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Comparability Study between Digital and Visual Colorimeter by using of Chlorine Indicators of DpD No.1 and DpD No.3 under practical conditions

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Summary
All public drinking water system was required to measure the levels of residual chlorine in a practically accurately instruments to ensure that the water was adequately disinfected. This experimental study was carried out to compare under practical condition in laboratory the test results of free and total chlorine in the water samples between digital colorimeter and visual colorimeter by using of chemical indicator reagents of ((DpD number (1)) for testing of free chlorine in water samples, and ((DpD number (3)) for testing of total chlorine in water samples. The experiments lasted from (1/10/2011 to 1/5/2012). The study was conducted in the Laboratories of Al-Kufa Technical Institute in Al-Kufa city that belong to Al-Najaf governorate about 165 Km to the south of Baghdad, and 60 km to the south of Babylon governorate.

200 experiments were done in the laboratory, by made of 2 experiments in each day through a standards laboratory conditions.

There was a highly statistical significant difference (p=0.000), in comparing between digital calorimeter and visual colorimeter of both free and a total chlorine test results.

There was a highly differences in the mean when was comparison of the digital colorimeter with the visual colorimeter of both all free and total chlorine experiment.

There was a strong direct correlation between digital colorimeter experimental results and contact time in both all free and total chlorine experiments, while there was a weak direct correlation between visual colorimeter and contact time in all free and total chlorine experiments.

From the all tested results of experiment that was derived from this study, the study recommend to practically adaptation of a digital colorimeter instead of visual colorimeter in all the chlorine residual test results that was done by ministry of health inspectors in all governorates in monitoring of drinking water, and for more accurate and sensitive test result we recommend to adapted of digital colorimeter in all researches when tracing of chlorine residual of different water samples.

1. Introduction

Chlorine is one of the most widely used disinfectants. It is very applicable and very effective for the deactivation of pathogenic microorganisms. Chlorine can be easily applied, measures and controlled. Is persistent and relatively cheap [1]. Chlorination is one type of disinfection used in drinking water and it is one of the best disinfecting processes because it is possible to maintain and measure a residual level of chlorine in the distributed water. This allows for continual monitoring of the process and minimizes the potential for re-growth of pathogenic organisms throughout the distribution pipes When chlorine is added to water for disinfection purposes, it usually starts reacting with dissolved organic and inorganic compounds in the water [2].

When chlorine is added to drinking water, it proceeds through a series of reactions, some of the chlorine reacts first with organic materials and metals in the water and is not available for disinfection (this is called the chlorine demand of the water), the remaining chlorine concentration after the chlorine demand is accounted for is called (total chlorine and free

chlorine residual), that used as a monitoring measurement by system operators. [3]. The (free chlorine):- which is the chlorine available to inactivate disease-causing organisms, and thus a measure to determine the notability of water, The remaining chlorine concentration after the chlorine demand is accounted for is called (total chlorine) [4]. The free Cl2 residual should be about 0.2 mg/L at the extreme ends of the network system and the total residual chlorine should be about 1ppm [5]. Disinfection is the most important step in the water treatment process to destroy pathogenic bacteria and other harmful agents. Chlorination is a very common and effective method for the disinfection of drinking water, and it has been the single most important process for assuring the bacteriological safety of potable water supplies [6].

Public water supplies are required to measure the level of residual disinfectants to ensure the water is adequately disinfected. DPD is a chemical indicator that reacts with the chlorine present and basically dyes the water a pink color that will indicate the chlorine level, making measurements more consistent and accurately [7].

Visual colorimeter use a powder or tablet chemical DPD (N,N diethyl-p-phenylene diamine) that causes a color change to pink in the presence of chlorine. The color wheels are simpler because to measure the intensity of the color change, the field worker uses a color wheel to visually match the color to a numerical free or total chlorine reading. The test kit can be used to measure free chlorine and/or total chlorine (using different chemicals in the kit).

Digital colorimeters are the way to measure free chlorine and/or total chlorine residual in the field. These colorimeters use the DPD tablets or powder into a vial of sample water that causes a color change to pink and automatically determining and displaying the color intensity (the free and/or total chlorine residual) digitally [8].

1.1 Study Objectives

The aim of this study is to compare under practical condition in laboratory the test results of free and total chlorine in the water between digital colorimeter and visual colorimeter by using of chemical reagents (N, N-diethyl-p-phenylenediamine) :-

1- DpD number (1) for testing of free chlorine in water.
2- DpD number (3) for testing of total chlorine in water.

2. Materials and Methods

2.1-Study Design: An experimental study.
2.2-Period of the Study: The experiments lasted from (1/10/2011 to 1/5/2012).

2.3-Place of the Study

The study was conducted in the Laboratory of Al-Kufa Technical Institute in Al-Kufa city, that belong to Al-Najaf governorate about 165Km to the south of Baghdad, and 60km to the south of Babylon governorate (9).

2.4 -Apparatus and Materials

2.4.1 - Apparatus:

Apparatus	Manufactures Company
1-Portable digital colorimeter. **2-Portable digital pH-meter.** **3-Portable Visual colorimeter.** **4-Micropipettes.** **5-1000 ml container.**	**1- Lovibond (England).** **2-Selecta (Germany).** **3-Lovibond (England).** **4-Inspiron (Germany).** **5-New century (Egypt).**

2.4.2 -Chemical Materials Used

Materials	Manufactured company
1-Free Chlorine Reagent (D.P.D no. (1) – (0.001 - 5.0 ppm). **2 Total Chlorine Reagent (D.P.D no. (3) – (0.001 - 5.0 ppm).** **3- Buffer solution (KOH).**	**1- Lovibond (England).** **1- Lovibond (England).** **3- Germany**

2.5-Methods

2.5.1 –Design of the Experiments

200 experiments was done In the laboratory, by made of 2 experiments in each day for comparing between Digital and Visual Colorimeter through used of (DpD no.1 and DpD no.2) chlorine chemical test reagent for free and total residual chlorine through **a standards laboratory conditions**:-

1. The volume of distilled water samples that prepared was the same in all experiments (1000 ml).
2. The pH of water samples was controlled in (7.5) by titration of buffer solution (potassium hydroxide KOH).
3. The same proportion of chlorine powder (5 ppm) was added to the all water volume (1000 ml).
4. 10 ml was taken from water samples in the same time for digital and visual colorimeter and then tasted in each experiment.

(1000 ml) of distilled water was prepared in the laboratory, then (5 ppm) of chlorine like of powder was add to the water, then we titrate of potassium hydrochloride solution (KOH) for made of constant level of pH in (7.5) and this controlling pH was done by used of digital pH meter.

These standard conditions were made for each experiment but the difference of them was in a time of selection of water samples that made in a different contact time (the time when chlorine adds and test), (the first experiment was done in the minute of one after addition of chlorine powder to the 1000 ml, and the second experiment in another day was done in the minute of tow after addition of chlorine powder, and so on the last experiment number 100 was done in the minute of 100).

In the first experiment, tow samples of 10 ml of water was taking after contact time of one minute of chlorine addition for testing of free chlorine, one samples of 10 ml was add to the tube of Digital colorimeter and then taken the result and at the same time other 10 ml of water sample was add to the visual colorimeter and then the result was reading.

The second experiment was done at the same conditions in another day but the contact time was change, this mean the difference between first or next experiment was one minute.

2.6 –Digital Colorimeter Test Procedure:-

Portable digital colorimeter was used in each experiment to measure Cl_2 concentration in drinking water samples:-

1. The tube of the colorimeter was filling with 10 ml of water samples and putted in a devise.
2. Then the (zero) buttons was turned on.
3. The DPD (no.1 or no.3) powder was add to the water samples for test of free or total chlorine.
4. Then the button 1 or 2 was turned on for chosen the free or total chlorine.

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5. Finally the button of (read) was turned on, and then the reading was appearing in a digital screen in (ppm).

2.7-Vissual Colorimeter Test Procedure:-

1. The tube of the devise was filling with the 10 ml of the water samples.
2. Then the DPD (no.1 or no.3) powder was added to the water samples for test of free or total chlorine.
3- After spend 1 minute in case of free chlorine and 2 minute in case of total chlorine the water sample was compare with a special color disc wheel of the devise by used the researcher eye, and the result was obtained.

2.8 – pH control:-

Portable digital pH meter was used in this study to control of the concentration of hydrogen ion in water samples by titration of potassium hydroxide in to water samples for reaching at the constant standard level of (7.5) .

2.9 - Data Analysis

Descriptive and analytical statistics were carried out by utilizing the statistical package for social science (S.P.S.S) version 17.

Z-test was applied to obtain any significant statistical differences at level of **P<0.05**. Between the digital and visual colorimeter test results In addition, Pearson correlation was applied between colorimeters and contact time (minute).

3. Results

Table (1): The experiments results of Digital and Visual Chlorimeter at the laboratory by using (DPD no. 1) Free Chlorine reagent at different contact time.

Experiments at Different Contact time (minute)	Free Chlorine Reagent (DPD no. 1)	
	Digital Chlorimeter	Visual Chlorimeter
1 minute	0.01	0.00
2 minute	0.01	0.00
3 minute	0.01	0.00
4 minute	0.01	0.00
5 minute	0.02	0.00
6 minute	0.02	0.00
7 minute	0.03	0.00
8 minute	0.03	0.00
9 minute	0.05	0.00
10 minute	0.12	0.00
11 minute	0.13	0.00
12 minute	0.16	0.00
13 minute	0.17	0.00
14 minute	0.20	0.00
15 minute	0.25	0.20
16 minute	0.28	0.20
17 minute	0.30	0.20
18 minute	0.33	0.20
19 minute	0.42	0.20
20 minute	0.44	0.20

21 minute	0.49	0.20
22 minute	0.51	0.20
23 minute	0.51	0.20
24 minute	0.55	0.40
25 minute	0.61	0.40
26 minute	0.63	0.40
27 minute	0.65	0.40
28 minute	0.70	0.40
29 minute	0.72	0.40
30 minute	0.72	0.40
31 minute	0.74	0.40
32 minute	0.75	0.40
33 minute	0.76	0.40
34 minute	0.78	0.40
35 minute	0.82	0.40
36 minute	0.83	0.40
37 minute	0.83	0.40
38 minute	0.84	0.40
39 minute	0.85	0.40
40 minute	0.88	0.40
41 minute	0.90	0.40
42 minute	0.92	0.40
43 minute	0.94	0.40
44 minute	0.99	0.40
45 minute	1.20	0.60
46 minute	1.23	0.60
47 minute	1.31	0.60
48 minute	1.40	0.60
49 minute	1.43	0.60
50 minute	1.46	0.60
51 minute	1.47	0.60
52 minute	1.52	0.60
53 minute	1.54	0.60
54 minute	1.55	0.60
55 minute	1.57	0.60
56 minute	1.59	0.60
57 minute	0.61	0.60
58 minute	1.62	0.60
59 minute	1.63	0.60
60 minute	1.64	0.60
61 minute	1.65	0.60
62 minute	1.70	0.60
63 minute	1.71	0.60
64 minute	1.72	0.60
65 minute	1.74	1.00
66 minute	1.75	1.00
67 minute	1.76	1.00
68 minute	1.77	1.00
69 minute	1.81	1.00

70 minute	**1.82**	**1.00**
71 minute	**1.83**	**1.00**
72 minute	**1.84**	**1.00**
73 minute	**1.86**	**1.00**
74 minute	**1.86**	**1.00**
75 minute	**1.87**	**1.00**
76 minute	**1.87**	**1.00**
77 minute	**1.88**	**1.00**
78 minute	**1.90**	**1.50**
79 minute	**1.93**	**1.50**
80 minute	**1.94**	**1.50**
81 minute	**1.94**	**1.50**
82 minute	**1.97**	**1.50**
83 minute	**2.00**	**1.50**
84 minute	**2.01**	**1.50**
85 minute	**2.10**	**1.50**
86 minute	**2.21**	**1.50**
87 minute	**2.29**	**1.50**
88 minute	**2.32**	**1.50**
89 minute	**2.34**	**1.50**
90 minute	**2.40**	**1.50**
91 minute	**2.41**	**1.50**
92 minute	**2.44**	**1.50**
93 minute	**2.48**	**1.50**
94 minute	**2.55**	**1.50**
95 minute	**2.62**	**1.50**
96 minute	**2.75**	**1.50**
97 minute	**2.76**	**1.50**
98 minute	**2.80**	**1.50**
99 minute	**2.83**	**1.50**
100 minute	**2.85**	**1.50**

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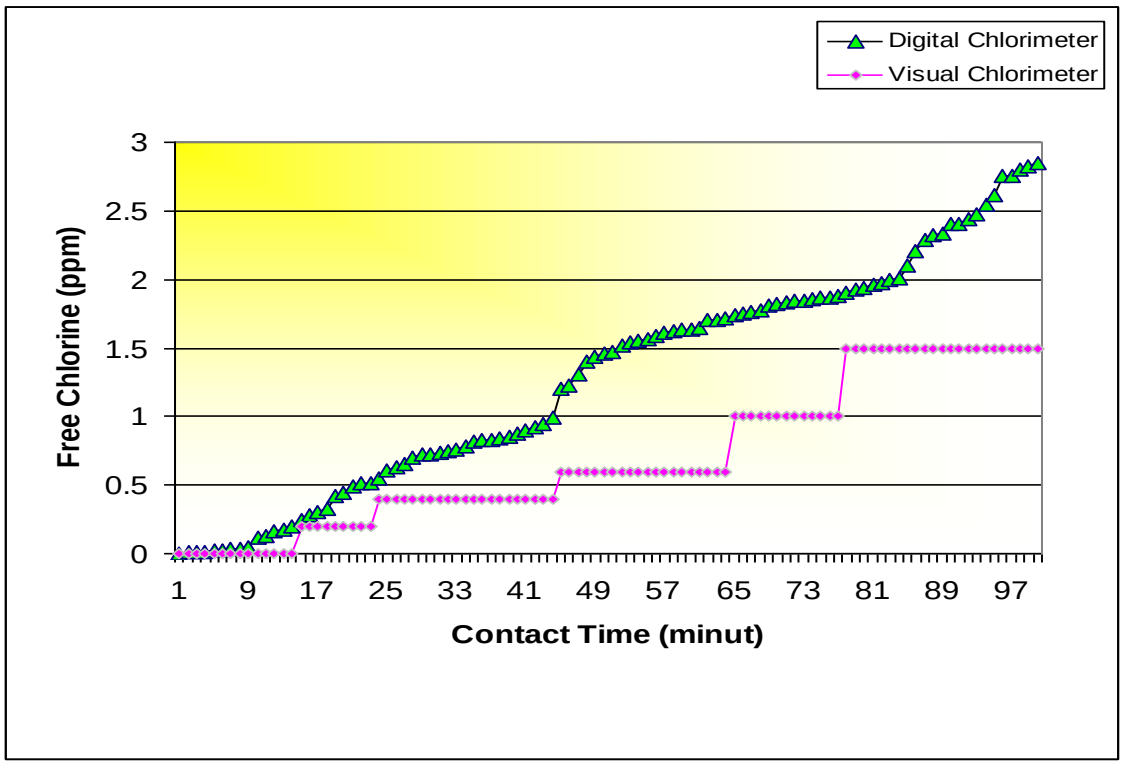

P = 0.000 / HS

Figure (1): The experiments results of Digital and Visual Chlorimeter at the laboratory by using (DPD no. 1) Free Chlorine reagent at the different contact time.

Table (2): Summary statistics comparing Digital and Visual Chlorimeter of Free Chlorine by using (DPD no.1).

Statistics	Free Chlorine (DPD no.1)	
	Digital Chlorimeter (ppm)	Visual Chlorimeter (ppm)
Mean	1.289	0.704
Std. Deviation	±0.823	± 0.521
Minimum	0.01	0.00
Maximum	2.85	1.50
Z test	Z= -5.489 *P = 0.000	

(*HS)

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Table (3): The correlation value in comparing each of digital and visual colorimeter with the contact time (minute) of all experiments of free chlorine chemical reagent (DPD no.1) in the laboratory.

Free Chlorine (DPD no.1)	R
Digital colorimeter X Contact time (minute)	0.992
Visual colorimeter X Contact time (minute)	0.330

Table (4): The experiments results of Digital and Visual Chlorimeter at the laboratory by using (DPD no.3) Total Chlorine reagent at different contact time.

Experiments at Different Contact time (minute)	Total Chlorine Test (ppm) / DPD no.3)	
	Digital Chlorimeter	Visual Chlorimeter
1 minute	0.01	0.00
2 minute	0.01	0.00
3 minute	0.02	0.00
4 minute	0.03	0.00
5 minute	0.03	0.00
6 minute	0.04	0.00
7 minute	0.04	0.00
8 minute	0.05	0.00
9 minute	0.05	0.00
10 minute	0.23	0.2
11 minute	0.23	0.2
12 minute	0.28	0.20
13 minute	0.31	0.20
14 minute	0.25	0.20
15 minute	0.25	0.20
16 minute	0.29	0.20
17 minute	0.31	0.20
18 minute	0.35	0.20
19 minute	0.43	0.20
20 minute	0.48	0.20
21 minute	0.50	0.20
22 minute	0.53	0.20
23 minute	0.54	0.20
24 minute	0.56	0.40
25 minute	0.62	0.40
26 minute	0.65	0.40
27 minute	0.70	0.40
28 minute	0.72	0.40
29 minute	0.74	0.40
30 minute	0.74	0.40
31 minute	0.74	0.40
32 minute	0.76	0.40
33 minute	0.77	0.40
34 minute	0.78	0.40

35 minute	**0.84**	**0.60**
36 minute	**0.84**	**0.60**
37 minute	**0.85**	**0.60**
38 minute	**0.86**	**0.60**
39 minute	**0.87**	**0.60**
40 minute	**0.91**	**0.60**
41 minute	**0.93**	**0.60**
42 minute	**0.98**	**0.60**
43 minute	**0.99**	**0.60**
44 minute	**0.99**	**0.60**
45 minute	**1.23**	**0.60**
46 minute	**1.26**	**0.60**
47 minute	**1.33**	**0.60**
48 minute	**1.42**	**0.60**
49 minute	**1.45**	**0.60**
50 minute	**1.49**	**0.60**
51 minute	**1.49**	**0.60**
52 minute	**1.54**	**0.60**
53 minute	**1.58**	**0.60**
54 minute	**1.56**	**0.60**
55 minute	**1.62**	**1.00**
56 minute	**1.63**	**1.00**
57 minute	**1.64**	**1.00**
58 minute	**1.65**	**1.00**
59 minute	**1.65**	**1.00**
60 minute	**1.65**	**1.00**
61 minute	**1.66**	**1.00**
62 minute	**1.71**	**1.00**
63 minute	**1.72**	**1.00**
64 minute	**1.73**	**1.00**
65 minute	**1.75**	**1.00**
66 minute	**1.76**	**1.00**
67 minute	**1.77**	**1.00**
68 minute	**1.78**	**1.00**
69 minute	**1.82**	**1.00**
70 minute	**1.84**	**1.00**
71 minute	**1.84**	**1.00**
72 minute	**1.85**	**1.50**
73 minute	**1.87**	**1.50**
74 minute	**1.87**	**1.50**
75 minute	**1.87**	**1.50**
76 minute	**1.90**	**1.50**
77 minute	**1.91**	**1.50**
78 minute	**1.92**	**1.50**
79 minute	**1.94**	**1.50**
80 minute	**1.94**	**1.50**
81 minute	**1.97**	**1.50**
82 minute	**1.98**	**1.50**
83 minute	**2.03**	**1.50**

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84 minute	**2.06**	**1.50**
85 minute	**2.13**	**1.50**
86 minute	**2.23**	**1.50**
87 minute	**2.31**	**1.50**
88 minute	**2.33**	**1.50**
89 minute	**2.35**	**1.50**
90 minute	**2.42**	**1.50**
91 minute	**2.45**	**1.50**
92 minute	**2.49**	**1.50**
93 minute	**2.49**	**1.50**
94 minute	**2.56**	**1.50**
95 minute	**2.64**	**1.50**
96 minute	**2.82**	**2.00**
97 minute	**2.83**	**2.00**
98 minute	**2.89**	**2.00**
99 minute	**2.92**	**2.00**
100 minute	**2.98**	**2.00**

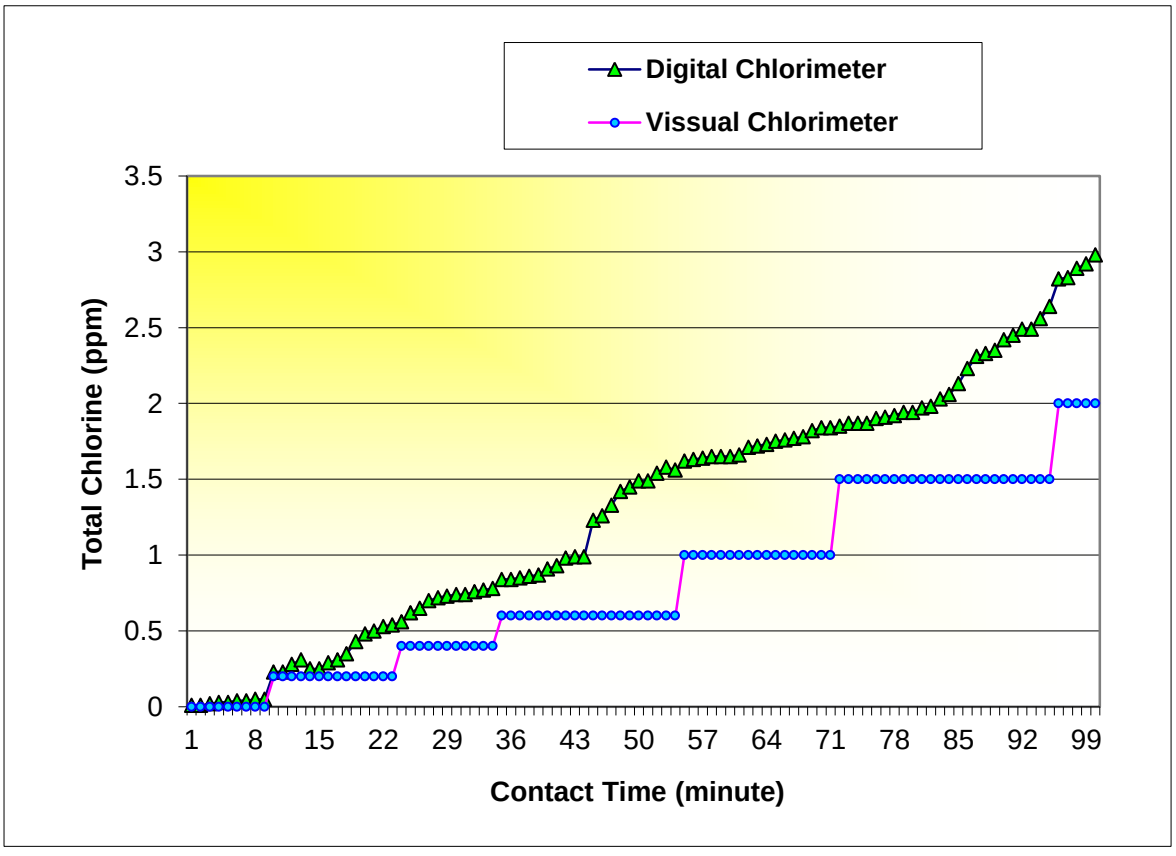

Figure (2): The experiments results of Digital and Visual Chlorimeter at the laboratory by using (DPD no.3) Total Chlorine reagent at different contact time.

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Table (5): Summary statistics comparing Digital and Visual Chlorimeter of Total Chlorine by using chemical reagent of (DPD no.3).

Statistics	Total Chlorine (DPD no.3)	
	Digital Chlorimeter (ppm)	Visual Chlorimeter (ppm)
Mean	1.316	0.833
Std. Deviation	± 0.825	± 0.599
Minimum	0.01	0.00
Maximum	2.98	2.00
Z test	Z= 4.335 *P = 0.000	

(*HS)

Table (6): The correlation value in comparing each of digital and visual colorimeter with the contact time (minute) of all experiments of Total chlorine (DPD no.1 chemical reagent) in the laboratory.

Total Chlorine (DPD no.3)	R
Digital colorimeter X Contact time (minute)	0.991
Visual colorimeter X Contact time (minute)	0. 418

4- Discussion

In the present study, the entire laboratory experiments between the digital and the visual colorimeter of free and total chlorine by using chemical reagents of (DpD no.1 and DpD no.3) showed a highly statistical significant difference, this difference seems to be tolerable for practical purposes.

In the present study, there was a finding that the free chlorine mean of digital colorimeter was higher than the free chlorine of visual colorimeter for all experiments, and there was a highly statistical significant difference between them. The same results that were found in all experiments of total chlorine that was used of chemical reagents of (DpD no.3).

These results agree with that mentioned by alien from university of Colorado in united state[10], who found that there was a highly statistical significant difference when was comparing between digital and visual colorimeter in used of DpD chemical reagents.

In addition, the same result was shown by Johnson, in an experimental study in university of York in England [11].

In the present study, the digital colorimeter in free chlorine experiments was giving a reading in the first minute of the contact time while the visual colorimeter was giving the reading in the experiment at the minute (14) of the contact time, and in the total chlorine the digital colorimeter was giving a reading in the first minute of the contact time while the visual colorimeter was giving the reading in the experiment at the minute (9) of the contact time. This might be due to, the accuracy of the digital colorimeter was higher than visual colorimeter in both experiments of free and total chlorine.In the present study, there was a direct strongly correlated between results of digital colorimeters in both testes of free and

total chlorine, that when increasing in contact time (minute) there was increasing in chlorine reading in ppm, while in visual colorimeter there was a direct weakly correlated in both testes of the experiments of free and total chlorine.

These results were explained by Wolfgang Adolph, in SGS institute in England, [12], who showed that there was a relation between increasing of contact time when chlorine was adds to the drinking water for disinfection and the sensitivity of colorimeter test results.

In addition, the same result was shown by smith, of national water association in Canada [13], who showed that, there was a strongly relation between increasing of contact time and the sensitivity of colorimeter reading.

5-Conclusions and Recommendations

5.1- Conclusions:

The following conclusions can be derived from this study:

1. There was a highly statistical significant difference (p=0.000), in a compare between digital calorimeter with the visual colorimeter in both free and a total chlorine test results of 200 experiments at the same practical condition when a tested reagents DPD no. (1) and no. (2) was used.
2. The digital colorimeter was giving a reading of (0.01) after one minute of the contact time at the first experiment, while the visual colorimeter was didn't giving any reading (0.00) at a first one minute of the contact time in both free and total chlorine experiments, this mean that the digital colorimeter was more sensitive than visual colorimeter.
3. In the experiment after a100 minute was spending of a contact time when addition of chlorine to the water sample the maximum value of the digital colorimeter was a higher than the maximum value of visual colorimeter of both free and total chlorine meter, this mean the digital colorimeter was more sensitive in reading.
4. There was a highly differences of the mean in comparison of the digital colorimeter with the visual colorimeter of both free and total chlorine experiment.
5. There was a direct strongly correlated between digital colorimeter and contact time in both free and total chlorine experiments.
6. there was a direct weakly correlated between visual colorimeter and contact time in free and total chlorine experiments.

5.2-Recommendation:

1. From the all tested results of experiment that was derived from this study we recommend to practically adaptation of a digital colorimeter instead of visual colorimeter in all the chlorine residual test results that was done by ministry of health in all governorates when monitoring of drinking water in any time.
2. For more accurate and sensitive test result we recommend to adapted of digital colorimeter in all researches when tracing of chlorine residual in any water samples.

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دراسة مقارنة بين جهاز قياس الكلور الرقمي وجهاز قياس الكلورالعيني بواسطة استخدام كواشف الكلور الدي بي دي رقم 1 والدي بي دي رقم 3 تحت ظروف قياسية

فولاذ عبد الرضا محسن
ماجستير صحة المجتمع
قسم صحة المجتمع / المعهد التقني الكوفة

الخلاصة

ان كل منظومة ماء شرب بحاجة لقياس مستويات الكلورين المتبقي باجهزة دقيقة عمليا للتاكد من ان الماء تم تنقيته بصورة مظبوطة.

اجريت هذه الدراسة التجريبية للمقارنة تحت ظروف قياسية في المختبر نتائج فحوصات الكلور الحر والكلي في نماذج الماء بين جهاز قياس الكلور الرقمي وجهاز قياس الكلور العيني بواسطة استخدام الكواشف الكيمياوية ((الدي بي دي رقم (1)) لقياس الكلورين الحر في نماذج الماء, واستخدام ((الدي بي دي رقم (3)) لقياس الكلورين الكلي في نماذج المياه. استمرت هذه الدراسة من (2011/10/1 الى 2012/5/1) . تمت الدراسة في مختبرات المعهد التقني الكوفة والتابع لمحافظة النجف الاشرف حوالي 165 كم للجنوب من بغداد, و60 كم للجنوب من محافظة بابل. 200 تجربة قد تم اجرائها في المختبر, بواسطة العمل بتجربتين في كل يوم تحت ظروف قياسية في المختبر.كان هنالك فروق معنوية احصائية كبيرة (p=0.000) عند المقارنة بين جهاز قياس الكلور الرقمي مع جهاز قياس الكلور العيني لكل من فحوصات الكلور الحر والكلور الكلي. كان هنالك فرق كبير في المتوسط الحسابي عند المقارنة بين الجهازين بالنسبة لكل فحوصات الكور الحر والكلي.

كان هنالك ارتباط موجب وقوي بين نتائج تجارب جهاز الكلور الرقمي ووقت التلامس لكل من فحوصات الكلور الحر والكلي, بينما كان هنالك ارتباط موجب وظعيف بين نتائج تجارب جهاز قياس الكلور العيني ووقت التلامس لكل من فحوصات الكلور الحر والكلي.

من جميع نتائج التجارب المعمولة والمستخلصة من هذه الدراسة, توصي الدراسة من تبني الاستخدام العملي لجهاز قياس الكلورالرقمي بدلا من جهاز قياس الكلور العيني في جميع فحوصات الكلور المتبقي من قبل المفتشين التابعين لوزارة الصحة في جميع المحافظات عند مراقبة مياه الشرب. كما توصي الدراسة لنتائج اكثر دقة وحساسية من تبني استخدام جهاز قياس الكلور الرقمي في جميع البحوث للتقصي عن الكلور الحر والمتبقي في مختلف نماذج المياه.