

# Disinfection Byproduct Formation from the Preparation of Instant Tea

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Two instant tea samples formed as much DBPs as aquatic humic substances under the same reaction conditions, although the concentration of tea used for consumption typically is much higher than the concentration of humic substances in natural waters. At typical tea concentrations, substantial levels of TOX (164–196  $\mu\text{g/L}$  as chloride) were generated when chlorinated at 4 mg/L. The TOX formed exceeded the Swiss limit of 25  $\mu\text{g/L}$  as referenced by Fleischacker and Randtke (1983). Use of boiled water in preparation of instant tea is suggested if the residual free chlorine in the tap water is high.

**Keywords:** Disinfection byproducts; DBPs; chlorination; instant tea; tap water

## INTRODUCTION

It is now well established that the practice of chlorination in drinking water treatment produces numerous organic disinfection byproducts (DBPs) with potential adverse health impacts. Humic substances occurring naturally in water sources serve as the major precursors for the reaction with chlorine to produce a variety of DBPs, a large percentage of which are halogenated (Glaze et al., 1979; Christman et al., 1980, 1983; Miller and Uden, 1983; Seeger et al., 1985). Trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), halo ketones (HKs), chloropicrin (CPN), chloral hydrate (CH), cyanogen chloride (CNCl), and cyanogen bromide (CNBr) are all identified chlorination byproducts.

Humic materials have a wide range of molecular weights and sizes, ranging from a few hundred to as much as several hundred thousand atomic mass units (Stevenson, 1994). Substantial evidence shows that humic substances consist of a skeleton of alkyl/aromatic units cross-linked mainly by oxygen and nitrogen groups with the major functional groups being carboxylic acid, phenolic and alcoholic hydroxyls, ketone, and quinone groups. The structures of fulvic acids are somewhat more aliphatic and less aromatic than humic acids; and fulvic acids are richer in carboxylic acid, phenolic, and ketonic groups. Two hypothetical chemical structures of humic acid and fulvic acid are shown in Figure 1 (Schnitzer and Khan, 1972; Stevenson, 1994); however, a wide variety of structural models were proposed by others (Stevenson, 1985; Leenheer et al., 1995; Schulten, 1996).

Tea polyphenols or tea tannins, as they are called, bear some resemblance to humic substances in both color and structure and, accordingly, have the potential to react with the chlorine residual present in tap water

to form DBPs. The four national surveys of free chlorine residuals in drinking water compiled in the disinfectants/DBP rule proposal (USEPA, 1994) show that free chlorine residuals in drinking water were as high as 5.2 mg/L, with a range of survey medians from 0.33 to 1.4 mg/L. Therefore it is very likely that reactions between free chlorine residual and tea polyphenols can take place during the preparation of instant tea, since water directly from the tap is typically used. A review paper on published information has shown that chlorine undergoes oxidation/substitution reactions with several model food compounds and forms byproducts with potential toxicity (Fukayama et al., 1985).

Second only to water, tea is the most widely consumed beverage in the world today with annual per capita consumption exceeding 40 L (International Tea Committee, 1990). There are three general types of tea produced: green (unfermented), oolong (partially fermented), and black (fully fermented). Instant tea, usually a powder, is generally prepared by the aqueous extraction of black tea followed by concentration and drying. It is also possible to make instant tea from green tea; however, this kind is not common in the North America and Europe (Huang and Ferraro, 1992). Instant tea is manufactured in several countries, but production and consumption in the United States is greater than in the rest of the world (*Kirk-Othmer Encyclopedia of Chemical Technology*, 1983).

## CHEMISTRY OF TEA

The outstanding chemical characteristic of tea leaves is their very high concentration of polyphenolic material. Their approximate amounts in fresh leaf, green, and black teas are in the range of 30–35%, 10–25%, and 8–21%, respectively (Lunder, 1992). The most abundant of polyphenols are a group of flavanols which usually constitutes 20–30% of the dry matter. The flavanols of tea belong to the group known as catechins (*Kirk-Othmer Encyclopedia of Chemical Technology*, 1983). In addition to flavanols, tea contains other polyphenols, caffeine, amino acids, and others. A rep-

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**Table 1. Composition of Tea**

(a) Composition of Tea Leaves	
composition	dry wt, <sup>a</sup> %
flavanols (catechins)	17–30
flavonols and flavonol glycosides	3–4
leucoanthocyanins	2–3
polyphenolic acids and depsides	~5
total polyphenols	~30
caffeine	3–4
amino acids and protein	~19
simple carbohydrates	~4
organic acids	~0.5
polysaccharides	~13
ash	~5
cellulose	~7
lignin	~6
lipids	~3
pigments	~0.5
volatiles	0.01–0.02

(b) Polyphenolic Composition of Tea	
composition	w/w, %
unprocessed tea (green tea)	
flavanols (catechins)	17–30
flavonols and flavonol glycosides	3–4
phenolic acids	5
fermented tea (black tea)	
thearubigins	15–20
theaflavins	1–2
bisflavonols	2–4
phenolic acids	4
unchanged flavanols	1–3
flavonols and flavonol glycosides	2–3

(c) Composition of Black Tea Leaves	
composition	dry wt, <sup>b</sup> mg/g
caffeine	4.0
catechin	2.3
epicatechin	4.1
epicatechin gallate	8.0
epigallocatechin	10.5
epigallocatechin gallate	16.6
flavonol glycosides	0.5
theaflavin	2.5
theaflavin gallate	4.1
theaflavin digallate	2.5
thearubigins	59.4
amino acids and protein	190
fiber	300
ash	50
carbohydrate	70

<sup>a</sup>Summation does not equal 100% due to approximation of individual component percentages. <sup>b</sup>Summation does not equal 1000 mg/g—some components may have not been included.

representative analysis of fresh leaf is given in Table 1a (Sanderson, 1972). The polyphenolic composition of tea is shown in Table 1b (Lunder, 1992).

The manufacturing process converts freshly harvested leaf to products of commerce. Black tea is the result of promoting the oxidation of fresh leaf catechins by atmospheric oxygen through catalysis by tea polyphenolase. The most significant change that occurs during the manufacture of black tea is the conversion of the colorless catechins to a complex mixture of orange-yellow to red-brown substances and the development of a large number of volatile compounds. During the formation of black tea, approximately 15% of tea catechins remain unchanged and approximately 10% are oxidized to theaflavin, theaflavic acid, and bisflavanol. About 75% of the catechins are converted to a complex, poorly defined, highly colored, incompletely separated group of substances known as thearubigins whose

molecular weight ranges from 700 to 40 000 Da (*Kirk-Othmer Encyclopedia of Chemical Technology*, 1983). The general composition of black tea leaves is presented in Table 1c (Balentine, 1992).

Some typical structures of catechins, theaflavin, theaflavic acid, bisflavanol, and thearubigins are shown in Figure 2. Because dihydroxybenzene moieties with two free meta-positioned OH-groups have been hypothesized to be responsible for the formation of chloroform during chlorination (Rook, 1977; de Leer et al., 1985), all compounds in Figure 2 are potential DBP precursors.

## OBJECTIVE

DBP formation and chlorine consumption were investigated in the preparation of instant tea with water containing chlorine residual. Aquatic humic substances were included and compared to the instant tea samples in terms of DBP formation and chlorine consumption under selected laboratory chlorination and chloramination conditions which included low tea concentrations. The target compounds of DBPs in this research were shown in Figure 3. In addition, DBP formation and chlorine consumption in realistic instant tea samples (typical instant tea concentrations) chlorinated at a maximum allowable level of free chlorine residual (4 mg/L) were also investigated.

## MATERIALS AND METHODS

**Materials.** Two instant tea samples, Lipton Natural Decaf Iced Tea Mix (Lipton) and Nestlé Iced Tea (Nestea), were obtained from a local supermarket. According to the labels, they were 100% unsweetened instant tea powder without any addition of flavorants. Aquatic humic substances were obtained from two blackwater rivers in Florida, the Santa Fe River (SFR) and the St. Marys River (St MR), a eutrophic lake (Newnans Lake, abbreviated as NL DOC), and a surficial groundwater source in a planted pine forest (Orange Heights, abbreviated OH DOC). The aquatic humic substances were extracted through a XAD-8 column and eluted by backflushing with 0.1 M NaOH; the 0.1 M NaOH solutions of concentrated aquatic humic substances were then eluted through a cation exchange column to convert the humic substances to the H<sup>+</sup> form. The aquatic humic substances were frozen at -40 °C and freeze-dried to provide the humic materials in dried form.

All DBP calibration standards (except cyanogen halides), internal standards, and surrogate standards used in this research were purchased from AccuStandard Inc., Aldrich Chemical Co., Supelco Inc., and ULTRA Scientific. CNCl standards were in situ synthesized in this laboratory or purchased in a methanol solution (Protocol Analytical Supplies, Inc.). The in situ synthesized CNCl standard has been demonstrated to be comparable with the purchased commercial standards (Wu et al., 1998). CNBr was purchased from Fisher Scientific Co. as solid crystals.

All other chemicals employed in this study were reagent grade or better (Fisher Scientific Co.). The reagent water used was Type 1 water (APHA, 1995) produced by Barnstead NANOpure ultrapure water system. Sodium hypochlorite solutions prepared from reagent grade NaOCl were used as a source of free chlorine. Preformed monochloramine was prepared by dropwise addition of equal volumes of NaOCl dosing solution (5000 mg/L as Cl<sub>2</sub>) into a buffered NH<sub>4</sub>Cl solution at pH 9.0 (4773 mg/L as NH<sub>4</sub>Cl) in a well-stirred Erlenmeyer flask on ice in a concentration ratio of 4 mg of Cl<sub>2</sub> to 1 mg of N. Preliminary experiment and literature review (Smith and Singer, 1994; Cowman and Singer, 1996) showed that the resulting solution had at least 96% conversion of free chlorine into monochloramine and no residual free chlorine was detected. Monochloramine solutions were prepared fresh on the day of each chloramination.

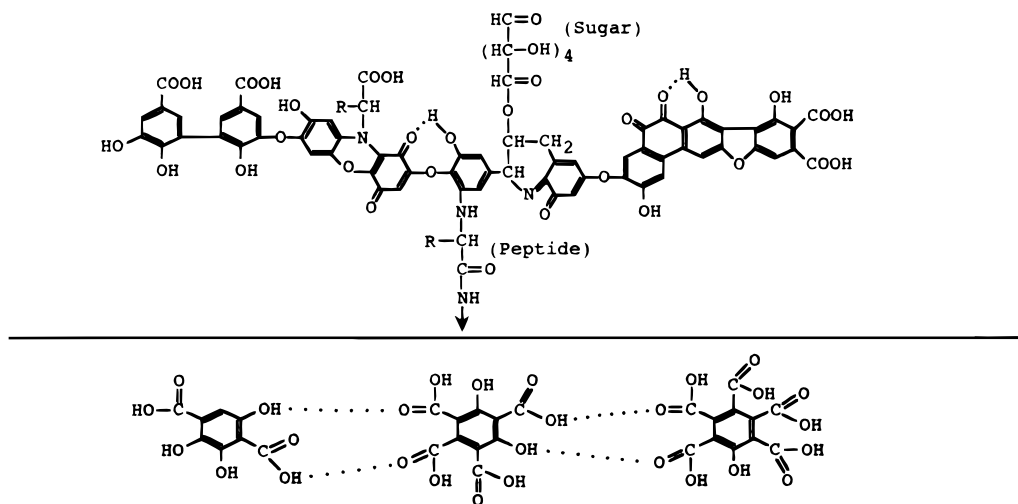


Figure 1. Hypothetical structures of humic acid and fulvic acid.

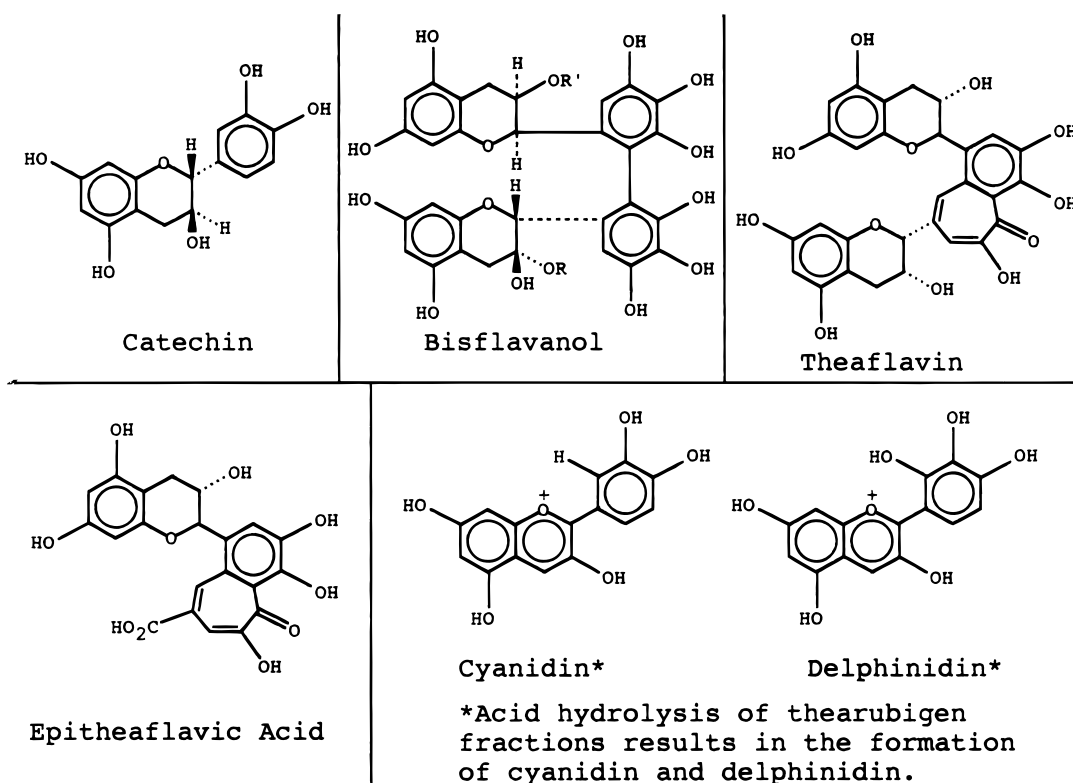


Figure 2. Some typical structures of the polyphenols found in black tea.

**Parameters.** Preliminary disinfectant demand experiments were run to determine the appropriate chlorine and chloramine dosages for subsequent DBP formation experiments. DBP formation was not measured in these preliminary experiments. For the first set of the experiments, tea samples and humic substances were dissolved in pH  $7 \pm 0.1$  buffer solutions and chlorinated with sodium hypochlorite at 25 °C in the absence of light and bromide ion. At the end of 24 h, samples were analyzed for chlorine residuals. For the second set of the experiments, chloramination was performed in a manner similar to chlorination. The two sets of experiments were studied under a series of conditions shown in Table 3a. Three chlorine/NPOC levels were performed to investigate the effect of chlorine dosages on the extents to which chlorine reacted with the tea samples and humic substances.

The water samples prepared from those instant tea powders and aquatic humic substances were then studied for DBP formation in a series of experiments performed under a series

of conditions shown in Table 3b. Chlorine and chloramine doses were chosen to achieve the chlorine and chloramine residual concentrations of at least 0.6 and 2.4 mg/L, respectively, at the end of the 24-h reaction period for all samples based on the results of disinfectant demand experiments. Although the chlorine residual after 24 h in realistic instant tea would rarely, if ever, be a nonzero value, a chlorine residual was maintained for the diluted tea samples (NPOC = 5 mg/L). This allows an equitable comparison to the humic samples. A chlorine residual at the end of the reaction period is specified in typical DBP formation potential tests used to characterize waters containing aquatic humic substances (APHA 5710B, 1995; Cowman and Singer, 1996). Seasonal averages of  $\text{Br}^-$  for 100 utilities in the U.S. were reported to range from 2 to 429  $\mu\text{g/L}$  (Amy et al., 1994). The  $\text{Br}^-$  concentration of 250  $\mu\text{g/L}$  was chosen in this research to give a sufficiently high impact on species distribution between chlorinated and brominated DBPs, while keeping the  $\text{Br}^-$  concentration within a reasonable range.

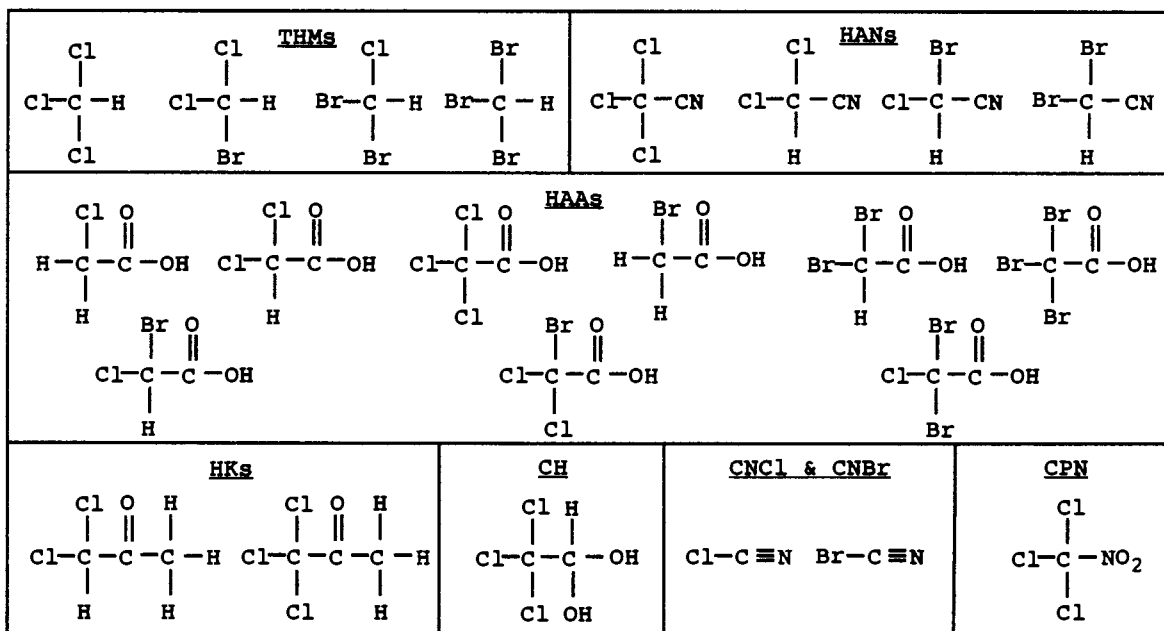


Figure 3. Target DBPs.

Table 2. Elemental Composition of the Humic Substances and Instant Tea Samples Expressed as Percent by Weight

source	moisture	ash <sup>b</sup>	elements <sup>a</sup>				N/C, <sup>d</sup> ×10
			C	H	N	O <sup>c</sup>	
SFR	1.65	1.15	49.41	3.69	0.77	46.13	0.13
St MR	0.62	0.43	51.17	3.82	0.61	44.41	0.10
OH DOC	1.20	2.35	50.48	4.10	0.49	44.93	0.08
NL DOC	0.28	6.62	50.23	4.60	0.79	44.38	0.13
Lipton	8.21	31.5	54.22	6.34	2.29	37.15	0.36
Nestea	8.56	17.7	57.84	6.81	4.56	30.79	0.68

<sup>a</sup> Corrected for moisture and ash content. <sup>b</sup> Represents approximate inorganic content. <sup>c</sup> Calculated by difference. <sup>d</sup> Molar ratios.

Table 3. Experimental Conditions: (a) Disinfectant Demand Experiment; (b) DBP Formation Experiment

parameters	a	b
temp, °C	25 ± 2	25 ± 2
pH	7.0 ± 0.1	7.0 ± 0.1, 8.5 ± 0.1
Br <sup>-</sup> concn, µg/L	0	0, 250
NPOC, <sup>a</sup> mg/L	5	5
chlorine dose, mg/L	6, 9, 12.5	12.5
chlorine dose/NPOC	1.2, 1.8, 2.5	2.5
chloramine dose, mg/L	3, 4.5, 6.25	6.25
chloramine dose/NPOC	0.6, 0.9, 1.25	1.25
contact time, h	24	24

<sup>a</sup> Nonpurgeable organic carbon.

**Experimental Design and Methods.** For DBP formation investigation, chlorination was conducted in borosilicate glass vials (nominally 40 mL) sealed with Teflon-faced septa. Each experiment was conducted with five vials. The first two vials were used for UV254 measurement before chlorination and for chlorine residual analysis at the end of the 24-h reaction period, respectively. UV254 absorbances were measured by standard method 5910 UV-absorbing organic constituents (APHA, 1995) for UV254 absorbance on a Perkin-Elmer model 552 double beam grating spectrophotometer. The chlorine residual concentrations were analyzed by standard method 4500-Cl G DPD colorimetric method (APHA, 1995) on a Milton Roy Spectronic 21 UV spectrophotometer. The remaining vials were used for EPA method 551.1, EPA method 552.2, and microliquid/liquid ( $\mu$ -LLE) extraction for cyanogen halide

measurements (Scimienti et al., 1994). At the end of the 24-h reaction period, different dechlorinating agents were added to terminate the DBP formation according to different methods used.

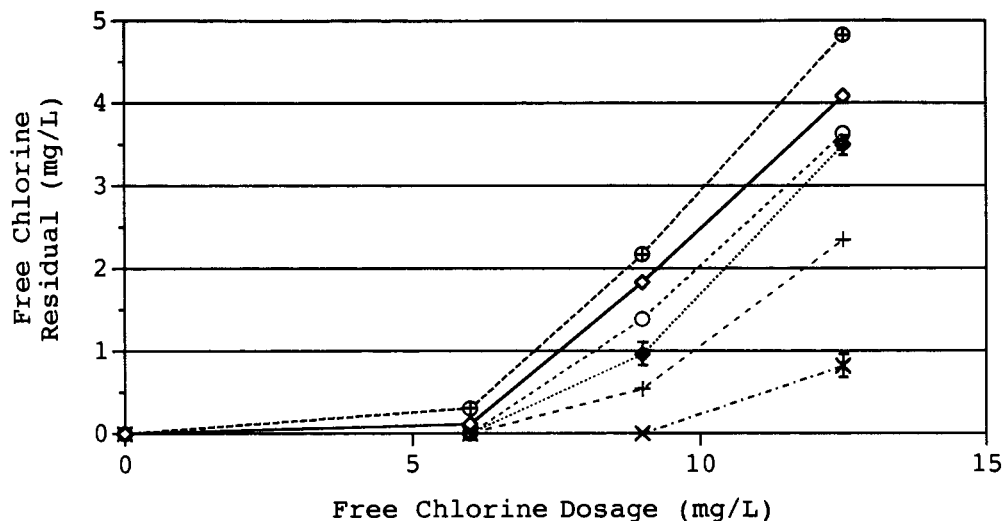
Chloramination was performed in a manner similar to chlorination using the freshly prepared monochloramine solutions as mentioned before. No dechlorinating agent was added to the samples in chloramination for EPA method 551.1 and EPA method 552.2 analyses. The two methods specify the use of ammonium chloride as the dechlorinating agent for chlorinated samples, and the two methods do not call for the removal of monochloramine prior to extraction. Therefore, at the end of the 24-h reaction period the samples in chloramination were stored as they were at 4 °C and were extracted on the next day. However, the addition of ascorbic acid to dechlorinate the samples for cyanogen halide measurement was practiced in this research as specified in the aforementioned method (Scimienti et al., 1994).

The DBPs formed in chlorination and chloramination were determined by EPA method 551.1, EPA method 552.2, and  $\mu$ -LLE for cyanogen halide, using a Perkin-Elmer AutoSystem gas chromatograph (GC) equipped with an electron capture detector (ECD). Analytical separation was achieved with a 0.53-mm i.d., 30-m fused silica capillary column (DB-5ms) with 1.5- $\mu$ m film thickness (J&W Scientific). Selected samples were analyzed with GC/mass spectrometers (GC/MS), which will be discussed later.

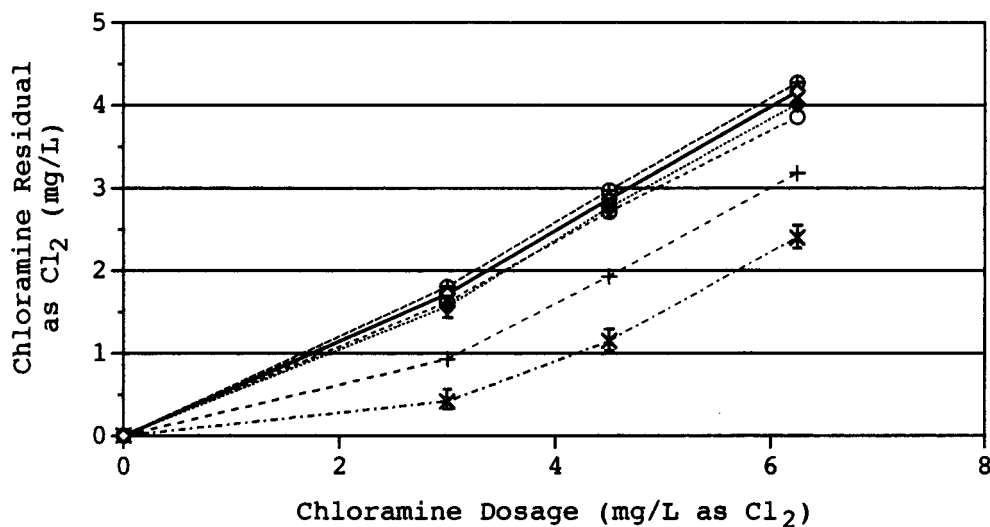
The NPOC concentration of the tea samples and the humic substances samples used in the previously discussed chlorination and chloramination experiments was 5 mg/L. The chlorination experiment extended to realistic instant tea samples of NPOC = 925 and 1175 mg/L, respectively, for Lipton and Nestea samples. The aforementioned high NPOC concentrations were obtained by dissolving 2.9573 g of tea powder to 1 L of Type 1 reagent water at room temperature adjusted to pH 7 by phosphate buffer (0.7 g to 8 fl oz of water, according to the preparation suggestion on labels).

The maximum residual free chlorine level in the proposed disinfectants/DBP rule is 4.0 mg/L (USEPA, 1994); accordingly all realistic instant tea samples were dosed at 4.0 mg/L free chlorine in an open container to simulate the highest level of free chlorine that consumers should encounter in public water supplies in the U.S. The free chlorine contact time was initially set to be 4 h. However, as will be discussed later, the free chlorine dissipated instantaneously; therefore, virtually no contact time longer than 1 min was needed in the realistic tea segment of the study.





**Figure 4.** Free chlorine residual for the humic substances and tea samples in the absence of bromide ion at pH 7 after 24 h. —◇—, SFR; —○—, OH DOC; —+—, Lipton; —◆—, St MR; —⊗—, NL DOC; —×—, Nestea.



**Figure 5.** Chloramine residual for the humic substances and tea samples in the absence of bromide ion at pH 7 after 24 h. —◇—, SFR; —○—, OH DOC; —+—, Lipton; —◆—, St MR; —⊗—, NL DOC; —×—, Nestea.

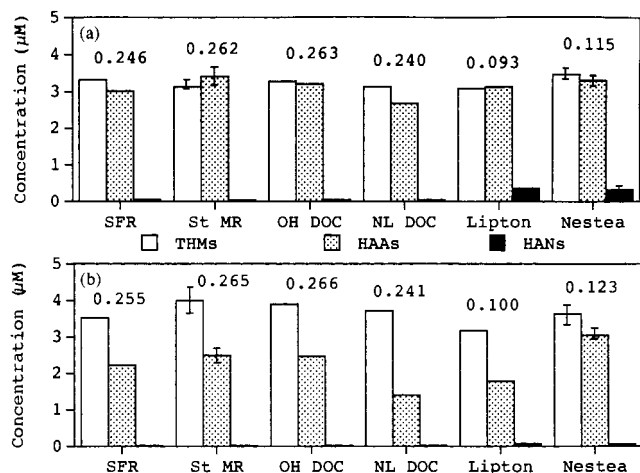
In realistic tea experiments, the free chlorine residual was measured by standard method 4500-Cl D amperometric titration method (APHA, 1995) using a CL Titrimeter model 397 (Fisher Scientific Co.); this method, although introduced specifically for water analysis, was used in this study for free chlorine determination in the realistic tea samples because it is not subject to interference from the color of the sample. The DBPs formed were determined by EPA method 524.2, using a GC/MS (5840A GC/5985 MS, Hewlett-Packard), and EPA method 625, using a GC/MS (AutoSystem GC/QMASS, Perkin-Elmer). The former is a purge-and-trap (P&T) GC/MS method, and the latter is a liquid/liquid extraction followed by GC/MS analysis. TOX analysis was performed by using standard method 5320 B adsorption-pyrolysis-titrimetric method (APHA, 1995).

**Elemental Composition.** Elemental analyses of the instant tea samples and aquatic humic substances were carried out using a Carlo Erba Model 1106 CHN analyzer in duplicate. The moisture and ash content of each sample were measured by drying in an evacuated (11 mg Hg) vacuum oven at 60 °C for 24 h and ignition at 750 °C for 2 h, respectively, in duplicate. The results of these analyses are presented in Table 2.

## RESULTS AND DISCUSSION

**Disinfectant Demand.** Chlorine dose and chlorine residual data are portrayed in Figure 4, while chlora-

mine dose and residual data are shown in Figure 5. The shapes of the curves in these figures are similar for tea and aquatic humic substance samples, although the chlorine demands for the tea samples were greater than those for the humic samples. At initial disinfectant doses of 12.5 mg/L ( $Cl_2/NPOC$  ratio of 2.5) in chlorination and 6.25 mg/L as  $Cl_2$  ( $Cl_2/NPOC$  ratio of 1.25) in chloramination, the free and combined chlorine demands, respectively, for the Lipton sample (10.1 and 3.1 mg/L as  $Cl_2$ ) and the Nestea sample (11.9 and 3.9 mg/L as  $Cl_2$ ) were both higher than for any of the humic samples. Although there may have been some chlorine demand not associated with DBP formation, the higher chlorine demands associated with the tea samples as compared to the humic samples may indicate a comparably higher DBP formation. Luong et al. (1982) proposed that the activation of the humic structure through oxidation reactions produces active sites followed by substitution reactions with oxidant to produce halogenated organics. The increase in the 24-h chlorine demand as the chlorine dosage increases may have been caused by greater chlorine reactivity in oxidation and substitution reactions with tea samples as compared with humic substances.



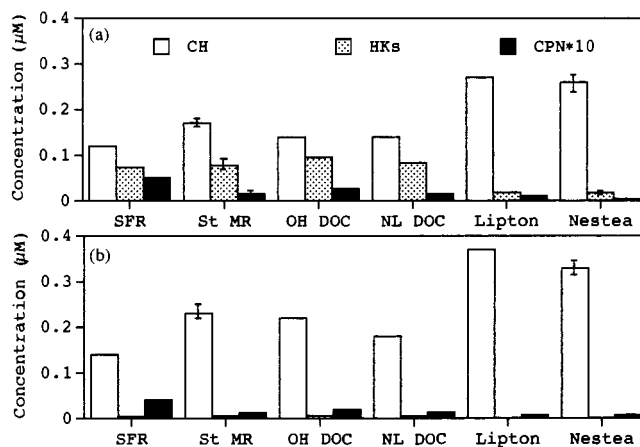
**Figure 6.** Comparison of THM, HAA, and HAN formation between the tea samples and the aquatic humic substances in the absence of bromide ion. (a) pH 7 with UV254 absorbance ( $\text{cm}^{-1}$ ); (b) pH 8.5 with UV254 absorbance ( $\text{cm}^{-1}$ ).

Between the two tea samples, there was a significant difference in the nitrogen content (Table 2). Reckhow et al. (1990) hypothesized that nitrogen groups and activated aromatic carbons serve as sites that are particularly reactive to chlorine, producing chlorinated byproducts. The higher chlorine demand of Nestea (11.9 mg/L) compared to that of Lipton (10.1 mg/L) may be attributed to the higher N content in the Nestea.

In DBP formation experiments, it is important to have a chlorine residual present at the end of the reaction period. Accordingly, a free chlorine dosage of 12.5 mg/L was used in the chlorination experiments to provide a minimum of 0.6 mg/L residual at the end of the 24-h reaction period, and a chloramine dosage of 6.25 mg/L as  $\text{Cl}_2$  was used in the chloramination experiments, providing a minimum residual 2.4 mg/L as  $\text{Cl}_2$ . In addition, the highest chloramine dose of 6.25 mg/L as  $\text{Cl}_2$  was used thereafter in subsequent DBP formation experiments in order to achieve sufficient DBP detection sensitivity since chloramination forms much less DBPs compared to chlorination.

**Chlorination.** Figure 6 shows that the two tea samples formed as much THMs, HAAs, and HANs as the aquatic humic substances under the same reaction conditions. It is interesting to note that the UV254 absorbance values of the two tea samples (ranging from 0.093 to 0.123  $\text{cm}^{-1}$ ) are considerably lower than the values for those aquatic humic substances (ranging from 0.240 to 0.266  $\text{cm}^{-1}$ ), while the tea samples still formed concentrations of DBPs comparable to those of the aquatic humic substances. It is also interesting to note that the higher chlorine demands for the two tea samples did not result in higher DBP formation, indicating that the oxidation reactions are probably favored over substitution reactions for the tea samples compared to the aquatic humic substances. However, Figure 6 also shows that the Nestea sample formed higher concentrations of THMs and HAAs than the Lipton sample, which is consistent with the prediction based on chlorine consumption.

In addition to THMs, HAAs, and HANs, all the other target compounds listed in Figure 3 were found in chlorinated tea samples, except cyanogen halides, which are unstable in the presence of free chlorine (Xie and Reckhow, 1992). Figure 7 shows that CH concentrations reported in the tea samples were consistently



**Figure 7.** Comparison of CH, HK, and CPN formation between the tea samples and the aquatic humic substances in the absence of bromide ion. (a) pH 7; (b) pH 8.5.

higher than those found in the aquatic humic substances, perhaps implying haloaldehydes were favored chlorinated byproducts in the chlorination of tea polyphenols. However, the formation of dichloropropanone, trichloropropanone (DCPO and TCPO are collectively called HKs), and CPN in the tea samples was less compared to the aquatic humic counterparts. It has been reported that TCPO (DCPO not quantitated) was the only DBP that showed higher yields for the fulvic fractions over the corresponding humic fractions; and a higher methyl ketone content in the fulvic fraction was proposed to be responsible for the higher TCPO yields (Reckhow et al., 1990). Figure 2 shows the typical structures of the polyphenols found in black tea; none of which contains methyl ketone moieties. The lower CPN (a N-containing DBP) concentration found in tea samples is noteworthy because the higher N content in the tea samples (Table 2) resulted in higher HAN formation but lower CPN formation compared to the aquatic humic substance samples. The N contents of the two tea samples were the highest, but no corresponding comparably high CPN concentrations were observed.

The effect of pH on DBP formation was similar for chlorination of both the humic and tea samples. The increasing trend for THM formation and decreasing trend for HAA formation with increasing pH have been well documented elsewhere (Stevens et al., 1989). The two trends were also shown in this research presented in Figure 6. Data shown in Figure 6 also suggest base-catalyzed hydrolysis of HANs since the HANs concentrations at pH 8.5 were lower than at pH 7.0. This is particularly evident for the tea samples. Base-catalyzed hydrolysis of HKs and CPN was also suggested by the data in Figure 7.

The effect of bromide ion on DBP formation was similar for chlorination of both the humic and tea samples. The addition of 250  $\mu\text{g/L}$  bromide ion caused changes in the THM, HAN, and HAA species distribution—decreasing chlorinated DBP concentrations while increasing bromine-containing DBP concentration. The presence of bromide ion led to reduced yields of HKs, CH, and CPN, since their brominated analogues were not quantitated in this research. Although the total mass concentrations of the THMs, HAA, and HANs increased during chlorination of the humic and tea samples, their molar yields were not substantially altered.

**Table 4. Results of TOX Analysis**

source	TOX ( $\mu\text{g/L}$ as chloride)
Lipton	196
Nestea	164
Nestea spike <sup>a</sup>	192

<sup>a</sup> Nestea spiked with 250  $\mu\text{g/L}$  bromide ion.

**Chloramination.** For the two tea samples, chloramination produced less than 2.4% of the THMs produced by chlorination, and HAA formation by chloramination was from 83 to 91% lower than by chlorination. In addition to THMs and HAAs, all the target DBPs listed in Figure 3 were found in chloraminated waters containing tea samples except trichloroacetonitrile (TCAN) and CNBr. TCAN formation was less than 0.09  $\mu\text{g/L}$  in chlorinated tea samples; therefore, the absence of TCAN in chloraminated tea samples is not surprising, since HANs are formed at lower amounts with chloramines as reported elsewhere. CNBr was not detected in any of the chloraminated samples. CNCl was detected for all samples; lower CNCl concentrations were found in the tea samples as compared to the aquatic humic samples. This may suggest that there was no simple correlation between the N content and CNCl formation.

**Realistic Instant Tea Samples.** The proposed maximum residual free chlorine level of 4.0 mg/L was used in the instant tea preparation as discussed before. Repeated analyses showed that the free chlorine of 4 mg/L present in Lipton and Nestea tea samples was quickly dissipated. The quick disappearance of free chlorine was expected due to both its reactivity and the large number of organic compounds found in these tea samples (NPOC  $\approx$  1000 mg/L).

Because the  $\text{Cl}_2/\text{NPOC}$  ratio of the reaction mixture was comparatively small (approximately 4/1000 mg/mg) as opposed to those normally encountered in water treatment (0.5/1–3/1 mg/mg), the DBPs formed, if any, were not likely to be extensively chlorinated or oxidized. In other words, reaction products were not likely to be small fragments of larger molecules and their identification by GC or GC/MS might not be possible. It was assumed that much of the organically bound halogen in this realistic tea study occurred in unidentified halogenated macromolecules. P&T GC/MS analysis for volatile organics of the realistic tea samples encountered peak overlapping interference and broadly unresolved humps on chromatograms, probably due to the vast amounts of volatile organic aroma present in tea. Serious foaming was observed in liquid/liquid extraction for semivolatile organic analysis; in addition, the apparent denaturation of tea components (floclike or cloudlike) appearance in acidified samples made any subsequent procedures difficult.

The unidentifiable DBPs formed were either too large in molecular weight to be separated by GC column or could not be concentrated due to aforementioned analytical difficulties. However, those byproducts might be simple to detect by TOX. Korshin et al. (1997) reported that approximately 15% of the 7-day TOX in their water samples was produced in the first half minute of reaction, and concluded that the virtually instantaneous appearance of TOX is possible during the chlorine/organic reaction. The results of TOX analysis of the realistic tea samples are listed in Table 4, which shows that TOX formed during the preparation of instant tea using a realistic free chlorine dose exceeded the Swiss

limit of TOX of 25  $\mu\text{g/L}$  as referenced by Fleischacker and Randtke (1983), although there are no current federal regulations for TOX in the United States. Specific compounds that compose the TOX generated in the free chlorination of the instant teas were not identified and, therefore, their health consequences cannot be determined. On the other hand, specific chlorinated organics of health significance were produced for both humic and tea samples of low concentrations. Accordingly, identification of the specific compounds associated with the tea TOX would be important to assess any health implications connected with the preparation of instant tea directly from chlorinated tap water. In light of this, the use of boiled water in the preparation of instant tea is suggested if the residual free chlorine is determined to be high in the particular distribution system.

The non-chlorinated byproducts in the realistic tea samples also deserve some discussion. As discussed previously, the oxidation reactions are probably favored over substitution reactions for the tea samples compared to the aquatic humic substances. Therefore, non-chlorinated byproducts may result from the oxidation of tea polyphenols by chlorine more preferably than aquatic humic substances. This causes property changes of the integrity of tea beverage. Cao et al. (1996) found that black and green teas ranked high in their antioxidant capacities as compared to 22 vegetables investigated in their research. However, the antioxidant capacities of teas may be decreased by reacting with the chlorine residual (an oxidant) in tap water. Although little is known about the human health effects of the non-chlorinated oxidized tea content, they are of interest because large amounts of polyphenolic compounds in tea are ingested by tea drinkers. Average tea consumption is 7–9 g/day/person in Qatar, Ireland, the United Kingdom, and Iraq, 4.5–7 g/day/person in Hong Kong, New Zealand, and Turkey, and about 1 g/day/person in the United States and China (WHO, 1991). Since polyphenolic material in black teas is about 20–30% of the dry solids in tea extract, the total polyphenolic ingestion in humans is therefore in the range of 0.3–1 g/day/person. However, more research is needed to fully evaluate the formation of the non-chlorinated oxidized tea content and the property changes of the integrity of tea beverage with chlorine residual in tap water.

## CONCLUSIONS

In DBP formation experiments, the two tea samples formed as much THMs, HAAs, and HANs as the aquatic humic substances under the same reaction conditions even though the UV254 absorbances of the two tea samples (ranging from 0.093 to 0.123  $\text{cm}^{-1}$ ) are considerably lower than the values of those aquatic humic substances (ranging from 0.240 to 0.266  $\text{cm}^{-1}$ ). It is also interesting to note that the higher chlorine demands for the two tea samples did not result in higher DBP formation, indicating that the oxidation reactions are probably favored over substitution reactions for the tea samples compared to the aquatic humic substances.

At realistic tea concentrations, substantial levels of TOX (164–196  $\mu\text{g/L}$  as chloride), as compared to the Swiss limit of 25  $\mu\text{g/L}$ , were generated when chlorinated at 4 mg/L. Use of boiled water in preparation of instant tea is suggested if the residual free chlorine in the tap water is high.



## ACKNOWLEDGMENT

We thank Dr. Michael D. Annable and Charles J. Schmidt of the University of Florida for allowing use of GC/ECD and GC/MS instrumentation.

## LITERATURE CITED

- Amy, G. L.; Siddiqui, M.; Zhai, W.; DeBroux, J.; Odem, W. *Survey of Bromide in Drinking Water and Impacts on DBP Formation*; AWWARF: Denver, CO, 1994.
- APHA; AWWA; WEF. *Standard Methods for Examination of Water and Wastewater*, 19th ed.; 1995.
- Balentine, D. A. Manufacturing and chemistry of tea. In *Phenolic Compounds in Food and Their Effects on Health II*; American Chemical Society: Washington, DC, 1992; pp 102–117.
- Cao, G.; Sofic, E.; Prior, R. L. Antioxidant capacity of tea and common vegetables. *J. Agric. Food Chem.* **1996**, *44*, 3426–3431.
- Christman, R. F.; Johnson, J. D.; Pfaender, F. K.; Norwood, D. L.; Webb, M. R. Chemical identification of aquatic humic chlorination products. In *Water Chlorination: Environmental Impact and Health Effects*, Jolley, R. L., et al., Eds.; Ann Arbor Science Publ.: Ann Arbor, MI, 1980; Vol. 3, pp 75–83.
- Christman, R. F.; Norwood, D. L.; Millington, D. S.; Johnson, J. D. Identity and yields of major halogenated products of aquatic fulvic acid chlorination. *Environ. Sci. Technol.* **1983**, *17*, 625–628.
- Cowman, G. A.; Singer, P. C. Effect of bromide ion on haloacetic acid speciation resulting from chlorination and chloramination of aquatic humic substances. *Environ. Sci. Technol.* **1996**, *30*, 16–24.
- de Leer, E. W. B.; Sinninghe Damsté, J. S.; Erkelens, C.; de Galan, L. Identification of intermediates leading to chloroform and C-4 diacids in the chlorination of humic acid. *Environ. Sci. Technol.* **1985**, *19*, 512–522.
- Fleischacker, S. J.; Randtke, S. J. Formation of organic chlorine in public water supplies. *J. Am. Water Works Assoc.* **1983**, *75*, 132–138.
- Fukayama, M. Y.; Tan, H.; Wheeler, W. B.; Wei, C. I. Reactions of aqueous chlorine and chlorine dioxide with model food compounds. *Environ. Health Perspect.* **1986**, *69*, 267–274.
- Glaze, W. H.; Peyton, G. R.; Saleh, F. Y.; Huang, F. Y. Analysis of disinfection byproducts in water and wastewater. *Intern. J. Environ. Anal. Chem.* **1979**, *7*, 143–160.
- Huang, M. T.; Ferraro, T. Phenolic compounds in food and cancer prevention. In *Phenolic Compounds in Food and Their Effects on Health II*; American Chemical Society: Washington, DC, 1992; pp 8–34.
- International Tea Committee Ltd. *Annual bulletin of statistics*; London, 1990.
- Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed.; John Wiley & Sons: New York, 1983; Vol. 22, pp 628–644.
- Korshin, G. V.; Li, C. W.; Benjamin, M. M. The decrease of UV absorbance as an indicator of TOX formation. *Water Res.* **1997**, *31*, 946–949.
- Leenheer, J. A.; Wershaw, R. L.; Reddy, M. M. Strong-acid, carboxyl-group structures in fulvic acid from the Suwannee River, Georgia. 2. major structures. *Environ. Sci. Technol.* **1995**, *29*, 399–405.
- Lunder, T. L. Catechins of green tea: antioxidant activity. In *Phenolic Compounds in Food and Their Effects on Health II*; American Chemical Society: Washington, DC, 1992; pp 114–120.
- Luong, T. V.; Peters, C. J.; Perry, R. Influence of bromide and ammonia upon the formation of trihalomethanes under water-treatment conditions. *Environ. Sci. Technol.* **1982**, *16*, 473–479.
- Miller, J. W.; Uden, P. C. Characterization of nonvolatile aqueous chlorination products of humic substances. *Environ. Sci. Technol.* **1983**, *17*, 150–157.
- Reckhow, D. A.; Singer, P. C.; Malcolm, R. L. Chlorination of humic material: byproduct formation and chemical interpretations. *Environ. Sci. Technol.* **1990**, *24*, 1655–1664.
- Rook, J. J. Chlorination reactions of fulvic acids in natural waters. *Environ. Sci. Technol.* **1977**, *11*, 478–482.
- Sanderson, G. W. *Structural and Functional Aspects of Phytochemistry*; Academic Press: New York, 1972; pp 247–316.
- Schnitzer, M.; Khan, S. U. *Humic Substances in the Environment*; Marcel Dekker: New York, 1972; p 196.
- Schulten, H. R. Three-dimensional, molecular structures of humic acids and their interactions with water and dissolved contaminants. *Int. J. Environ. Anal. Chem.* **1996**, *64*, 147–162.
- Scilimenti, M. J.; Hwang, C. J.; Speitel, G. E. The simultaneous determination of cyanogen chloride and cyanogen bromide in chloraminated waters by a simplified microextraction GC/ECD technique. In *Proc. AWWA WQTC*; AWWA: Denver, CO, 1994; pp 489–507.
- Seeger, D. R.; Moore, L. A.; Stevens, A. A. Formation of acidic trace organic byproducts from chlorination of humic acids. In *Water Chlorination: Chemistry, Environmental Impact and Health Effects*, Jolley, R. L., et al., Eds.; Lewis Publ.: Chelsea, MI, 1985; Vol. 5, pp 859–873.
- Smith, M. E.; Singer, P. C. Impact of ozonation on cyanogen chloride formation. In *Proc. AWWA WQTC*; AWWA: Denver, CO, 1994; pp 925–945.
- Stevens, A. A.; Moore, L. A.; Miltner, R. J. Formation and control of nontrihalomethane disinfection byproducts. *J. Am. Water Works Assoc.* **1989**, *81*, 54–60.
- Stevenson, F. J. Geochemistry of soil humic substances. In *Humic Substances in Soil, Sediment, and Water*; Aiken, G. R., et al., Eds.; Wiley: New York, 1985; pp 13–52.
- Stevenson, F. J. *Humus Chemistry: Genesis, Composition, Reactions*; Wiley: New York, 1994.
- USEPA. *Proposed Disinfectants/Disinfection Byproduct Rule*. *Fed. Reg.* **1994**, *59*, 145, 38668–38829.
- WHO International Agency for Research on Cancer *IARC Monogr. Carcinog. Risk Hum.* **1991**, *51*, 207–271.
- Wu, W. W.; Chadik, P. A.; Schmidt, C. J. An in situ synthesis of cyanogen chloride as a safe and economical aqueous standard. *Water Res.*, in press.
- Xie, Y.; Reckhow, D. A. Stability of cyanogen chloride in the presence of sulfite and chlorine. In *Proc. AWWA WQTC*; AWWA: Denver, CO, 1992; pp 1761–1777.

Received for review February 17, 1998. Revised manuscript received May 9, 1998. Accepted June 10, 1998.

JF9801466