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## **MINIMIZING THE CHLORINATION BY-PRODUCTS BY OPTIMIZING THE CHLORINE DOSE AND TEMPERATURE**

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### **Abstract**

Disinfection of water by chlorine produces a number of halogenated disinfection by-products (DBPs). Trihalomethanes (THMs) and haloacetic acids (HAAs) are the dominant species found in finished drinking water. Several toxicological studies shown some disinfection by-products (DBPs), including certain (THMs) and (HAAs), to be carcinogenic in laboratory animals. Due to all these potential problems associated with the formation of disinfection by-products (DBPs) during the free chlorination of drinking water have been well documented and due to the health risks associated with them, the US Environmental Protection Agency (USEPA) began regulating the levels of these disinfection by-products (DBPs) in finished drinking water in 1979. Many researchers suggested different procedures in order to minimize the concentrations of the formed DBPs. These procedures based upon the decreasing of the natural organic matter (NOM) in the raw water e.g. ultrafiltration (UF)–nanofiltration (NF) combined membrane process which showed better removal efficiency of NOM. Another studies suggested usage of another disinfectants e.g. ozone. This study aimed to minimize the concentrations of the (DBPs) via the optimization of the added chlorine dose which complies with the microbiological requirements. Also the effect of temperature on the formed DBPs was studied. The results showed that the concentrations of the various (DBPs) are inversely proportional with the temperature. Also this study suggested another procedure to calculate the most suitable chlorine dose.

### **Introduction**

Aqueous chlorine is one of the most versatile and effective chemical oxidants. Its uses include the oxidation of manganese, color removal, control of off-tastes and odors, and a flocculent aid. Unfortunately chlorine also forms potentially mutagenic and carcinogenic by-products, especially when it is used in the treatment of surface water by the conventional procedure. A variety of precursor compounds are probably involved; humic and fulvic acid (themselves a complex mixture of compounds), chlorophyll, and other components or metabolites of algae and bacteria grow in municipal water supplies <sup>(1)</sup>. Disinfection of water by chlorine produces a number of halogenated disinfection by-products (DBPs). Among these, trihalomethanes (THMs) and haloacetic acids (HAAs) which represent the dominant species found in finished drinking water. Since chlorination by-products were

discovered in drinking water in 1974, several toxicological studies shown DBPs, including certain (THMs) and (HAAs), to be carcinogenic in laboratory animals. A recent work on the laboratory rats showed that the exposure to a three of the nine haloacetic acids (dichloro (DCAA), dibromo (DBAA) and monobromochloro acetic (MBCAA)) singly or in combination together causes another health problems to the animals that were subjected to this work<sup>(2)</sup>.

Due to all these potential problems associated with the formation of DBPs during the free chlorination of drinking water have been well documented and due to the health risks associated with them, the US Environmental Protection Agency (USEPA) began regulating the levels of these DBPs in finished drinking water in 1979 <sup>(3)</sup>. Concerns regarding the carcinogenic effects of HAAs led the Environmental Protection Agency the Stage 1 Disinfectant / DBP rule that regulates the sum of five haloacetic acids at a maximum contaminant level of 60  $\mu\text{g/L}$  in finished drinking water. These five acids are monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), and dibromoacetic acid (DBAA). Another group of these DBPs, the THMs are also regulated in the same rule which established a maximum contaminant level of the sum of trihalomethanes (THMs) of 80  $\mu\text{g/L}$ . The regulated trihalomethanes (THMs) are, chloroform ( $\text{CHCl}_3$ ), dichlorobromomethane ( $\text{CHCl}_2\text{Br}$ ), dibromochloromethane ( $\text{CHBr}_2\text{Cl}$ ), and bromoform ( $\text{CHBr}_3$ ). Also this rule regulated the maximum contaminant level for the 2,2-dichloropropionic acid (Dalapon) at 200  $\mu\text{g/L}$ <sup>(4)</sup>

Many researchers suggested different procedures in order to minimize the concentrations of the formed DBPs. These procedures based upon the decreasing of the (NOM) in the raw water e.g. ultrafiltration (UF)–nanofiltration (NF) combined membrane process which showed better removal efficiency of NOM <sup>(5)</sup>. Another procedures suggested that the usage of another disinfectants rather than the chlorine e.g. ozone will prevent the formation of the HAAs and the THMs. <sup>(5)</sup>. The present study is aiming to minimize the DBPs specially the five HAAs (MCAA, DCAA, TCAA, MBAA, and DBAA) and dalapon which are formed during the chlorination of a fresh surface water collected from the Nile. The main idea is based on the optimization of the chlorine doses that is comply with the microbiological requirements; the effect of the pH values and the temperature on the DBPs formation was studied.

## Experimental

### Materials and Methods

Two sets of Nile water were collected from the intake of El-Fustat water plant. Each set consisted of seven samples of one liter volume. These samples were used in a two jar tests at two different temperatures (17°C & 27°C) to evaluate the effect of temperature beside the effect of the added chlorine doses on the formation of chlorination by-products which are resulted from the chlorination of a surface water of the same matrices. The conditions of the two jars are summarized in Tables (1&2):

#### *Equipment and supplies*

1. Phipps & Bird Stirrer model 7790-402
2. Glass beakers of one liter volume
3. Glass pipettes of 10 ml
4. Amber glass bottles with Teflon faced septa and open top screw cap of different volumes.

#### *Reagents and chemicals:-*

1. 0.028N chlorine stock solution (i.e. 1.0 mg/ml).
2.  $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$  "Alum" solution of strength (10 mg/ml).

#### *Procedure*

1. Fill six beakers with one liter of the raw water and put them on the stirrer.
2. Add 2.5 ml from the alum solution of (10 mg/ml).
3. Add 1.5, 3.0, 4.5, 6.0, and 7.5 ml from the chlorine stock solution on (1.0 mg/ml).
4. Turn the stirrer on at high settings for about 3 minutes for good mixing of the added chemicals.
5. Put the stirrer on low settings for 15 minutes to complete the flocculation process.
6. Turn the stirrer off and let the samples for 10 minutes to complete the settling process.
7. Distribute each sample on the bottles of each analysis taking in consideration the percussions of the sample collection of each analysis.

#### *Haloacetic acids & dalapon determination*

It was carried out according to the USEPA method No 552.1.

*Determination of trihalomethanes (THMs)*

It was carried out according to the USEPA method No 501.2.

*Microbiological analyses:-*

The main goal of this study was to determine the optimum chlorine dose added that will kill all the harmful bacteria that may exist in the raw water.

*Determination of the Faecal Coliform Bacteria:-*

The determination of the Faecal Coliform (FC) was carried out according to the Standard Method No. 9222D. This method is based on the Membrane Filtration (MF) technique. The (MF) method uses an enriched lactose medium and incubation of  $44.5 \pm 0.2^\circ\text{C}$  for selectivity.

*Determination of the Total Coliform Bacteria:-*

The determination of the Total Coliform (TC) was carried out according to the Standard Method No. 9222B <sup>(6)</sup>. This method is based on the Membrane Filtration (MF) technique.

*Determination of Heterotrophic Plate Count:-*

The determination of the Heterotrophic Plate Count (HPC) was carried out according to the Standard Method No. 9215B. <sup>(7)</sup> In this method the produced colonies are relatively small and compact, showing low tendency to encroach on each other than those produced by surface growth.

*Disinfection By-Products Formation Potential:-*

It was carried out according to the Standard Method No. 5710 <sup>(8)</sup>. In this method an excess chlorine dose of known concentration is added to a buffered raw water sample and then incubated at  $25^\circ\text{C}$  for 7 days to allow the reaction of the disinfection by-products formation to approach completion. This excess dose must give a free chlorine residual at the end of the seven days of 3 to 5 mg  $\text{Cl}_2/\text{L}$ . After these seven days the chlorinated water is taken and analyzed for THMs, HAAS, and Dalapon according to the previously mentioned methods of analyses.

*Apparatus:-*

- Incubator, to maintain temperature of  $25 \pm 2^\circ\text{C}$ .
- Bottles, glass, with TFE-lined screw caps to contain 245 to 255 ml, 1-L, 4-L.
- Vials, glass, 25 or 40 ml with TFE-lined screw caps.
- pH meter accurate to within  $\pm 0.1$  unit.

*Procedure:-*

- a) Add 3.5 & 4.0 ml of standardized sodium hypochlorite solution of strength 1 mg  $\text{Cl}_2/\text{L}$  to a two raw water samples in an two amber screw capped bottles of volumes 250 ml.
- b) Add 5 ml phosphate buffer to maintain the pH at  $7.0 \pm 0.2$
- c) Do not let any head space in the bottles.
- d) Incubate the bottles in an incubator at a temperature  $25 \pm 2^\circ\text{C}$  for seven days.
- e) After the seven days measure the residual free chlorine in each sample which must be between 3 to 5 mg  $\text{Cl}_2/\text{L}$ .
- f) Analyze the THMs, HAAS, and Dalapon according to the mentioned methods.
- g) Note: the chlorine doses added (3.5 & 4.0 mg  $\text{Cl}_2/\text{ml}$ ) to the 250 ml sample ( $\approx$  14 & 16 mg  $\text{Cl}_2/\text{L}$ ) yields residual free chlorine (3.02 & 3.2 mg  $\text{Cl}_2/\text{L}$ ) after the seven days.

**Results and Discussion:**

The first goal of this study is the minimizing of the chlorination by-products (HAAS, Dalapon, and THMs) by minimizing the added chlorine doses which complying with the microbiological requirements; the effect of temperature was also studied. In addition this study investigated the formation potentials of the HAAS, dalapon, and the THMs i.e. the maximum concentrations of these compounds that may yielded from the addition of a very high dose of chlorine to a NOM containing water (raw water). This investigation gives an indication to the chlorination by-products precursors' content in the raw water.

*Concentration Levels and the Formation Potential of HAAs*

The HAAs were determined under the previously mentioned circumstances at ( $27^\circ\text{C}$  &  $17^\circ\text{C}$ ). Data illustrated in Fig. (1) showed that the absence of all the HAAs in the samples No. 1 and No. 2 due to the absence of chlorine. After the addition of the first chlorine dose (1.5 mg/L) the TCAA was the only haloacetic acid that was formed at a concentration of 21.02  $\mu\text{g}/\text{L}$ . With increasing the added chlorine dose (3 mg/L) the DCAA started to appear at a concentration of 13.41  $\mu\text{g}/\text{L}$ . Addition of higher chlorine doses (4.5, 6.0, and 7.5 mg/L) increased the concentrations of these two compounds. The TCAA was the major compound that was formed with increasing the added chlorine doses (Fig. 1). The behavior of these two compounds reflected on the THAAS at these conditions where the THAAs increased gradually with the increasing of the chlorine addition.

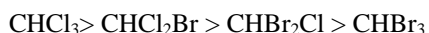
Data illustrated in Fig.(2) showed also the absence of all the HAAs in the samples No 8 and No. 9 due to the absence of chlorine. After the addition of chlorine (1.5 mg/L), the TCAA was the only haloacetic acid that formed at a concentration of 28.02  $\mu\text{g/L}$  which is greater than the TCAA that recorded in the sample No.3 Table (3). Evidently, the decreasing in the reaction temperature increases the concentration of TCAA and this is due to the increasing in the chlorine gas solubility. Generally, the TCAA showed higher concentrations at 17°C than at 27°C. With increasing the added chlorine dose (3 mg/L) the DCAA and the DBAA started to appear at concentrations of 8.93 $\mu\text{g/L}$  and 2.958 $\mu\text{g/L}$ , respectively. Addition of higher chlorine doses (4.5, 6.0, and 7.5 mg/L) increased the concentrations of these two compounds. The TCAA was the major compound that was formed with increasing the added chlorine doses.. Also this situation reflected on the THAAs at these conditions where the total of the HAAs increased gradually with increasing chlorine addition, see Fig. (2). In general, THAAs at the relatively low temperature of 17°C in general were greater than the recorded concentrations at 27°C.

Obviously, the concentrations of the formed by-products were directly proportional with the added chlorine doses. This fact means that if we optimize the added chlorine doses as lower as possible (as we can) in complying with the microbiological requirements, we will minimize the concentrations of the formed chlorination by-products.

The data illustrated in Table (3) represents the results of the regulated five haloacetic acids formation potential (HAASFP). This formation potential reaction was carried out by two samples that were injected by two chlorine doses of 14 and 16 mg/L and incubated at 25°C for seven days. These data showed that after these seven days the major HAA was the DCAA rather than the TCAA. This observation indicates that although the TCAA is the most predominant product in the freshly produced water but it is also more degradable than the DCAA and this conclusion is coincides with the rest of the regulated five HAAs.

#### *Concentration Levels and the Formation Potential of THMs:*

As chlorination by-products the THMs concentration levels were investigated in this bench scale study. Data illustrated in Figs. (3&4) showed the absence of all the THMs compounds due to the absence of the chlorine. As more chlorine was added, these compounds were appeared in the following order:



Also the bromoform started to be formed at the lower temperature (17°C) but it was absent at the relatively high temperature (27°C). The observed values of the TTHMs were lower than those of the THAAs as shown from the results of Figs. (3&4), especially at the lower temperature (17°C).

The data illustrated in Table (4) represents the results of the regulated four trihalomethanes formation potential (THMFP). This formation potential reaction was carried out as in case of the THAAFP. These data showed that after these seven days the major THM was  $\text{CHCl}_3$  and then  $\text{CHCl}_2\text{Br}$  followed by  $\text{CHBr}_2\text{Cl}$  and finally at 16 mg/L chlorine dose the  $\text{CHBr}_3$ . Although the levels of TTHMs were lower than those of THAAs in the samples of the different chlorine doses but the formation potential reaction results that were matched with the field study showed on opposite situation ( i.e. TTHMFPs levels were greater than those of THAAFP). This may indicate that the formation reaction of the HAAS is faster than that of the THMs and then the THAAs appeared in the samples in a greater levels than those of the TTHMs, but when the formation reaction of both groups was allowed to be completed the actual arrangement appeared.

#### *Concentration Levels and the Formation Potential of Dalapon :*

The investigation of the concentration levels of the Dalapon as a chlorination by-product under these circumstances was important. Data illustrated in Figs. (5&6) showed that although there were no significant influences of the added chlorine doses, or the reaction temperature but the higher concentration levels appeared at the lower temperature (17°C).

The Dalapon formation potential showed the absence of the dalapon after the incubation for seven days of the reaction with 14 and 16 mg/L chlorine doses at 25°C (Table 5). This absence although the conditions of the reaction were available may explain the irregularity of the dalapon formation. On this basis the strongest reason is the complete and relatively degradation of the dalapon precursors into a shorter chains of one or two carbon atoms

#### *Adjustment of the Chlorine Doses with a Compliancy of the Microbiological Regulation:*

From the previous data, it is evident that the goal of minimizing the concentrations of the formed by-products can be achieved by decreasing the added

chlorine doses. This decreasing must be in compliance with the microbiological requirements, and therefore, we have to optimize the chlorine doses i.e. the addition of the lowest chlorine dose that kill all the microorganisms present in the raw water which permits a suitable residual chlorine dose maintains the disinfection of the drinking water through the distribution system. In order to achieve this goal, three microbiological parameters were chosen to be examined {total coliform (TC), faecal coliform (FC), and the heterotrophic plate count (HPC)} with regarding the minimum chlorine dose that would kill the microbiological contamination resources. These three parameters were regulated by the WHO in 1984 at {(FC<1 CFU/100ml)<sup>7</sup>, (TC<1 CFU/100ml)<sup>(8)</sup> and the Egyptian regulations for (HPC 50 unit / 1ml)} in the treated drinking water sample<sup>(9)</sup>.

Data illustrated in Figs. (7, 8 & 9) and Figs. (10, 11 & 12), which represent the results of the microbiological detection of the FC, TC, and PC at the two different temperatures (27°C & 17°C), showed that the maximum level with the FC, TC, and the PC were occurred in the raw water (Nile water). In addition, they also showed that the FC, TC, and the PC were occurred at higher levels at 17°C than those at the higher temperature (27°C). The addition, of alum reduces these contaminations to a great extent although there were no chlorine additions to such samples. Just the first chlorine dose (1.5 mg/L) was added beside the alum once (FC) and (TC) were reduced to <1 CFU/100ml and (TC) to 16 and 45 CFU/1ml at the two different temperatures of 27°C and 17°C, respectively. Although these levels are matched with the guideline values that are regulated by the WHO, the residual chlorine is still the important factor in this respect. Via the relations that are representing the TC, FC, and PC with both the added and the residual chlorine doses, it will be easy to determine the optimum chlorine doses that will verify the WHO microbiological regulations side by side with the safe residual chlorine dose which will be in accordance with the distribution system requirements.

## **Conclusion**

This study showed that the using of unreasonable doses of chlorine in the treatment of the fresh water to be a safe drinking water yields undesirable concentrations from the chlorination by-products. This problem can be solved by optimizing the used chlorine doses which are used in the treatment processes. This optimization is achieved by regarding the microbiological requirements i.e. using minimum chlorine dose that enough to kill the microorganisms and leave a suitable residual chlorine to maintain the disinfection through the distribution system. This



step can be achieved by the correlation between the microbiological parameters (FC, TC, and PC), added chlorine doses and the residual chlorine concentrations (Figs. 7-12). Such correlation gives us the ability to determine the most optimum chlorine dose that we can apply it on the treatment plant.

Also this study evaluates the role of the atmospheric temperature in the formation of the disinfection by-products which is an inverse proportion due to the increasing of the chlorine solubility in the lower temperatures. This fact can be used to minimize the concentrations of the formed by-products and makes us to be careful when we calculate the added chlorine doses in the cold times.

**Table (1)**

(27 °C)	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7
Cl <sub>2</sub> Dose (mg/L)	0	0	1.5	3.0	4.5	6.0	7.5
Alum Dose (mg/L)	0	25	25	25	25	25	25

**Table (2)**

(17 °C)	No. 8	No. 9	No. 10	No. 11	No. 12	No. 13	No. 14
Cl <sub>2</sub> Dose (mg/L)	0	1.5	3.0	4.5	6.0	7.5	0
Alum Dose (mg/L)	0	25	25	25	25	25	0

**Table (3): The Formation Potential of the Regulated Five Haloacetic Acids After Seven Days of Incubation at (25 °C)**

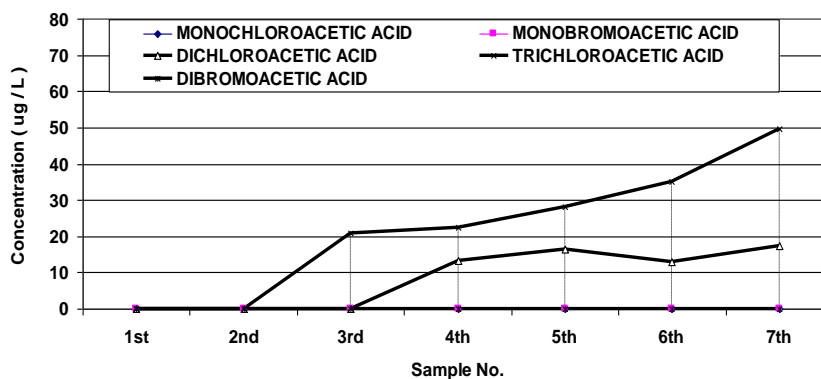
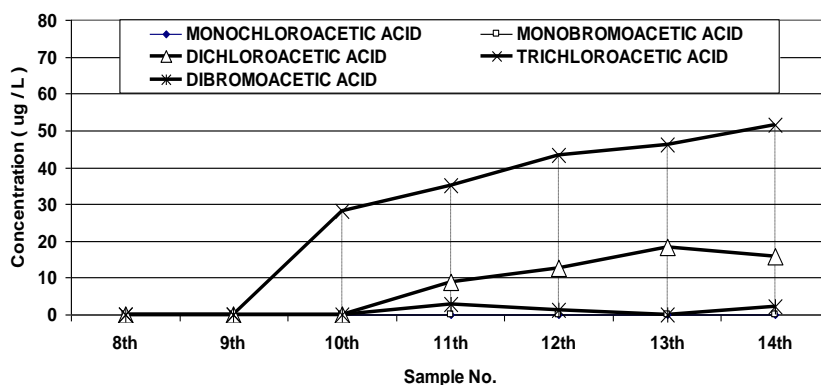
Chlorine Dose Added ( mg / L )	Compounds ( µg / L )					
	MCAA	MBAA	DCAA	TCAA	DBAA	Total
14 ( mg / L )	ND	ND	102.58	74.56	ND	177.14
16 ( mg / L )	ND	ND	116.65	89.24	ND	205.89

**Table (4): The Formation Potential of the Regulated Four Trihalomethanes After Seven Days of Inoculation at (25 °C)**

Chlorine Dose Added ( mg / L )	Compounds ( µg / L )				
	CHCl <sub>3</sub>	CHCl <sub>2</sub> Br	CHClBr <sub>2</sub>	CHBr <sub>3</sub>	Total
14 ( mg / L )	148.01	37.09	9.56	ND	194.66
16 ( mg / L )	161.45	40.41	10.54	1.09	213.49

**Table (5): The Formation Potential of 2,2'-Dichloropropionic Acid (Dalapon) After Seven Days of Incubation at ( 25 °C. )**

Compounds ( $\mu\text{g} / \text{L}$ )	Chlorine Dose Added ( $\text{mg} / \text{L}$ )	
	14 ( $\text{mg} / \text{L}$ )	16 ( $\text{mg} / \text{L}$ )
Dalapon	ND	ND

**Fig.(1): The Concentration Levels of the Regulated Five Haloacetic Acids Which Are Resulted from the Addition of Different Chlorine Doses at ( 27 °C. )****Fig.(2): The Concentration Levels of the Regulated Five Haloacetic Acids Which Are Resulted From the Addition of Different Chlorine Doses at ( 17 °C. )**

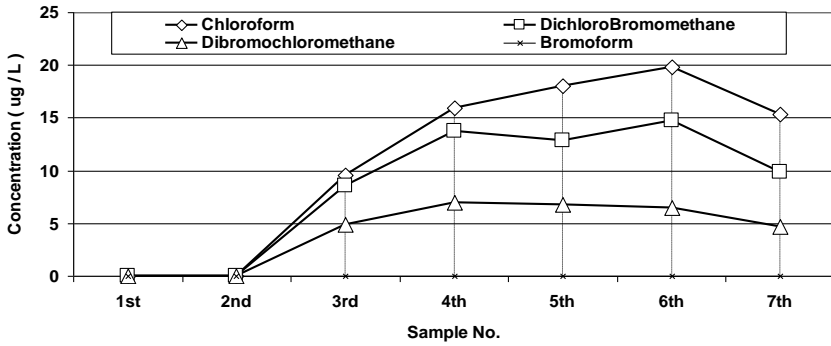


Fig.(3): The Concentration Levels of the Regulated Four Trihalomethanes Which Are Resulted From the Addition of Different Chlorine Doses At ( 27 °C. )

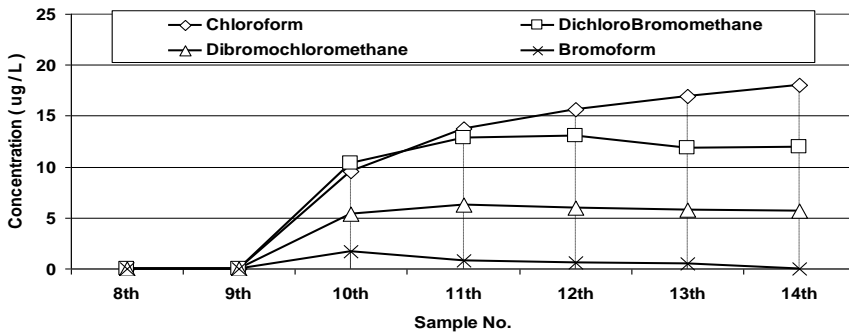


Fig.(4): The Concentration Levels of the Regulated Four Trihalomethanes Which Are Resulted From the Addition of Different Chlorine Doses At ( 17 °C. )

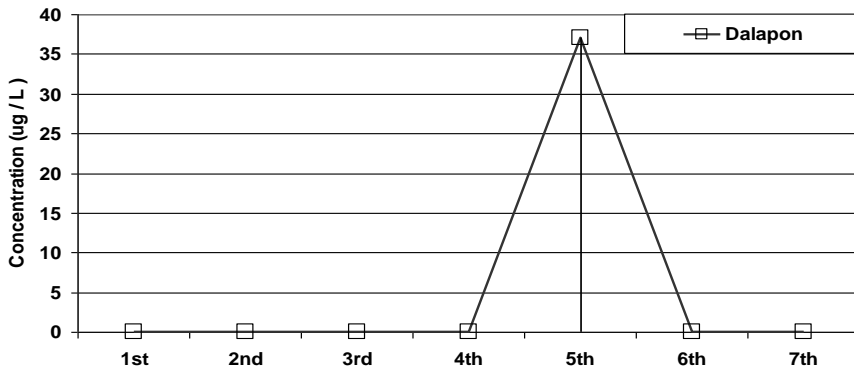


Fig. (5): The Concentration Levels of Dalapon at (27 °C)

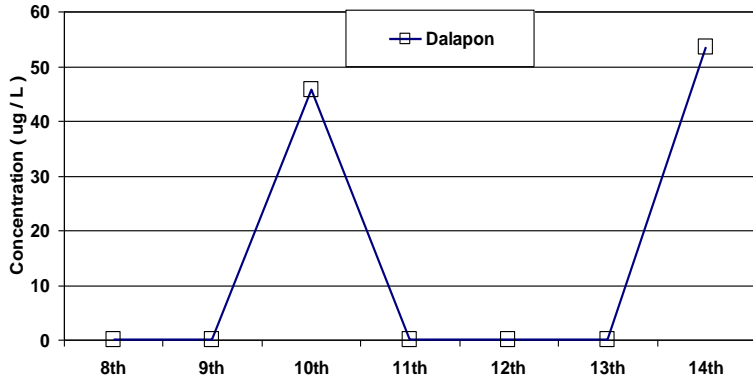


Fig. (6): The Concentration Levels of Dalapon at (17 °C)

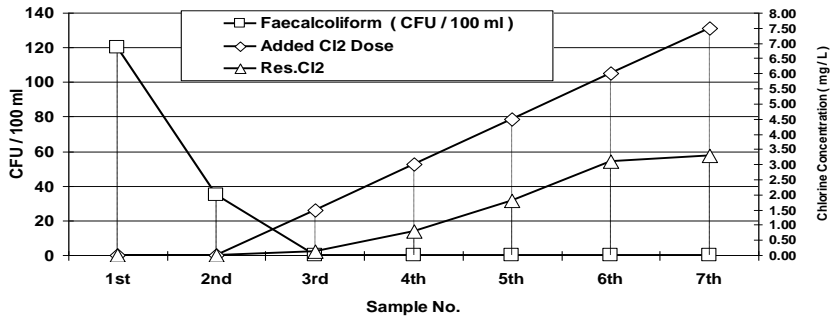


Fig.(7): The Relation Between the Faecal Coliform, Chlorine Dose Added& the Residual Chlorine Concentration At ( 27 °C. )

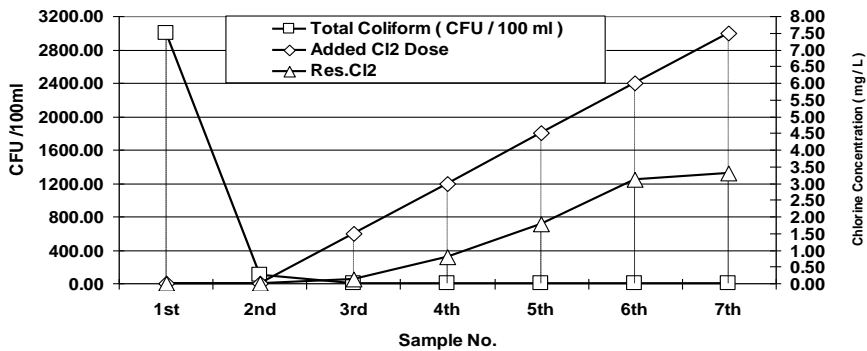


Fig.(8): The Relation Between the Total Coliform, the Chlorine Dose Added& the Residual Chlorine Concentration At ( 27 °C. )

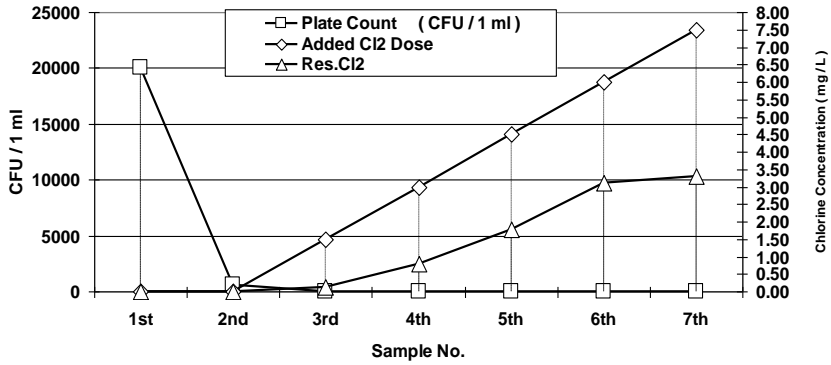


Fig.(9): The Relation Between the Total Plat Count, the Chlorine Doses Added& the Residual Chlorine Concentrations At ( 27 °C. )

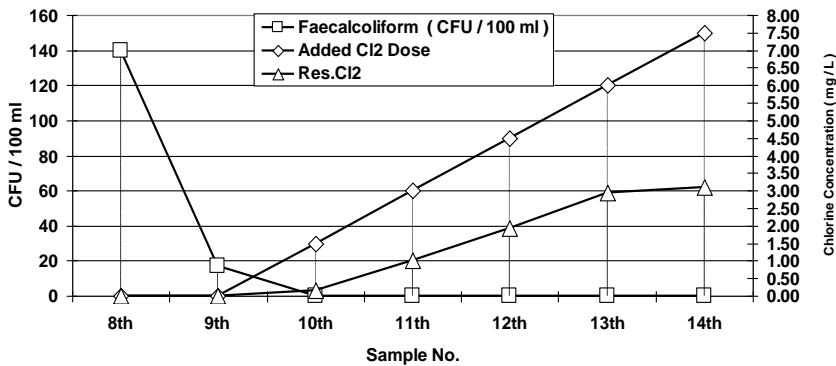


Fig.(10): The Relation Between the Faecal Coliform, Chlorine Doses Added& the Residual Chlorine Concentrations At ( 17 °C. )

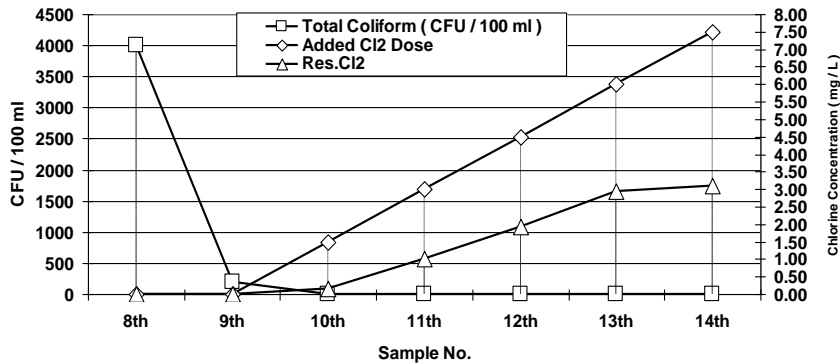


Fig.(11): The Relation Between the Total Coliform,Chlorine Doses Added& the Residual Chlorine Concentrations At ( 17 °C. )

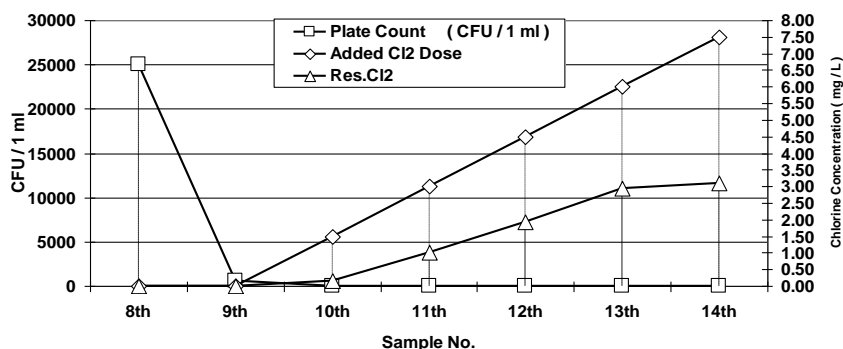


Fig.(12): The Relation Between the Total Plat Count, the Chlorine Doses Added& the Residual Chlorine Concentrations At ( 17 °C. )

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