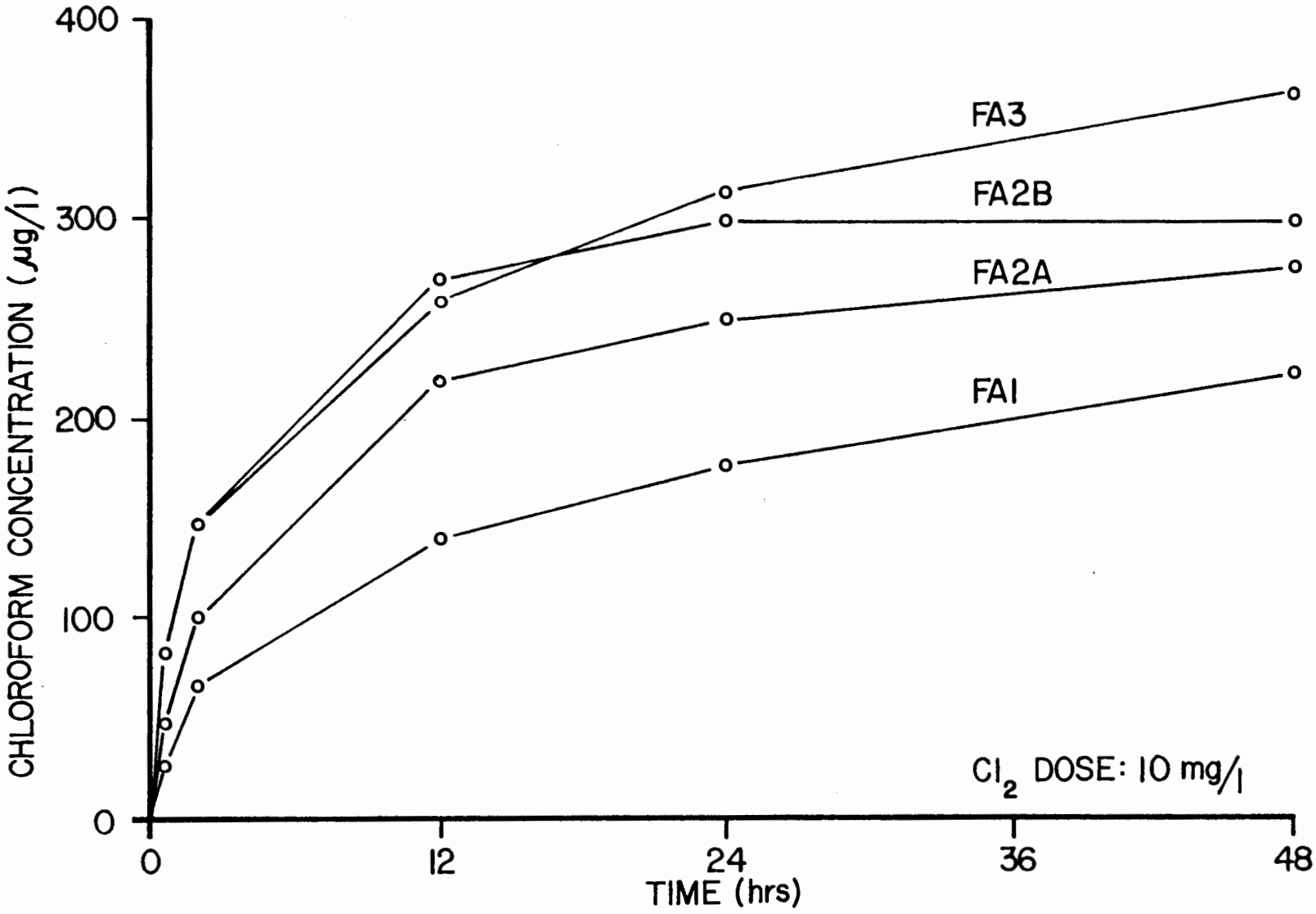


FIGURE 11

RESIDUAL CHLORINE VS. TIME FOR EXPERIMENTS IN FIGURE 9

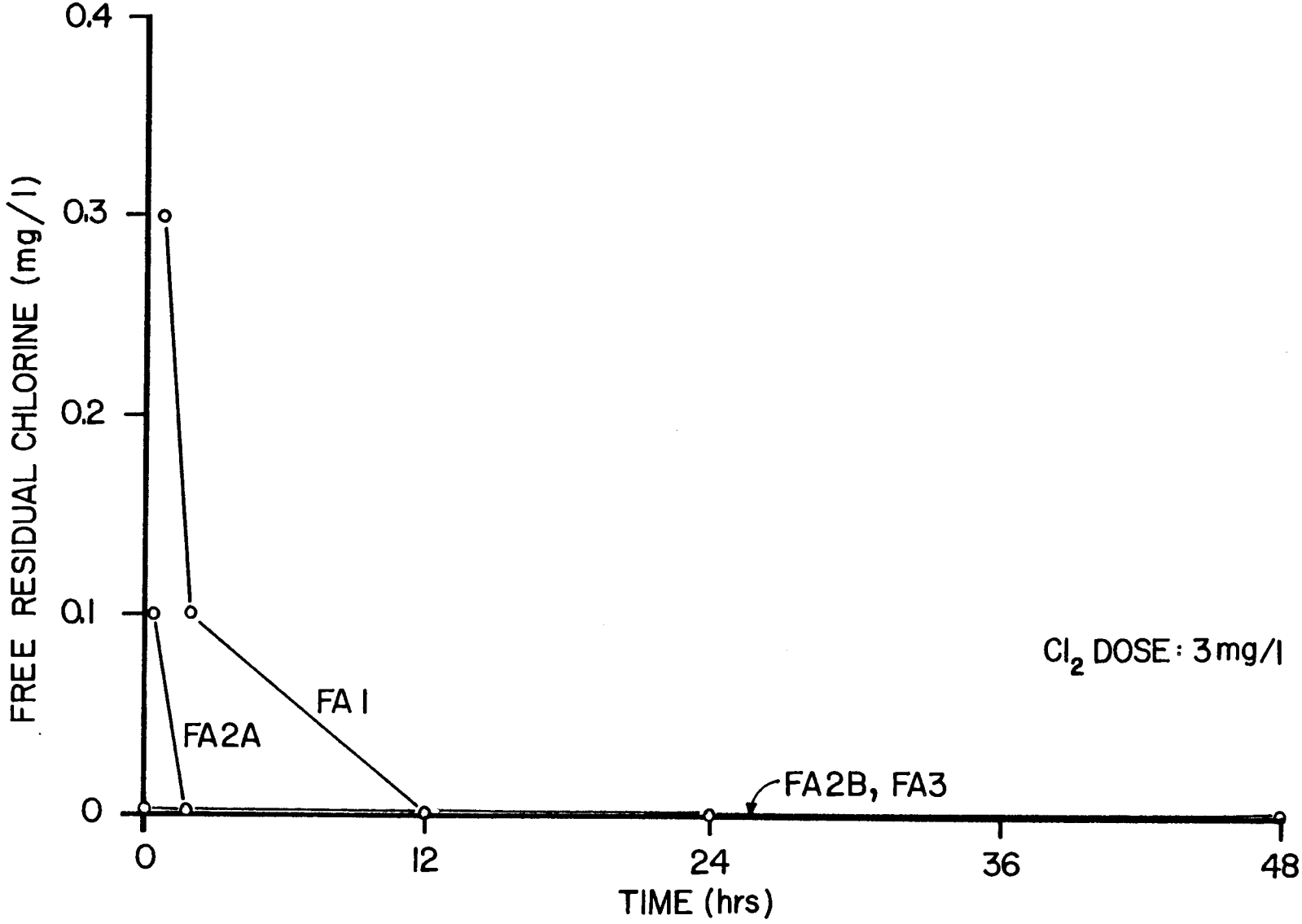


FIGURE 12
RESIDUAL CHLORINE VS. TIME FOR EXPERIMENTS IN FIGURE 10

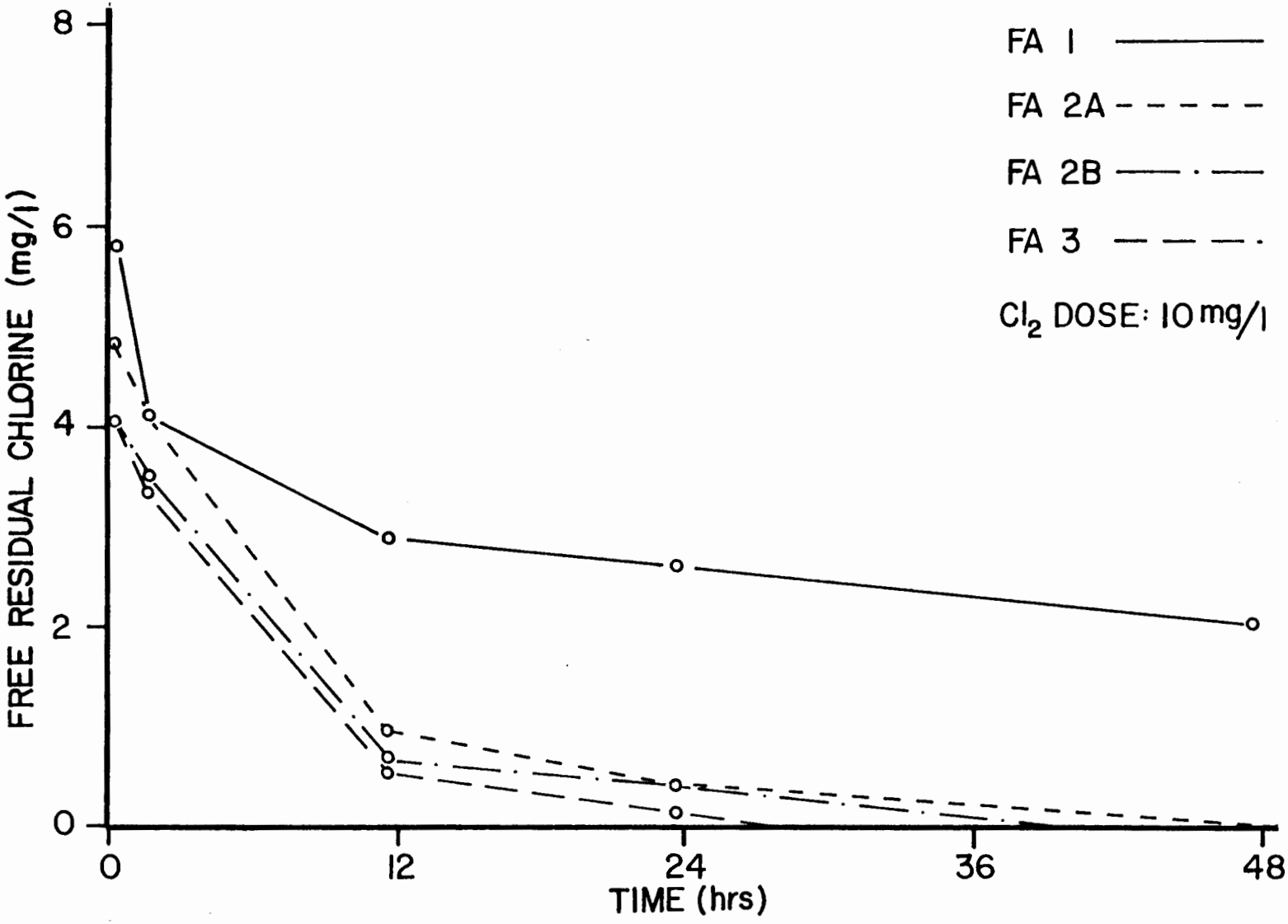


Table 11

48-hour Molar Yields of Chloroform for Fulvic Acid Fractions

Fraction	$CHCl_3$ Molar Yield at 48 hours*
FA 1	.0028
FA 2A	.0034
FA 2B	.0037
FA 3	.0045

*moles $CHCl_3$ @ 48 hours/moles of carbon initially present

Conditions: Initial fraction concentrations, 8 mg C/L
Initial chlorine, 10 mg Cl/L

(35) have concluded that the low molecular fulvic acid fraction is the predominant THM precursor. If the assumption can be made that the fulvic acid fractionation scheme used in this study did produce a molecular weight separation, the results of this series of experiment support the finding of Oliver and Visser. However, no direct evidence to support this assumption is available.

The chlorine consumption in this series of experiments was large and as the chloroform yield as a percentage of carbon atoms is low (.28-.45% from Table 11) so too is the chlorine yield. The chlorine yield (moles Cl in $CHCl_3$ produced/mole of initial chlorine), expressed in percent, was 2.5, 2.4, 2.6, and 3.2 for fractions FA 1, FA 2A, FA 2B, and FA 3, respectively, indicating that the great majority of chlorine atoms do not react to form trihalomethanes.

Chlorination reactions were also conducted at pH 7.0 in phosphate buffer. Results, expressed as mg $CHCl_3$/mg TOC, are presented graphically in Figures 13 and 14 (data are contained in Appendix). In these experiments, solutions of parent fulvic acid (FA) and fractions FA 1, FA 2, and FA 3 were compared. Ultimate yields of chloroform, as mg $CHCl_3$/mg TOC, were reasonably uniform for all fulvic acid fractions. Initial TOC levels in these runs ranged from 1.6 - 2.8 mg/ℓ. As can be seen by Figure 14, significant differences in chlorine consumed among fractions were observed which could not be fully explained by differences in initial TOC. In comparing these $CHCl_3$ yield results to those of the previous chlorination experiments, it appears that at pH 7.0, there do not appear to be significant differences in chloroform production for the fulvic acid fractions. The yields observed here, 176 - 243 mg $CHCl_3$/mg TOC, are slightly higher than those determined for fulvic acid by Oliver and Visser (35) and could easily be accounted for by differences in the source fulvic acid, experimental conditions, and the fractionation procedures used. In summary, it can be stated that fulvic fractions with varying distributions of chemical structures and functional groups, as identified by IR and NMR spectroscopy, can serve as precursors to significant generation of chloroform upon

FIGURE 13
CHLORINATION OF FULVIC ACID FRACTIONS AT pH 7.0

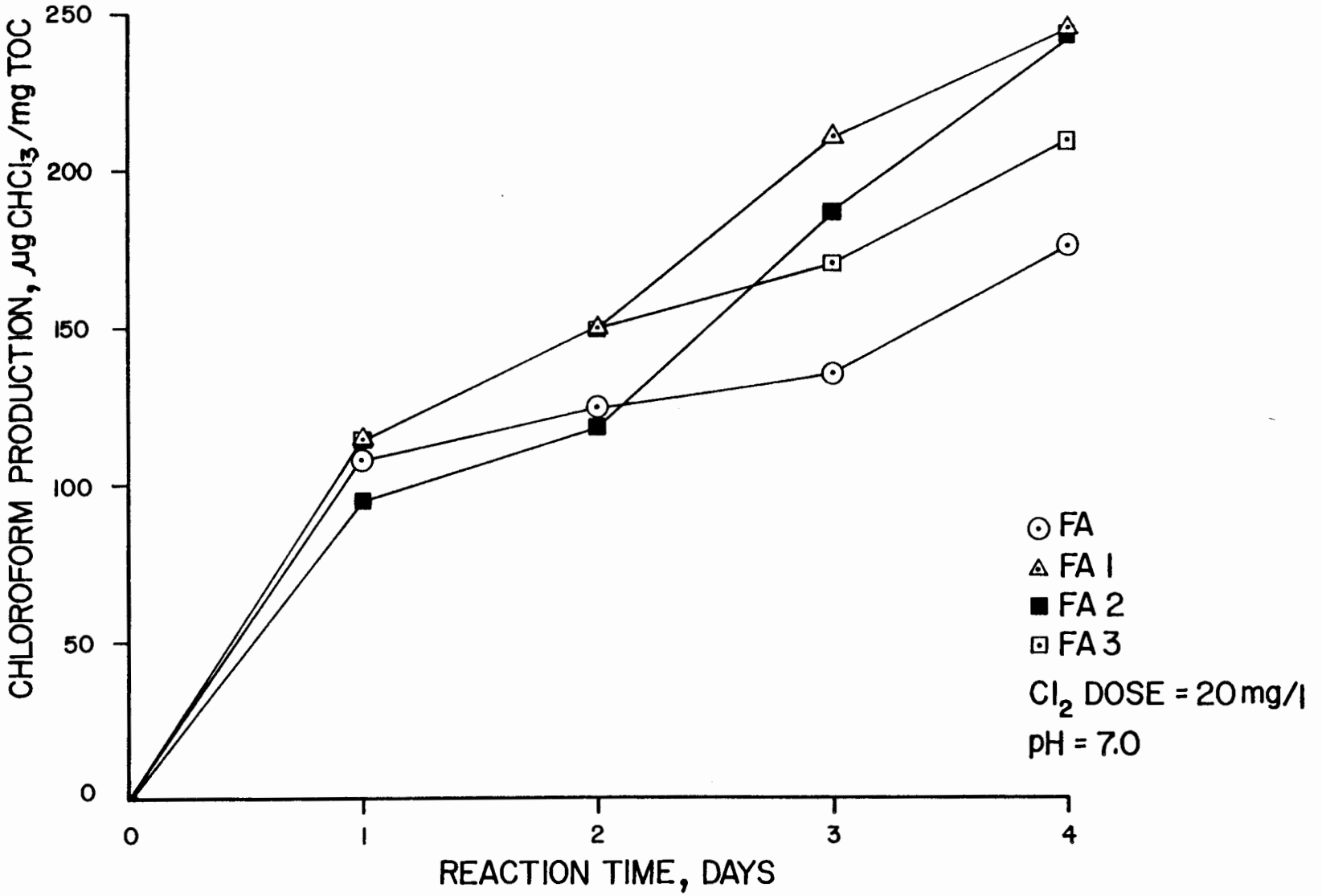
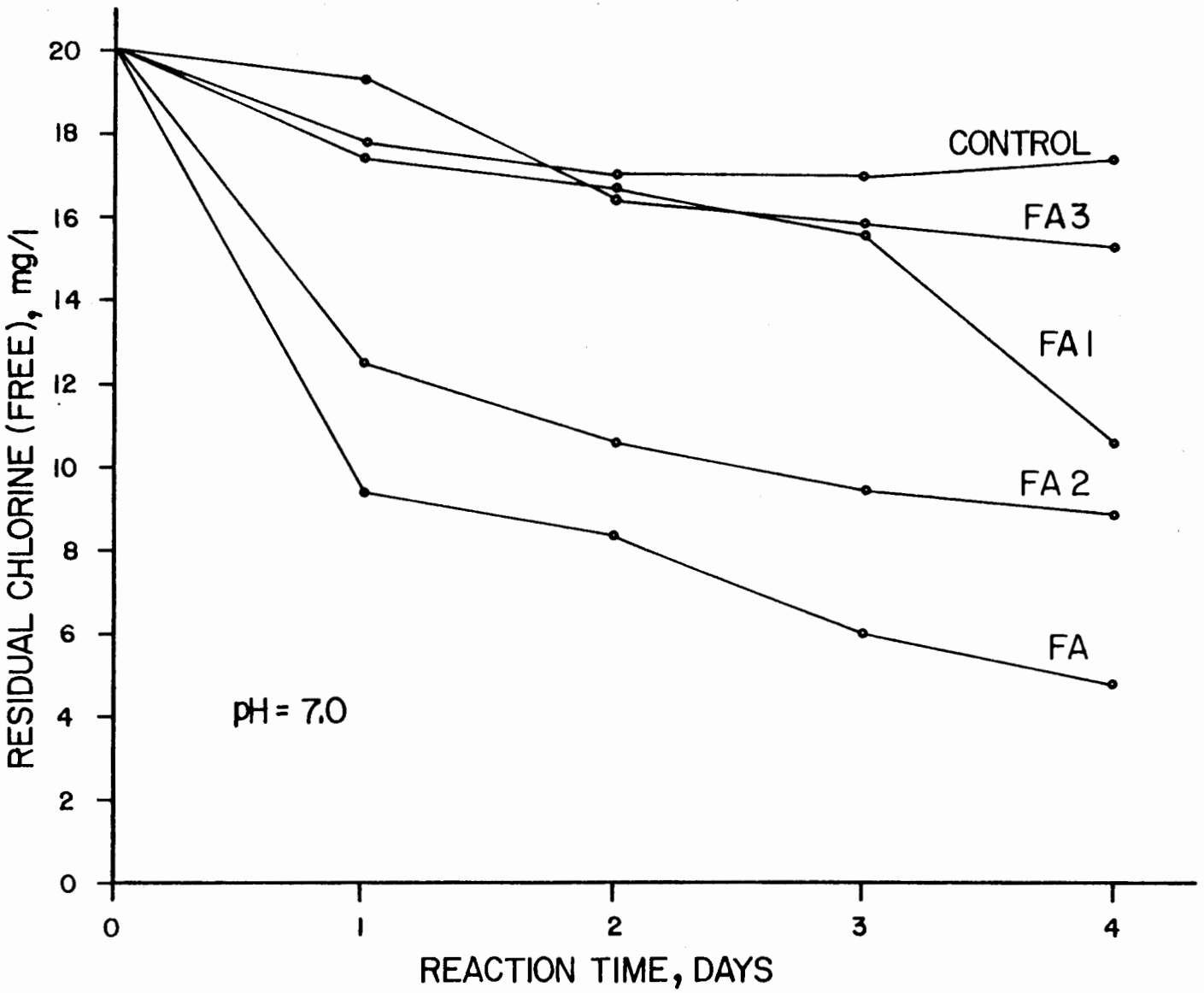


FIGURE 14
RESIDUAL CHLORINE VS. TIME FOR EXPERIMENTS IN FIGURE 13



chlorination.

Behavior of Fulvic Acid in Coagulation

As coagulation processes are currently relied upon for removal of humic materials in water treatment plants, it was decided to investigate the impact of coagulation on the distribution of fulvic acid fractions. Under conditions simulating conventional coagulation (see Experimental), solutions of fulvic acid were coagulated and the distribution of fulvic acid fractions in the residual fulvic acid was determined. Figures 15 and 16 present the Sephadex elution curves for fulvic acid and the residual fulvic acid remaining after coagulation. Percentage removals of fractions FA 1, FA 2A, FA 2B, and FA 3 were calculated from the measured overall removal and the respective relative areas under the elution curves. These data are shown in Table 12. This experiment demonstrates that coagulation with aluminum sulfate does not result in equal removal of all fulvic acid compounds, but is somewhat selective. In particular, the apparent low molecular weight fraction (FA 3) is most difficult to remove and in the residual fulvic acid mixture becomes a major fraction. In past studies of coagulation of humic materials, it has been noted that the maximum removal is approximately 90% and it has been surmised that some humic compounds are not amenable to removal by coagulation. This experiment provides evidence for this phenomenon and indicates that the apparent low molecular weight, predominantly aromatic compounds are not efficiently removed by coagulation processes.

The foregoing experiment was duplicated to assess reproducibility and the results are presented in Figures 17 and 18 as well as Table 13. In this experiment (Removal of Fulvic Acid by Coagulation - Experiment II) only fractions FA 1, FA 2, and FA 3 were investigated. Given the long and elaborate procedures involved in concentrating the residual fulvic acid and in the column chromatography, the agreement with Experiment I is deemed satisfactory.

To further explore the behavior of fulvic acid compounds during

FIGURE 15

SEPHADEX ELUTION CURVE FOR FULVIC ACID PRIOR TO COAGULATION - EXPERIMENT I

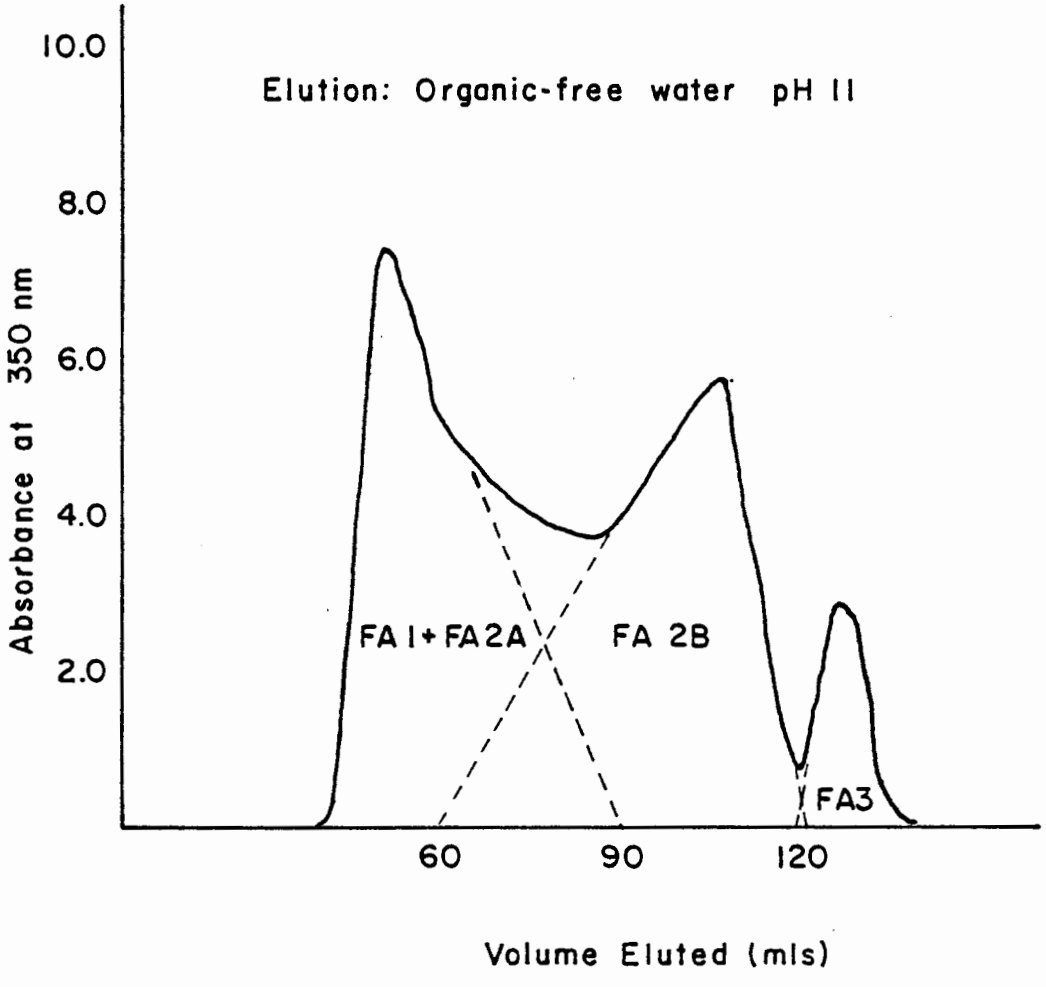


FIGURE 16

SEPHADEX ELUTION CURVE FOR RESIDUAL FULVIC ACID FOLLOWING COAGULATION - EXPERIMENT I

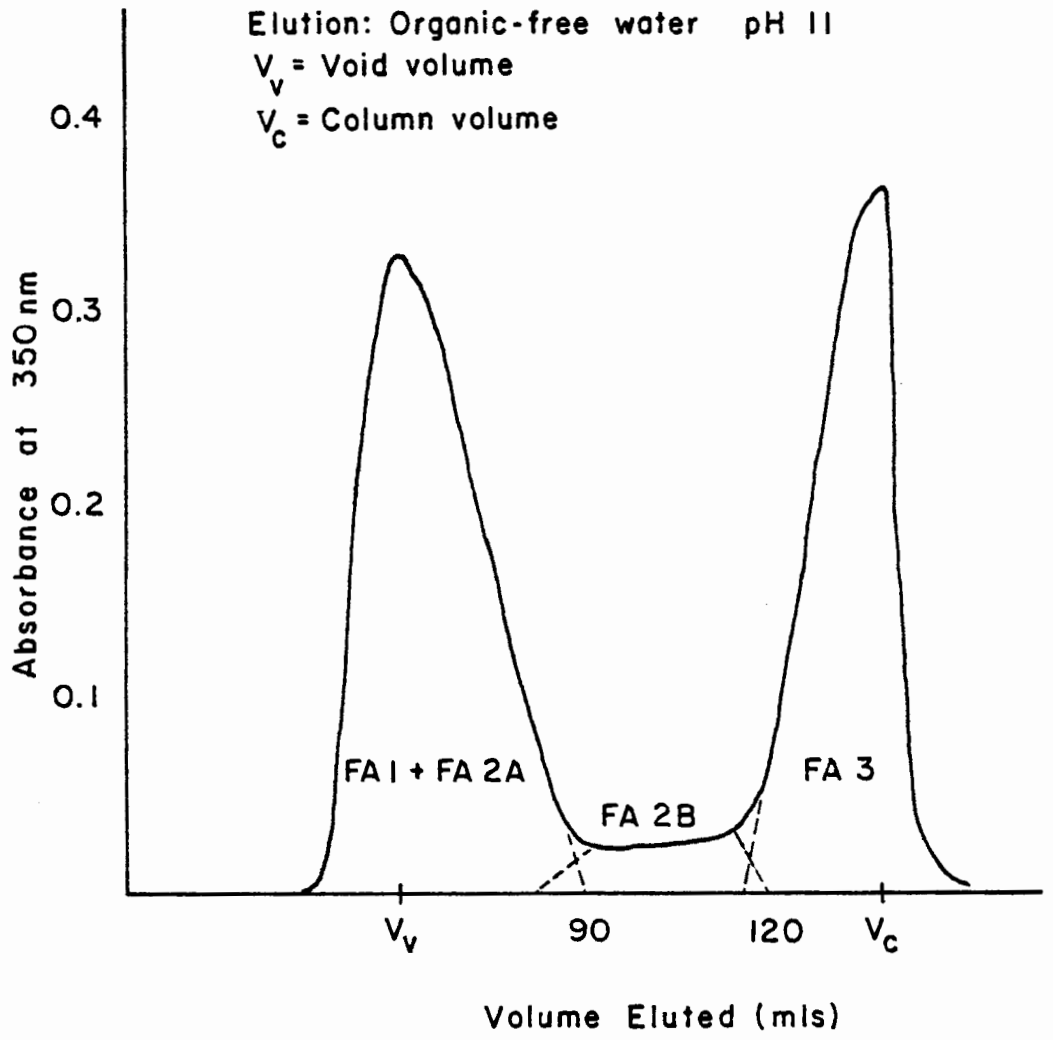


Table 12

Removal of Fulvic Acid by Coagulation - Experiment I

Fraction	Percentage Composition		
	Fulvic Acid	Residual Fulvic Acid after Coagulation	Percent Removal
FA 1	24.2	21.0	92.2
FA 2A	32.4	33.1	90.8
FA 2B	37.8	13.0	96.9
FA 3	5.6	32.9	47.7

Overall removal of fulvic acid was 91%

Aluminum sulfate was the coagulant

pH = 6

FIGURE 17
SEPHADEX ELUTION CURVE FOR FULVIC ACID
PRIOR TO COAGULATION - EXPERIMENT II

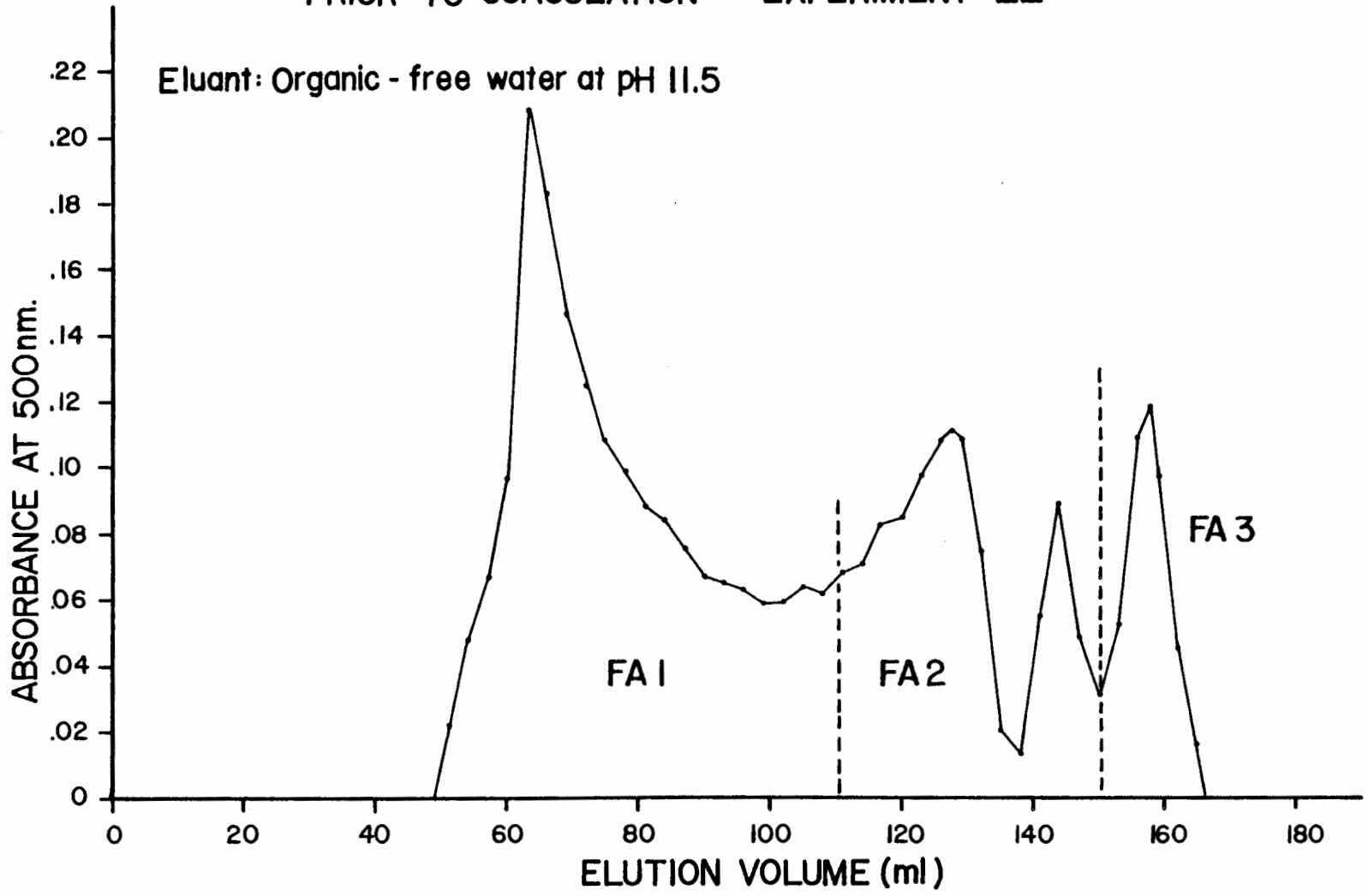


FIGURE 18
SEPHADEX ELUTION CURVE FOR RESIDUAL FULVIC ACID
FOLLOWING COAGULATION - EXPERIMENT II

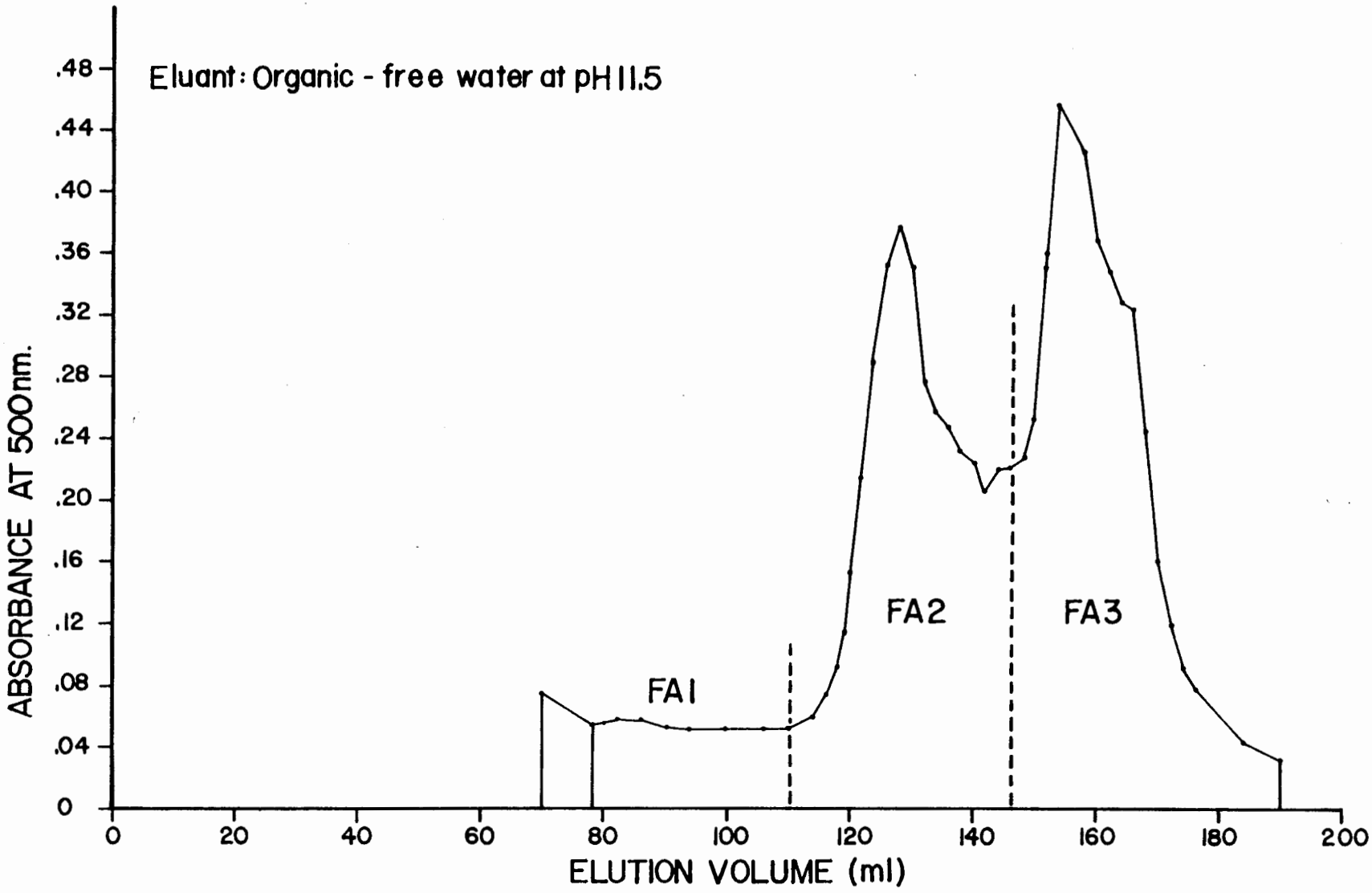


Table 13

Removal of Fulvic Acid by Coagulation - Experiment II

Fraction	Percentage Composition: Fulvic Acid	Residual Fulvic Acid after Coagulation	Percent Removal
FA 1	58.5	12.5	97.9
FA 2	30.5	41.8	86.9
FA 3	11.0	45.7	60.0

Overall removal of fulvic acid was 90.4%

Aluminum sulfate was the coagulant

pH = 6

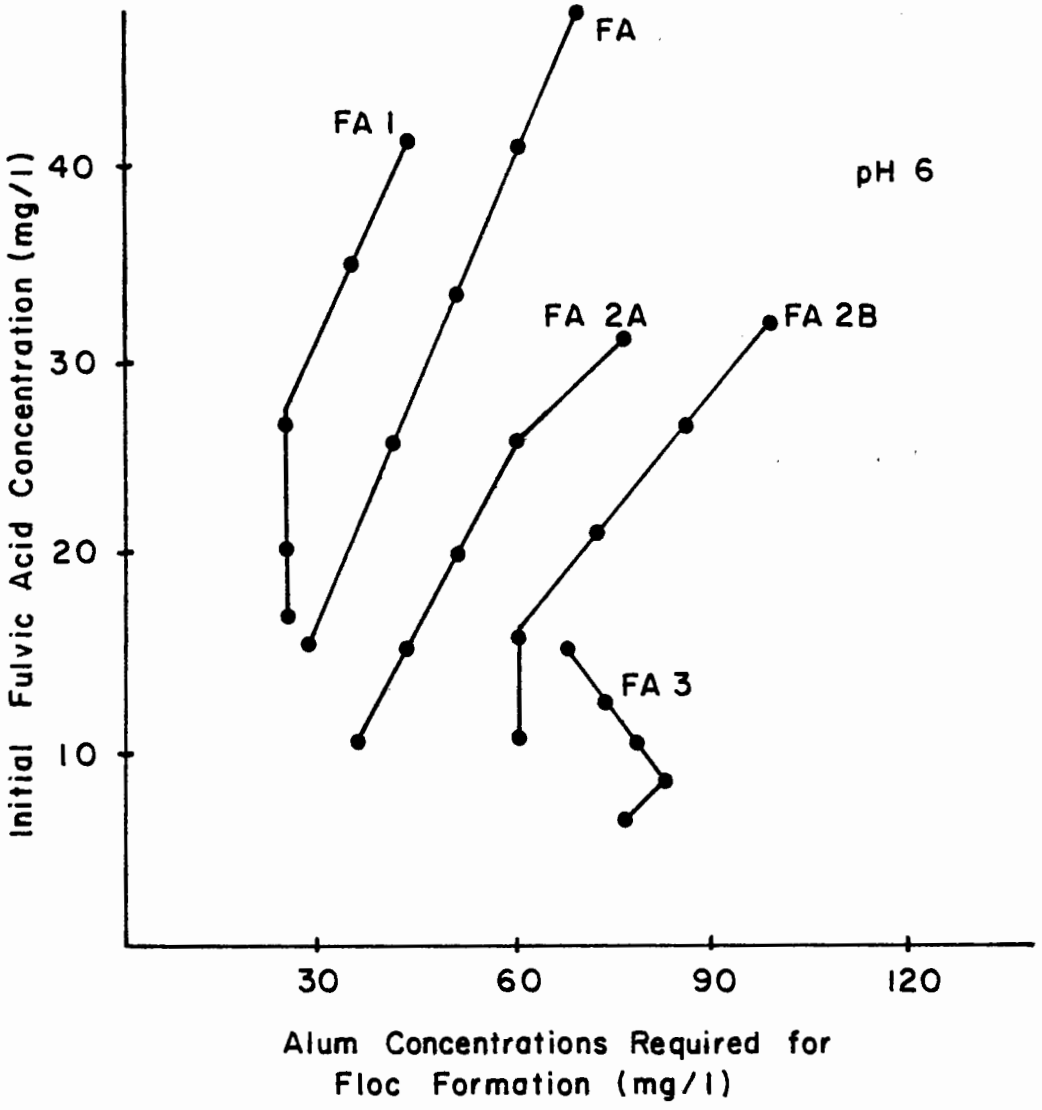
coagulation, the relationships between fraction concentration and alum dose required for flocculation were studied in controlled experiments. Individually, fulvic acid fractions were titrated with an aluminum sulfate solution at pH 6 until visible flocculation occurred. Schnitzer and Khan (36) have reported that aluminum forms complexes with fulvic acid and also forms a precipitate in the neutral pH region. The stoichiometry of this reaction is demonstrated in Figure 19 which also points out the very significant differences among fractions. It should be noted that no experimental evidence for the formation of an aluminum-fulvic acid complex is presented in this report, although it is assumed based upon the work of Schnitzer and Khan (36). The interpretation of Figure 19 for all fractions (including FA) except FA 3 is as follows. Aluminum forms a soluble mixed hydroxy-fulvic acid complex with fulvic acid until a certain ratio of aluminum to fulvic acid "saturates" the solution and a mixed aluminum hydroxy-fulvic acid precipitates from solution and is seen as the "floc" material. The behavior of fraction FA 3 is puzzling and is not easily explained.

Two conclusions may be drawn from these results. The apparent high molecular weight fulvic acid compounds are flocculated at much lower doses than apparent low molecular weight compounds. Fraction FA 2B requires approximately 3 times the alum dose than that for FA 1. Secondly, on a weight basis (and approximately so on a molar (as C) basis) the complexing ability of the fractions, in the range of experimental conditions studied, increases in the order FA 1, FA 2A, FA 2B, and FA 3. It is interesting that the same order was observed for the trihalomethane yields of the fractions (on a equimolar carbon basis) suggesting that the same functional groups might be involved in both metal complexation and trihalomethane formation.

Effect of Coagulation on Chloroform Yields of Fulvic Acid Fractions

In assessing the impact of coagulation on trihalomethane formation, an intriguing question arises. What is the effect of

FIGURE 19
STOICHIOMETRY OF THE REACTION OF
ALUMINUM SULFATE WITH FULVIC ACID FRACTIONS



coagulation on the reactivity of residual fulvic acid compounds with aqueous chlorine? This was investigated in a series of experiments in which the residual fulvic acid following coagulation was freeze concentrated and separated into component fractions on Sepahdex G-50 at pH 11.5. The fulvic acid fractions were freeze concentrated and reacted with chlorine in experiments conducted similarly to those at pH 7.0 reported previously. The experiment was performed in duplicate and each point in Figure 20 is an average of two values. (See data in Appendix). The initial TOC of the fractions ranged from 1.4 to 2.3 mg/ℓ. The chlorine dose was 20 mg/ℓ and residual chlorine was present throughout the reaction period.

The reactivities of the fulvic acid fractions decrease following coagulation with alum. The chloroform yields of the residual fulvic acid fractions, expressed as mg $CHCl_3$/mg TOC, decrease 60.1, 79.9, and 78.0 percent for FA 1, FA 2, and FA 3, respectively. Also, following coagulation, the fraction FA 1 yield is approximately twice that of FA 2 and FA 3. This finding is important in understanding the impact of coagulation on trihalomethane production. Contrary to the view of Babcock and Singer (18) that coagulation selectively removes trihalomethane precursors, these results show that the fulvic acid compounds remaining in solution following coagulation are intrinsically less reactive in the trihalomethane formation reaction. Presumably, chemical changes (i.e. complexation with metal coagulants) in the fulvic acid compounds are the causes of this phenomenon.

The type of humic compounds responsible for trihalomethane formation is important if enough of their chemistry and reactions in water treatment processes is known to enable an assessment of which treatment processes should best be employed to minimize trihalomethane production. Based upon the results presented previously, the percentage of the expected chloroform concentration attributable to each fulvic acid fraction, was calculated for a given water before and after coagulation. The results are given in Table 14 (see calculations and data in Appendix). Prior to coagulation, the major

FIGURE 20
CHLOROFORM YIELDS OF RESIDUAL FULVIC ACID FRACTIONS
FOLLOWING COAGULATION

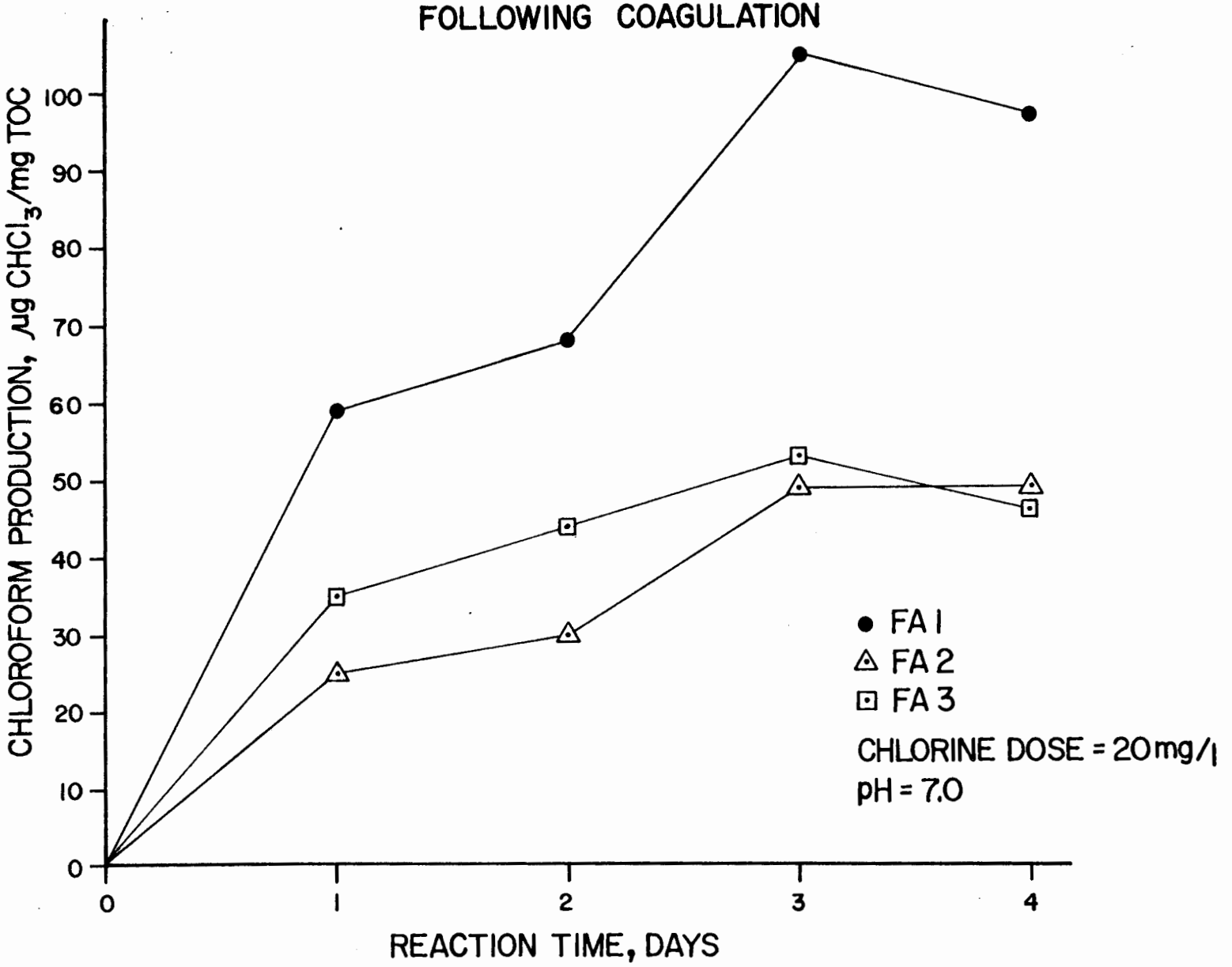


Table 14

Contribution of Fulvic Acid Fractions to Chloroform Production - Effect of Coagulation

	Chloroform Production (Calculated)			
	Before Coagulation		After Coagulation	
Fraction	$[CHCl_3]$, mg/L	% of total $CHCl_3$	$[CHCl_3]$, mg/L	% of total $CHCl_3$
FA 1	442	62.7	4.1	20.8
FA 2	180	25.5	5.9	30.1
FA 3	83	11.8	9.7	49.1
Total	705	-	19.7	-

Basis for calculation: Initial TOC = 5 mg/L

90.4% removal of TOC by coagulation

48 chloroform yields were used

fraction for trihalomethane production is FA 1 (62.7%) but FA 3 becomes the most important contributor in the coagulated water, representing approximately half of the total chloroform produced. The chloroform concentration expected following chlorination of coagulated waters containing fulvic acid, 19.7 μg/ℓ, is in good agreement with observations of many treatment plants including Durham, N.H., that the minimum trihalomethane level seems to be approximately 20-30 μg/ℓ. These calculations reinforce the previous observations that the apparent low molecular weight fraction of fulvic acid is the most important in regard to trihalomethane formation in those treatment plants employing coagulation processes.

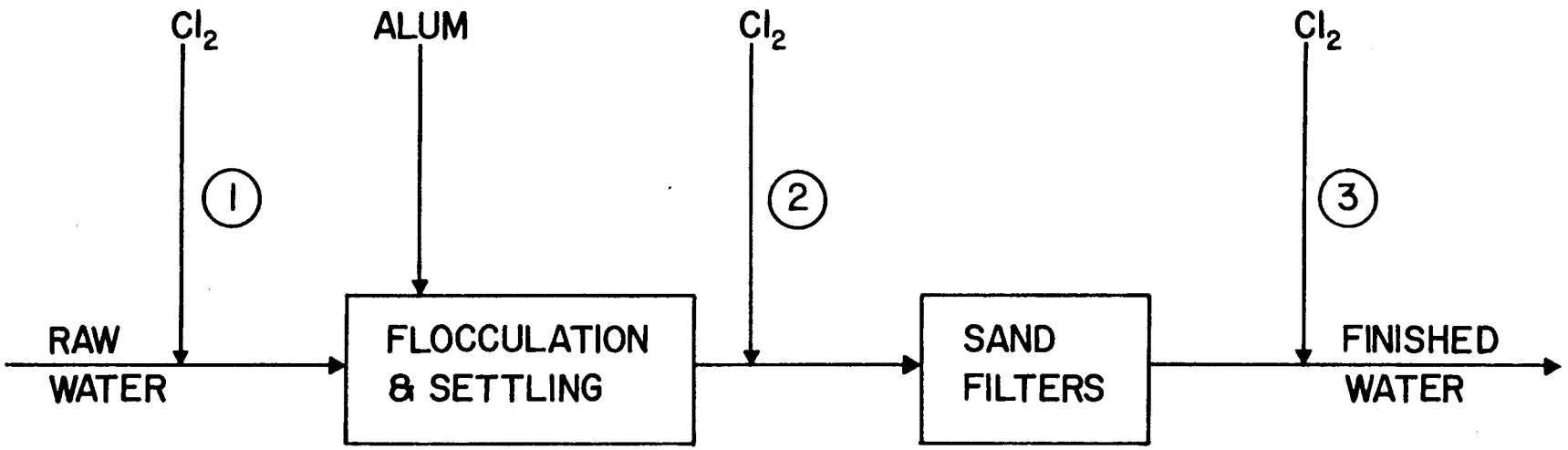
Effect of Simple Treatment Plant Changes on Trihalomethane Production at the Durham-UNH Water Treatment Plant

The water treatment plant in Durham, New Hampshire treats water taken from the Oyster River, a moderately-colored, small stream, and supplies the distribution system for this relatively small New England community and the University of New Hampshire. The treatment process utilizes raw water chlorination with chlorine gas, alum coagulation, open settling basins, rapid sand gravity filters and post chlorination with chlorine gas. The plant is also set up for alkali feed for pH adjustment (corrosion control), sodium fluoride addition and mid-point chlorination (between the settling basins and the filters), but chlorination at this point has never been used. The water treatment plant treats an average of 0.9 MGD and services a permanent population of about 4,500 people plus a resident student population estimated at 4,000. The treatment process is shown in schematic form in Figure 21.

A short term study was conducted in April, 1978 whose primary goal was to examine the effect of a change in chlorination practices on trihalomethane formation. The effects of chlorine contact time and sample storage temperature were also investigated. Referring to the treatment plant schematic in Figure 21, with chlorination occurring at points (1) and (3), daily samples of raw water, settled water and finished water were taken for a period of two weeks and

FIGURE 21

DURHAM, N.H. WATER TREATMENT
PLANT SCHEMATIC



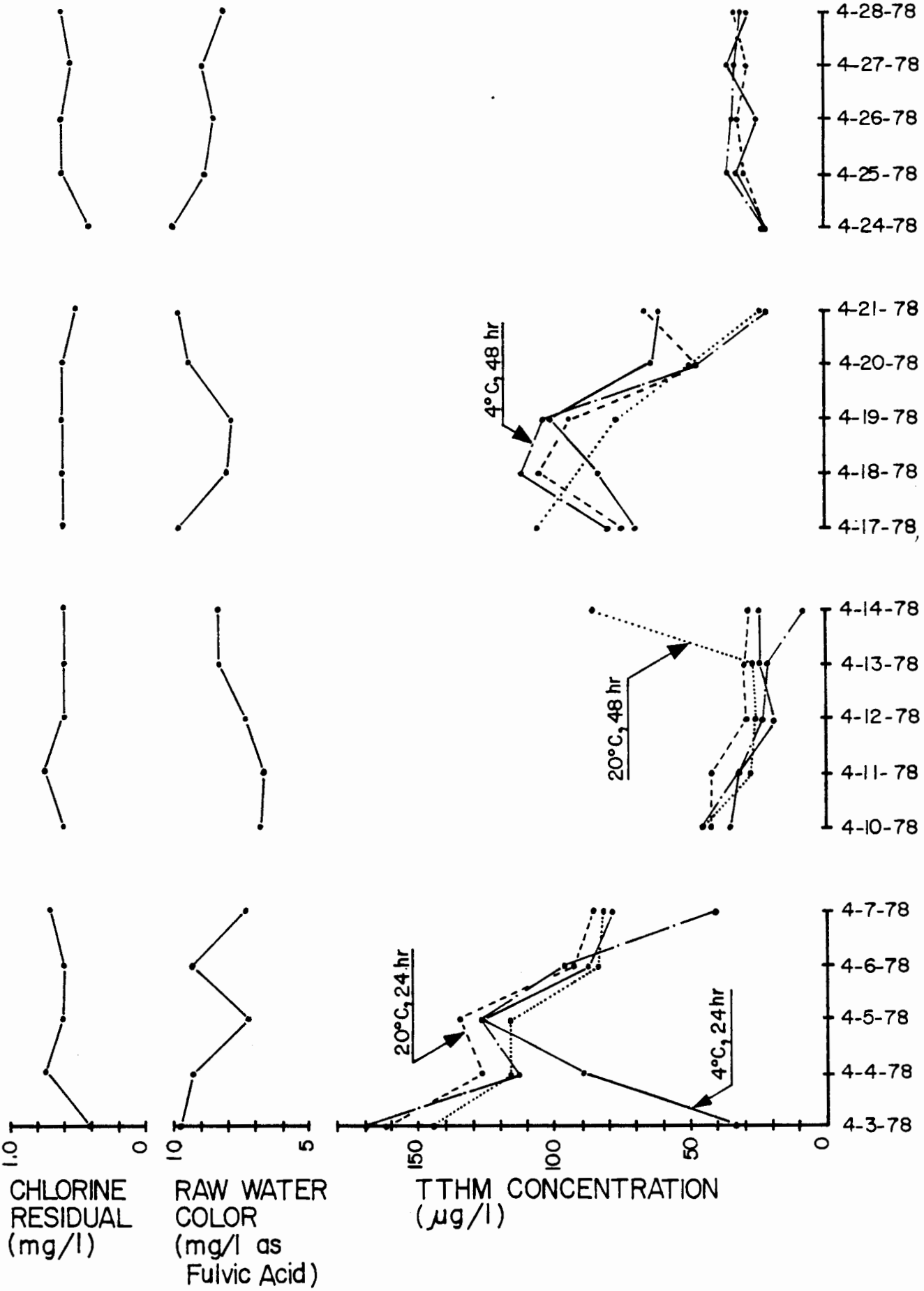
analyzed for color and trihalomethanes. Then the points of chlorination were changed to (2) and (3) and the sampling and testing procedure was repeated. Important variables such as temperature and contact time were controlled by taking multiple samples of finished water and storing them at two different temperatures for specified periods of time before quenching them with sodium thiosulfate to eliminate the chlorine residual and stop the reaction.

This was an in-plant study and as many plant operational parameters as possible were controlled. However, over a period of one month unavoidable changes in raw water quality, temperature, and other raw water variables undoubtedly did occur. As far as chlorination practices were concerned, the operator attempted to maintain the same chlorine residual in the finished water throughout the study period.

Results of the investigation are summarized in Figure 22 (see data in Appendix). Individual daily TTHM results (see Appendix) show a great deal of variation. Although longer contact times and higher storage temperatures generally resulted in higher TTHM concentrations in the water samples, this was not always true. Also, during the period of raw water chlorination, TTHM levels dropped off dramatically so that by the end of the two week period they were only 15 - 20 percent of the TTHM levels measured in samples collected on the first day of testing. When the process was switched to settled water chlorination, TTHM concentrations immediately increased to a level of about 50 - 70 percent of the TTHM concentrations measured in samples collected on the first day of testing (raw water chlorination), then again began to drop off dramatically to lower levels during the final week of testing.

Examination of the mean and standard deviation information (see Appendix) shows that most of the data variation occurred during the first and third weeks of testing - i.e. during the first week of raw water chlorination and during the first week of settled water chlorination. Since raw water color and chlorine residual remained fairly constant throughout the testing period, it appears that this phenomenon was related to some unknown variable related to the process

FIGURE 22
RESULTS OF DURHAM, N.H. IN-PLANT CHLORINATION STUDY



change. Once the operators had become familiar with the process change and the treatment process variables had stabilized, TTHM concentrations leveled out at a low level.

For these reasons, it is felt that comparisons of overall average TTHM concentrations is difficult and that conclusions drawn from these comparisons would be tenuous. Therefore, subsequent data analysis utilizes only the results of the second week of raw water chlorination and the second week of settled water chlorination. Comparison of average TTHM levels recorded during the second week of raw water chlorination with average TTHM levels recorded during the second week of settled water chlorination show that changing the point of chlorination resulted in reductions of average TTHM concentrations ranging from 15 percent to 27 percent among the samples stored at $20^{o}C$. No reduction of average TTHM concentrations was noted among the samples stored at $4^{o}C$.

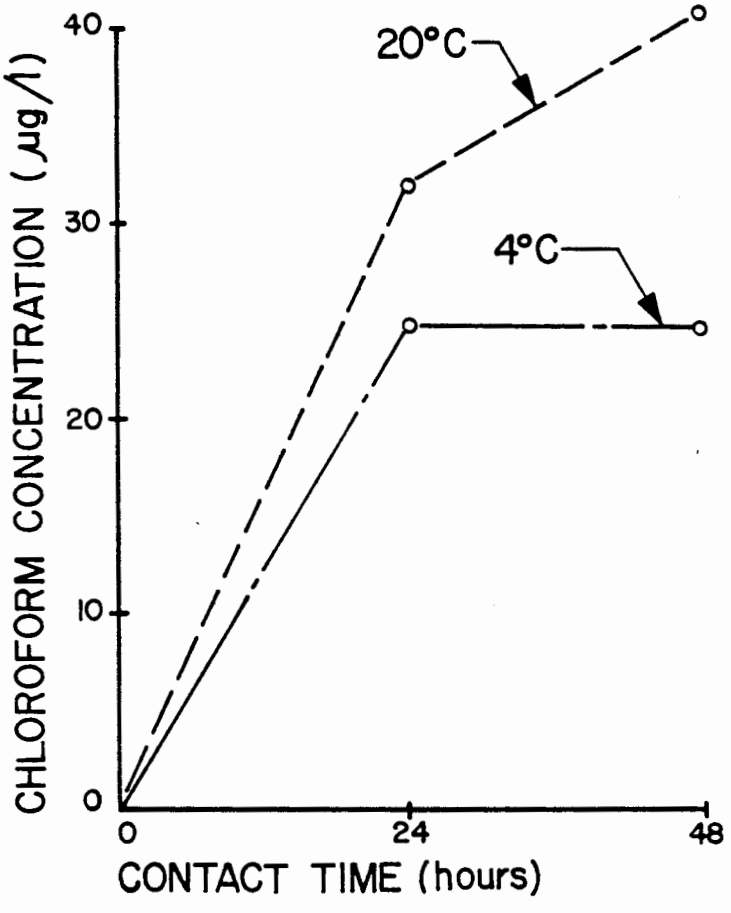
Raw water color remained low (mean of 8.46 mg/ℓ as fulvic acid) and fairly constant (standard deviation of 1.06 mg/ℓ) throughout the test period so no attempt was made to correlate raw water color with finished water TTHM levels. However, the mean raw water color during the second week of settled water chlorination (8.84 mg/ℓ as fulvic acid) was approximately 18 percent higher than the mean raw water color during the second week of raw water chlorination (7.47 mg/ℓ as fulvic acid). This is one possible explanation for the relatively small reduction in TTHM concentrations that resulted from changing the point of chlorination. If TTHM levels were expressed in terms of concentration per unit of raw water color, reductions of average TTHM concentrations ranging from 28 percent to 38 percent among the samples stored at $20^{o}C$ could be attributed to the change in the point of chlorination. Statistical analysis of these results (student's t-test) showed that there is a less than 90 percent probability that these differences in TTHM concentrations are statistically significant, undoubtedly due in part to the number of uncontrolled variables in water quality and plant operation. Also, the raw water color was low at this time and the relative importance of humic compounds as trihalomethane precursors in this

water supply at this time could not be determined.

The effect of sampling variables, time and temperature, is demonstrated in Figure 23. This figure shows the effect of these variables for raw water chlorination samples. Comparison of average chloroform levels in the second week of settled water chlorination showed no significant effects of storage temperature and contact time. Apparently, ultimate trihalomethane production had been limited by the amount of precursor present at the point of chlorination and the reaction was essentially complete before the first measurements were made at a contact time of 24 hours. The trends exemplified by one series of trihalomethane analyses (Figure 23) illustrate the care which should be given to sampling considerations and interpretation of data in trihalomethane studies.

FIGURE 23

EFFECT OF
STORAGE TIME AND TEMPERATURE ON
SAMPLES FOR CHLOROFORM ANALYSIS



CONCLUSIONS

The major conclusions of this study are presented below. The implications for water treatment plant design and operation lie in the understanding of the behavior of humic compounds in coagulation processes and the impact upon chlorination reactions. Additional research is warranted in the areas of alternative coagulants, solution conditions, and treatment processes to determine appropriate treatment strategies for the absolute minimization of trihalomethane formation in drinking waters.

1) Fractionation of soil-derived fulvic acid utilizing adsorption chromatography is a useful technique for the study of fulvic acid. Fractions exhibiting chemical differences were produced which enabled more definitive study of selected reactions of fulvic acid.

2) Fulvic acid was confirmed as a significant precursor to chloroform production upon chlorination. Furthermore, studies of fulvic acid fractions with methyl, alcoholic, phenolic, and carboxylate functional groups showed no major differences insofar as chloroform yield is concerned. Evidently, no single function group or chemical structure is responsible for chloroform production from fulvic acid.

3) The effect of coagulation on fulvic acid is twofold. Coagulation utilizing aluminum sulfate at pH 6 does not result in uniform removal of fulvic acid compounds. The apparent low molecular weight, primarily aromatic fraction of fulvic acid is poorly removed in coagulation processes. In addition, alum coagulation reduces the chloroform yield of compounds not removed by 60-80%. Coagulation, under the conditions employed in this study, does not selectively remove trihalomethane precursors but rather reduces the reactivity of these compounds with chlorine.

REFERENCES CITED

1. Federal Register, Vol. 43, No. 28, February 1978.

2. National Research Council, Drinking Water and Health. National Academy of Sciences, Wash. D.C., (1977).

3. Symons, J.M., Bellar, T.A., Carswell, J.K., DeMarco, J., Kropp, K.L., Robeck, G.C., Seeger, D.R., Slocum, C.J., Smith, B.L., and Stevens, A.A. National Organics Reconnaissance Survey for Halogenated Organics, J.AWWA 67: 634 (1974).

4. Wetzel, R.G., Limnology, W.B. Saunders Co. (1975).

5. Oden, S. Die Huminsauren, Kolloidchem. Beihefte 11: 75-98, (1919).

6. Black, A.P., and Christman, R.F. Characteristics of Colored Surface Waters, J.AWWA 55: 753-770 (1963).

7. Bordelon, B.R. Environmental Factors Affecting the Properties and Precipitation of Coloring Colloids in Aquatic Habitats, Masters Thesis, Louisiana State University, (1973).

8. Gjessing, E.T. Physical and Chemical Characteristics of Aquatic Humus, Ann Arbor Science, Inc. (1976).

9. Wershaw, R.L., and Pinckney, D.J. The Fractionation of Humic Acids from Natural Water Systems, J. Research of the USGS 1: 365, (1973).

10. Dubach, P., and Meta, N.C. The Chemistry of Soil Humic Substances, Soils and Fertilizers 26: 293 (1963).

11. Kemp, A.L. and Wong, H.K. Molecular Weight Distribution of Humic Substances from Lakes Ontario and Erie Sediments, Chemical Geol 14: 15-22 (1974).

12. Swift, R.S. and Posner, A.M. Gel Chromatography of Humic Acid, J. Soil Sci 22: 238-249, (1971).

13. Rashid, M.A. and King, L.H. Molecular Weight Distribution Measurements on Humic and Fulvic Acid Fractions from Marine Clays on the Scotian Shelf, Geochim. Cosmochim. Acta 33: 147-151, (1969).

14. Poirrier, M.A., Bordelon, B.R., and Laseter, J.L. Adsorption and Concentration of Dissolved Carbon-14 DDT by Coloring Colloids in Surface Waters. Environmental Science and Technology 6(12): 1033-1035, (1972).

15. Rook, J.J. Chlorination Reactions of Fulvic Acids in Natural Waters, Environmental Science and Technology 11: 478 (1977).

16. Zogorski, J.S., "Removal of Chloroform from Drinking Water", Univ. of Kentucky Water Resources Research Institute, Lexington, KY, Report #111, (1978).

17. Dallaire, G. "Are Cities Doing Enough to Remove Cancer-Causing Chemicals from Drinking Water?", Civil Engineering - ASCE: 88 (September, 1977).

18. Babcock, D.B. and Singer, P.C., "Chlorination and Coagulation of Humic and Fulvic Acids", J.AWWA 71: 149-52, (1979).

19. Oliver, B.G. and Lawrence, J., "Haloforms in Drinking Water: A Study of Precursors and Precursor Removal", J.AWWA, 71: 161-63, (1979).

20. Schnitzer, M. and Skinner, S.I. Alkali Versus Acid Extraction of Soil Organic Matter, Soil Sci. 105: 392-396, (1968).

21. Richard, J.J. and Junk, G.A. Liquid Extraction for the Rapid Determination of Halomethanes in Water, J.AWWA 69: 62, (1977).

22. Bellar, T.A. and Lichtenberg, J.J., "The Determination of Volatile Organic Compounds at the µg/ℓ Level in Water by Gas Chromatography", Journal American Water Works Association 66: 739, (December 1974).

23. Johnson, J.D. and Overby, R., "Stabilized Neutral Orthotolidine, SNORT, Colorimetric Method for Chlorine", Anal. Chem 41 (13): 1744-50, (1969).

24. Standard Methods for the Examination of Water and Wastewater, 14th ed., American Public Health Assoc., New York, (1975).

25. Ishiwatari, R., "Chemical Characterization of Fractionated Humic Acids from Lake and Marine Sediments", Chemical Geology 12: 113-26, (1973).

26. Sposito, G., et al., "Investigation of Fulvic Acid Extracted from Sewage Sludge Using Carbon 13 and Proton NMR Spectroscopy", Envr. Sci. & Tech. 12: 931-33, (1978).

27. Goh, K.M. and Stevenson, F.J., "Comparison of Infrared Spectra of Synthetic and Natural Humic and Fulvic Acids", Soil Sci. 112(6): 392-400, (1971).

28. Tan, K.H. and J.E. Giddens, "Molecular Weights and Spectral Characteristics of Humic and Fulvic Acids", GEODERMA 8: 221-229, (1972).

29. Vinkler, P., Lakatos, B., and J. Meisel, "Infrared Spectroscopic Investigations of Humic Substances and their Metal Complexes," GEODERMA 15: 231-42, (1976).

30. Stevenson, F.J. and K.M. Goh, "Infrared Spectra of Humic Acids and Related Substances," Geochimica and Cosmochimica Acta 35: 471-83, (1971).

31. Wilson, M.A. and K.M. Goh, "Proton Decoupled Pulse Fourier-Transform ^{13}C Magnetic Resonance of Soil Organic Matter," J. Soil Science 28: 645-52, (1977).

32. Grant, D., "Chemical Structure of Humic Substances," Nature 270: 709-10, (1977).

33. Templeton, G.D., "Trace Metal-Organic Matter Interactions During Early Diagenesis in Anoxic Estuarine Sediments," Ph.D. Dissertation, Department of Chemistry, University of New Hampshire, (1980).

34. Morris, J.C. and B. Baum, "Precursors and Mechanisms of Haloform Formation in the Chlorination of Water Supplies," Water Chlorination-Environmental Impact and Health Effects, Vol. 2, Jolley, R.L., Gorchev, H. and D.H. Hamilton, Jr., Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1978), p. 29-48.

35. Oliver, B.G. and Visser, S.A., "Chloroform Production from the Chlorination of Aquatic Humic Material: the Effect of Molecular Weight, Environment, and Season", Unpublished, (1979).

36. Schnitzer, M. and S.U. Khan, Humic Substances in the Environment (New York: Marcel Dekker, Inc., 1972).

APPENDIX

APPENDIX A. CHLORINATION OF FULVIC ACID FRACTIONS AT pH 7.0

Fraction	Time (hrs)	$[CHCl_3]$ µg/ℓ	$[TOC]_o$ mg/ℓ	µg $CHCl_3$/mg $[TOC]_o$	[Cl] mg/ℓ
FA	24	302	2.8	108	9.4
	48	351		125	8.3
	72	379		135	6.0
	96	494		176	4.9
FA 1	24	252	2.2	115	17.4
	48	333		151	16.7
	72	464		211	15.6
	96	534		243	10.6
FA 2	24	181	1.9	95	12.5
	48	225		118	10.6
	72	353		186	9.5
	96	458		241	8.9
FA 3	24	184	1.6	115	19.3
	48	241		151	16.5
	72	271		169	15.8
	96	334		209	15.3
Chlorine Control	0				17.8
	24				17.8
	48				17.0
	72				17.0
	96				17.4

APPENDIX B. CHLORINATION OF RESIDUAL FULVIC ACID FOLLOWING COAGULATION - RUN 1

pH = 7.0 (.1 M Phosphate buffer - see Experimental)

Cl_2 dose = 20 mg/ℓ

Fraction	Time(hrs)	$[CHCl_3]$, µg/ℓ	$[TOC]_{t=o}$, mg/ℓ	µg $CHCl_3$/mg$[TOC]_{t=o}$	$[Cl]_{free}$, mg/ℓ
Control (buffer & chlorine)	0	19	-		17.3
	24	18			18.9
	48	25			17.5
	72	28			18.5
	96	29			19.4
FA 1	24	78	1.4	56	13.3
	48	101		72	13.1
	72	138		99	12.2
	96	148		106	13.1
FA 2	24	68	2.9	23	15.2
	48	87		30	15.9
	72	143		49	15.2
	96	157		54	15.8
FA 3	24	79	2.3	34	12.2
	48	121		53	14.5
	72	137		60	13.3
	96	bad sample		-	13.1

CHLORINATION OF RESIDUAL FULVIC ACID FOLLOWING COAGULATION - RUN 2

pH = 7.0

Cl_2 dose = 20 mg/ℓ

Fraction	Time(hrs)	$[CHCl_3]$, mg/ℓ	$[TOC]_{t=o}$, mg/ℓ	μg $CHCl_3$/mg$[TOC]_{t=o}$	$[Cl]_{free}$, mg/ℓ
Control (buffer & chlorine)	0	20			18.5
	24	20			18.2
	48	27			17.9
	72	28			17.8
	96	29			19.2
FA 1	24	85	1.4	61	10.1
	48	90		64	13.1
	72	152		109	12.5
	96	123		88	15.8
FA 2	24	78	2.9	27	16.4
	48	83		29	15.2
	72	138		48	15.5
	96	125		43	16.0
FA 3	24	83	2.3	36	14.6
	48	80		35	13.9
	72	106		46	13.6
	96	105		46	14.3

APPENDIX C. CALCULATION OF CONTRIBUTION OF FULVIC ACID FRACTIONS TO CHLOROFORM PRODUCTION - EFFECT OF COAGULATION

Basis: Raw water before coagulation; TOC = 5 mg/ℓ

Assumptions: 1) Raw water contains only fulvic acid
2) mg TOC/unit weight is equal for all fulvic acid fractions

Data

	48 hr Chloroform Yields, μg $CHCl_3$/mg TOC	
Fraction	FA before Coagulated	Residual FA after Coagulation*
FA 1	151	68
FA 2	118	29.5
FA 3	151	44

Calculations

I. Before Coagulation (TOC = 5 mg/ℓ)

Fraction	mg/ℓ TOC**	$[CHCl_3]$, mg/ℓ	% of Total $[CHCl_3]$ due to Fraction
FA 1	2.925	151 x 2.925 = 442	62.7
FA 2	1.525	118 x 1.525 = 180	25.5
FA 3	.55	151 x .55 = 83	11.8
		TOTAL 705	

*Average of two runs (see Appendix B)

**See Assumption 2) above and Table 13 in text

II. After Coagulation (90.4% Removal of FA; Residual TOC = .48 mg/ℓ)

Fraction	mg/ℓ TOC	$[CHCl_3]$, mg/ℓ	% of Total $[CHCl_3]$ due to Fraction
FA 1	.06	68 x .06 = 4.1	20.8
FA 2	.2006	29.5 x .2006 = 5.9	30.1
FA 3	.2194	44 x .2194 = 9.7	49.1
		TOTAL 19.7	

APPENDIX D. DATA FOR DURHAM, NH IN-PLANT STUDY

CHLOROFORM CONCENTRATIONS DURING RAW WATER CHLORINATION

Finished Water Sample	$CHCl_3$ Concentration (µg/ℓ)			
	24 Hour Contact Time		48 Hour Contact Time	
	4°C Storage Temperature	20°C Storage Temperature	4°C Storage Temperature	20°C Storage Temperature
4/3/78	24.0	161.2	169.4	145.1
4/4/78	85.9	124.3	109.1	110.9
4/5/78	122.7	130.7	122.7	110.9
4/6/78	76.8	83.6	88.3	80.9
4/7/78	73.5	79.9	37.5	48.1
4/10/78	33.6	39.4	41.4	42.9
4/11/78	27.7	39.0	27.9	25.7
4/12/78	17.0	27.2	23.9	24.9
4/13/78	23.2	27.2	21.8	25.2
4/14/78	22.5	26.9	8.7	81.7
All data				
Mean	50.69	73.94	65.07	69.63
Standard deviation	36.28	50.00	53.88	42.76
1st week data				
Mean	76.58	115.94	105.40	99.18
Standard deviation	35.31	34.21	48.25	36.49
2nd week data				
Mean	24.80	31.94	24.74	40.08
Standard deviation	6.22	6.63	11.77	24.49

BROMODICHLOROMETHANE CONCENTRATIONS DURING RAW WATER CHLORINATION

Finished Water Sample	$CHBrCl_2$ Concentration (µg/ℓ)			
	24 Hour Contact Time		48 Hour Contact Time	
	4°C Storage Temperature	20°C Storage Temperature	4°C Storage Temperature	20°C Storage Temperature
4/3/78	3.3	3.6	4.0	3.5
4/4/78	3.7	3.5	3.3	3.2
4/5/78	4.3	4.3	4.0	4.3
4/6/78	9.8	7.7	7.9	7.8
4/7/78	6.4	6.1	2.6	3.1
4/10/78	2.5	3.0	3.1	3.1
4/11/78	2.9	2.9	2.5	2.4
4/12/78	2.2	2.2	2.4	2.3
4/13/78	2.3	2.3	2.3	2.2
4/14/78	2.1	2.2	--	4.0
All data				
Mean	3.95	3.78	3.57	3.59
Standard deviation	2.43	1.82	1.75	1.63
1st week data				
Mean	5.50	5.04	4.36	4.38
Standard deviation	2.68	1.82	2.06	1.97
2nd week data				
Mean	2.40	2.52	2.58	2.80
Standard deviation	0.32	0.40	0.36	0.76

CHLOROFORM CONCENTRATIONS DURING SETTLED WATER CHLORINATION

Finished Water Sample	$CHCl_3$ Concentration (µg/ℓ) 24 Hour Contact Time 4°C Storage Temperature	24 Hour Contact Time 20°C Storage Temperature	48 Hour Contact Time 4°C Storage Temperature	48 Hour Contact Time 20°C Storage Temperature
4/17/78	63.8	65.6	72.6	98.4
4/18/78	75.5	97.6	103.5	--
4/19/78	93.4	84.3	93.9	70.8
4/20/78	60.2	42.6	42.6	44.2
4/21/78	55.5	61.0	18.3	19.7
4/24/78	18.7	19.9	19.4	21.1
4/25/78	29.9	28.0	32.3	29.7
4/26/78	23.0	29.1	29.9	30.3
4/27/78	32.9	27.3	30.7	31.1
4/28/78	26.4	28.3	27.4	29.2
All data				
Mean	47.93	48.37	47.06	41.61
Standard deviation	25.34	27.18	31.29	26.27
1st week data				
Mean	69.68	70.22	66.18	58.28
Standard deviation	15.18	21.31	35.53	33.93
2nd week data				
Mean	26.18	26.52	27.94	28.28
Standard deviation	5.59	3.76	5.09	4.08

BROMODICHLOROMETHANE CONCENTRATIONS DURING SETTLED WATER CHLORINATION

Finished Water Sample	$CHBrCl_2$ Concentration (µg/ℓ)			
	24 Hour Contact Time		48 Hour Contact Time	
	4°C Storage Temperature	20°C Storage Temperature	4°C Storage Temperature	20°C Storage Temperature
4/17/78	6.1	5.8	7.0	7.5
4/18/78	6.7	6.8	7.8	6.5
4/19/78	7.4	9.4	8.3	6.4
4/20/78	4.4	5.0	4.4	4.8
4/21/78	5.9	5.2	2.3	2.0
4/24/78	2.2	2.2	2.2	2.4
4/25/78	2.6	2.8	2.7	2.5
4/26/78	2.7	3.0	2.9	3.0
4/27/78	3.1	2.9	3.5	3.2
4/28/78	3.4	3.4	3.7	4.0
All data				
Mean	4.45	4.65	4.48	4.23
Standard deviation	1.92	2.25	2.34	1.97
1st week data				
Mean	6.10	6.44	5.96	5.44
Standard deviation	1.12	1.80	2.54	2.15
2nd week data				
Mean	2.80	2.86	3.00	3.02
Standard deviation	0.46	0.43	0.61	0.64

COLOR ANALYSIS RESULTS

Date	Concentration (mg/ℓ as fulvic acid) Raw Water	Settled Water
4/3/78	9.78	--
4/4/78	9.33	--
4/5/78	7.11	--
4/6/78	9.33	--
4/7/78	7.33	--
4/10/78	6.89	--
4/11/78	6.67	--
4/12/78	7.33	--
4/13/78	8.22	--
4/14/78	8.22	--
4/17/78	9.78	0.60
4/18/78	8.00	0.60
4/19/78	7.78	2.75
4/20/78	9.33	2.75
4/21/78	9.78	1.25
4/24/78	10.00	2.00
4/25/78	8.89	1.25
4/26/78	8.44	0.60
4/27/78	8.89	2.25
4/28/78	8.00	1.00
Mean	8.46	1.51
Standard deviation	1.06	0.87

WATER TREATMENT PLANT OPERATIONAL DATA

Date	Gallons Treated	Chlorine Added			Chlorine Residual (mg/ℓ)
		Prechlorine (lb gas)	Midchlorine (gal HOCl)	Postchlorine (lb/gas)	
4/3/78	781,000	3	0	9	0.40
4/4/78	794,000	3		8	0.75
4/5/78	959,000	3		10	0.60
4/6/78	904,000	3		10	0.60
4/7/78	966,000	3		10	0.70
4/10/78	787,000	3		9	0.60
4/11/78	818,000	2		8	0.75
4/12/78	896,000	3		8	0.60
4/13/78	935,000	2		8	0.60
4/14/78	958,000	3	0	9	0.60
4/17/78	702,000	0	3	7	0.60
4/18/78	799,000		1	7	0.60
4/19/78	938,000		1.5	9	0.60
4/20/78	943,000			9	0.60
4/21/78	1,024,000			9	0.50
4/24/78	776,000			8	0.40
4/25/78	929,000			8	0.60
4/26/78	998,000			10	0.60
4/27/78	943,000			8	0.55
4/28/78	1,016,000	0	1.5	9	0.60

Note: Data source - water treatment plant records