

AN INVESTIGATION OF THE METHODS USED IN THE
DETERMINATION OF THE CHLORINE DEMAND OF
SETTLED SEWAGE

by

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I. INTRODUCTION

Chlorine is used in the treatment of sewage mainly to prevent an increase in the bacteria population, thereby protecting the receiving water from contamination. It is also used to solve special problems in the sewage treatment system, such as controlling odors in the sewer lines and in the sewage treatment system; controlling trickling filter flies and trickling filter foaming; controlling digester foaming; and reducing the B. O. D. of the sewage. Chlorine may be applied to sewage by one or a combination of the following methods: in the sewer lines before the sewage reaches the sewage treatment plant (Up-sewer chlorination); in the influent to the sewage treatment plant (Pre-chlorination); in the effluent to the sewage treatment plant (Post-chlorination); and at points within the sewage treatment plant (Plant-chlorination).

The amount of chlorine required depends upon the type of sewage treated and the degree of treatment given the sewage, wherein enough must be added to satisfy the demand of the organic material present in the sewage. When this demand has been satisfied, further addition will cause a residual chlorine content to be present in the sewage. The chlorine demand is defined as the amount of chlorine that is required to be added as chlorine water to satisfy the needs of all the compounds in the sewage and still have a 0.10 ppm. residual at the end of a fifteen minute contact period (2). Discrepancies in the

results obtained by the various methods employed in the determination of chlorine residuals offers the possibility of either too little or too much chlorine used in sewage chlorination.

This investigation of the methods used in the determination of the chlorine demand was made in an effort to determine the correlation which exists between the chlorine demand determination methods in settled sewage.

II. REVIEW OF LITERATURE

The starch iodide method was the original chlorine residual determination test (4); however, the end-point was difficult to distinguish due to the absorption of the free iodine by the sewage constituents (7) and (8). The ortho toluidine method was developed to eliminate this difficulty. This reagent will produce false end-points due to the presence of nitrites, manganese, or ferric iron in the sewage (2) and (4); however, by acidifying and by placing the sample in the dark during color development, this interference may be eliminated. Since the addition of acid to the ortho toluidine induced errors in the results obtained, the amperometric titrator was developed (6). Several variations of the amperometric titrator have been developed: Marks, Joiner, and Strandkov (8) developed the neutral amperometric method; Marks and Joiner (7) developed the acid amperometric method; and Strandkov, Marks, and Horchler (10) developed the starch amperometric method.

Marks, Joiner, and Strandkov (8) reported that the acid ortho toluidine and the neutral amperometric methods gave results which varied widely from sample to sample. Strandkov, Marks, and Horchler (10) found that a zero reading with acid ortho toluidine was obtained on a large number of chlorinated effluent samples which gave neutral amperometric residuals as high as 1.00 ppm. Heukelekian and Day (5) found a correlation between the acid ortho toluidine and

neutral amperometric methods using the method of least squares, wherein 1.2 to 1.6 ppm. amperometric residuals were required to produce a measureable ortho tolidine residual and the rate of increase was 2.00 ppm. amperometric residual for each ppm. increase in the ortho tolidine residual. Marks and Joiner (7) reported that the acid amperometric residuals were comparable with the acid ortho tolidine residuals.

Nusbaum and Meyerson (9), using the spot test to determine chlorine residuals by the p-aminodimethyl, neutral and acid ortho tolidine, and neutral and acid starch iodide methods, found good agreement between p-aminodimethyl, neutral ortho tolidine, and acid starch iodide methods; however, the acid ortho tolidine and neutral starch iodide methods did not have any relation to one another except that the chlorine demand was much higher than that of the other methods. Good agreement was obtained between the acid starch iodide and the neutral amperometric methods.

III. THE INVESTIGATION

Theory and Apparatus

When sewage is chlorinated at a neutral pH, sufficient chlorine (HOCl) must be added to react with the sewage constituents (X) other than the ammonia and complexed organic compounds -

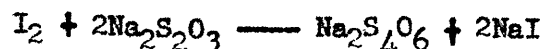
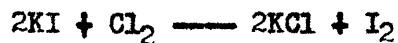


Further addition of chlorine will cause chlorine residuals in the form of chloramines to be present in the sewage -



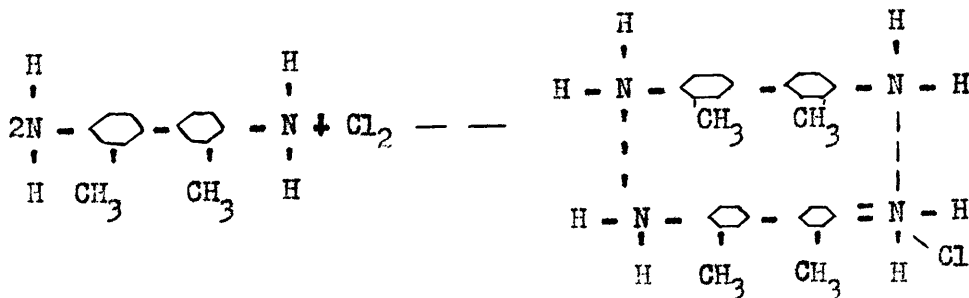
These chlorine residuals are formed by the reaction of the chlorine with ammonia and complexed organic compounds. The chlorine demand determination methods used in this investigation indicate the amount of combined chlorine residual present in chlorinated sewage.

Starch Iodide Methods: The following equations illustrate the reactions which take place in determination of the chlorine demand of sewage by the starch iodide method:



Potassium iodide (KI) combines with the combined forms of chlorine to liberate free iodine which upon addition of starch solution forms the characteristic blue color, providing a chlorine residual is present in the chlorinated sewage sample. Titration with sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) causes the blue color to disappear when all the free iodine has reacted with the sodium thiosulfate.

Acid Ortho Tolidine Method: The following equation illustrates the reaction which takes place in the determination of the chlorine demand by the acid ortho tolidine method (3):



When the pH is above 1.8, acid ortho tolidine plus the free and combined forms of chlorine react to form meriquinone of ortho tolidine due to the oxidation of the ortho tolidine by the chlorine. From a pH of 2.0 to over 6.0, chlorinated ortho tolidine appears to be a fairly good pH indicator (3). As the concentration of the total chlorine increases, the color developed by the meriquinone of ortho tolidine increases and standard color disks have been developed to determine the concentration of the total chlorine



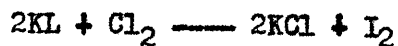
Figure 1

Amperometric Titrator (Left) and Ortho Tolidine
Comparator (Right).

present on this basis. Nitrites, ferric iron, and manganese also form with ortho tolidine the colors characteristic of chlorine and ortho tolidine.

A Wallace and Tiernan turbidity compensating comparator (Figure 1) was used to determine the chlorine residual present in the chlorinated sewage sample. This instrument consists of a standardized color disk, two sample tubes, and an eye piece. A comparison is made of the reaction of ortho tolidine and chlorine with that of the standard color disk.

Amperometric Methods: The following equations illustrate the reactions which take place in the determination of the chlorine demand by the amperometric methods (1):



Phenylarseneoxide reacts with either free chlorine or free iodine; however, it will not react with the combined forms of chlorine. Potassium iodide is added to liberate iodine from the combined forms of chlorine (1). When using this method in sewage determinations, a process of "back-titration" is employed. Potassium iodide is added to liberate iodine from the combined forms of chlorine which in turn reacts with the phenylarseneoxide. Since an excess of phenylarseneoxide is added to the sample, the remaining unreacted phenylarseneoxide must be titrated with free iodine; hence the

term "back-titration". Just before back-titrating with the iodine, the pH is lowered, by the addition of HCl, to approximately 2.5.

"When two electrodes are placed in contact with a solution and an electrical voltage is impressed, the current can flow only if the voltage is sufficient to cause a chemical reaction at both electrodes. The chemical reaction at the positive electrode is oxidation; that at the negative electrode is reduction. Current can flow only if oxidation occurs at the positive electrode and reduction occurs at the negative electrode. With a given impressed voltage, these reactions are possible and, if the proper reducing agent is in contact with the positive electrode and if the proper oxidizing agent is in contact with the negative electrode. In the determination of an oxidizing agent, such as chlorine, a large easily oxidized positive electrode is used. Under proper conditions, the current that can flow will depend only upon the concentration of the oxidizing agent which is reduced at the negative electrode (6)." The solution is agitated to increase the sensitivity of the negative electrode.

A Wallace and Tiernan Amperometric titrator was used (Figure 1), which consisted of a displacement cup, amperometric titrator (consisting of a microammeter, burette, porous cylinder, agitator cup, and sample jar), and reagent bottle.



Figure 2

Sampling Station at the Primary Clarifier Effluent
of V. P. I. Sewage Treatment Plant

Three modifications of the amperometric titrator were used in this investigation which are explained briefly below. The neutral and acid amperometric methods used the same reagents; however, the difference was the order in which the reagents were added to the chlorinated sewage sample. In the neutral amperometric method, the phenylarseneoxide plus potassium iodide was added to the chlorinated sewage sample followed by Hydrochloric acid solution; whereas, in the acid amperometric method, hydrochloric acid was added to the chlorinated sewage sample followed by the phenylarseneoxide plus potassium iodide. In both methods, the sample was then back-titrated with iodine; and the end-point noted in both of these methods by the permanent deflection of the microammeter needle. The starch amperometric method is a modification of the neutral amperometric method, wherein, starch solution is added prior to back-titrating with iodine and the appearance of the blue color indicated the end-point.

Sampling

All sewage samples were obtained from the primary clarifier effluent at the V. P. I. Sewage Treatment Plant, Blacksburg, Virginia, (Figure 2). Since only one-half of the primary clarifier was in operation during the summer months, these samples were taken from the middle of the eastern clarifier midway between the concrete

baffle and the effluent weir. The chlorine demand sample was obtained by employing a dipper to fill a five-gallon container with the sewage.

Procedure

Method of Chlorination: Each chlorine residual test used in this study required a separate time schedule so that the operator could set up the chlorinated sewage samples and run the desired chlorine residual test to determine the chlorine demand. The amperometric methods were set up for a four-minute time schedule; although the neutral amperometric method was later decreased to a two-minute schedule. The acid ortho toolidine method was set up for a six-minute schedule; but, when two turbidity compensating comparators were available, this time schedule was decreased to three minutes. Since the acid amperometric method and the acid ortho toolidine method were run from the same chlorinated sewage sample, their time schedule depended on the comparators available for use. The starch iodide methods were set up for a two-minute schedule.

The sewage, in the five-gallon container, was mixed and a 1500 ml. beaker was filled with the sewage. Two hundred and fifty mls. of the sewage were poured into a minimum of four and a maximum of eight 1000 ml. flasks. As the first chlorine dosage (see Appendices for preparation of chlorine solution) was added to 250 mls. of sewage,

the stop watch was started. Immediately after addition of the chlorine, the chlorinated sewage was mixed by rotating the flask for one minute. After a time lapse of 2, 3, 4, or 6 minutes depending on the chlorine residual test to be made, the next chlorine dosage was added to the following sewage sample which was mixed for one minute. This procedure was continued until the desired number of samples had been chlorinated.

When the fifteen minutes had elapsed from the time of the chlorination, the desired chlorine residual test was made. Another sample was run according to the time schedule so that a fifteen minute contact period was given to each chlorinated sample. During some of the runs, samples were being chlorinated while other samples were being tested for a chlorine residual; however, a sample was never chlorinated at the same time that a chlorine residual test was to be made.

Neutral Starch Iodide Method: The preparation of reagents which were used in the neutral starch iodide method is explained in the Appendices. When the 15 minute contact period ended, 2.5 mls. of potassium iodide solution was added to the sample. The sample was mixed and one ml. of starch solution was added. If a blue color appeared, the sample was titrated with 0.01 N sodium thiosulfate solution until the blue color disappeared.

Acid Starch Iodide Method: The preparation of reagents which were used in the acid starch iodide method is explained in the Appendices. When the fifteen minute contact period ended, 2.5 mls. of 50 per cent glacial acetic acid solution, followed by 2.5 mls. of potassium iodide, was added to the chlorinated sewage sample. The sample was mixed and one ml. of starch solution was added to the sample. If a blue color appeared, the sample was titrated with 0.01 N sodium thiosulfate until the blue color disappeared.

Acid Ortho Tolidine Method: The preparation of reagents used in the acid ortho tolidine method is explained in the Appendices. This chlorine residual test was made using a Wallace and Tiernan comparator. When the fifteen minute contact period ended, 15 mls. of the chlorinated sewage sample were poured into the sample tube which contained 0.75 mls. of acid ortho tolidine reagent. Another 15 mls. were poured into the other sample tube. After the sample tubes had been placed in the comparator, the comparator was placed in the dark for five minute color development. When the five minute period ended, the comparator was taken out of the dark and, by looking into the eye piece and rotating the color disk, the chlorine residual of the sample was obtained.

Neutral Amperometric Method: The preparation of reagents which were used in the neutral amperometric method is explained in the Appendices. This chlorine residual test was made using a Wallace and

Tiernan amperometric titrator. When the fifteen minute contact period ended, five mls. of 0.00564 N phenylarseneoxide plus potassium iodide was added to 200 mls. of the chlorinated sewage sample. After thorough mixing, two mls. of N hydrochloric acid was added to the sample, which was then titrated with 0.0282 N iodine solution. The permanent deflection of the microammeter needle to the right indicated the end-point.

Acid Amperometric Method: The preparation of reagents which were used in the acid amperometric method is explained in the Appendices. This chlorine residual test was made using a Wallace and Tiernan amperometric titrator. When the fifteen minute contact period ended, two mls. of N hydrochloric acid was added, with agitation, to the 200 mls. of chlorinated sewage sample. Then five mls. of 0.00564 N phenylarseneoxide solution was added and the sample titrated with the 0.0282 N iodine solution. The permanent deflection of the microammeter needle to the right indicated the end-point.

Starch Amperometric Method: The preparation of reagents which were used in the starch amperometric method is explained in the Appendices. This chlorine residual test required that a light be used to determine when the blue color appeared along with a Wallace and Tiernan amperometric titrator. When the fifteen minute contact period ended, five mls. of 0.00562 N phenylarseneoxide solution was added to 200 mls. of chlorinated sewage. After thorough mixing, two

mls. of N hydrochloric acid was added followed by one ml. of starch solution. The mixture was then titrated with 0.0282 N iodine solution to the blue color end-point.

Results

The data that was obtained by the chlorine demand determination methods is tabulated in Tables 1, 3, 4, 6, 7, 8, and 9, and the corresponding results plotted graphically in Figures 3, 4, 5, 6, 7, and 8. The method of least squares, which was used to correlate the obtained data is presented in Tables 2, 10, 11, 12, and 13 with the exception of the acid starch iodide and neutral amperometric chlorine demands which is presented in Table 5.

Table 1
Neutral and Acid Starch Iodide
Chlorine Demands

Date	Time	Chlorine Demand by Neutral Starch Iodide (ppm.)	Chlorine Demand by Acid Starch Iodide (ppm.)
August 21	12:00	4.44	4.20
August 21	1:00	4.64	4.62
August 22	9:05	3.48	3.14
August 22	11:30	4.56	4.18
August 22	12:30	4.00	3.05
August 28	10:15	4.02	3.54
August 28	11:40	5.16	4.82
August 28	12:40	4.46	3.66
August 29	10:15	3.20	2.80
August 29	11:40	4.40	4.20
August 29	12:40	6.00	5.45
August 29	1:45	5.60	3.80
August 29	3:00	4.20	3.20
August 30	9:30	3.80	2.80
August 30	11:30	4.60	4.00
September 17	9:50	2.50	1.90
September 17	10:40	2.90	2.30

Table 2

Correlation of Neutral and Acid Starch Iodide
Chlorine Demands

Number of Runs (n)	Acid Starch Iodide (x)	Neutral Starch Iodide (y)	(x) ²	(x)(y)
1	4.20	4.44	17.6400	18.6480
1	4.62	4.64	21.3444	21.4368
1	3.14	3.84	9.8596	12.0576
1	4.18	4.56	17.4724	19.0608
1	3.05	4.00	9.3025	12.2000
1	3.54	4.02	12.5316	14.2308
1	4.82	5.16	23.2324	24.8712
1	3.66	4.46	13.3956	16.3236
1	2.80	3.20	7.8400	8.9600
1	4.20	4.40	17.6400	18.4800
1	5.45	6.00	29.7025	32.7000
1	3.80	5.60	14.4400	21.2800
1	3.20	4.20	10.2400	13.4400
1	2.80	3.80	7.8400	10.6400
1	4.00	4.60	16.0000	18.4000
1	1.90	2.50	3.6100	4.7500
1	2.30	2.90	5.2900	6.6700
17	61.66	72.32	237.3810	274.1488

$$61.66 a + 17.00b - 72.32 = 0 \quad (1)$$

$$237.3810a + 61.66b - 274.1488 = 0 \quad (2)$$

Solve simultaneously for a

$$a = + 0.87$$

Substitute 0.87 for a in equation (1)

$$b = + 1.09$$

Equation of best fit ----- $y = 0.87x + 1.09$

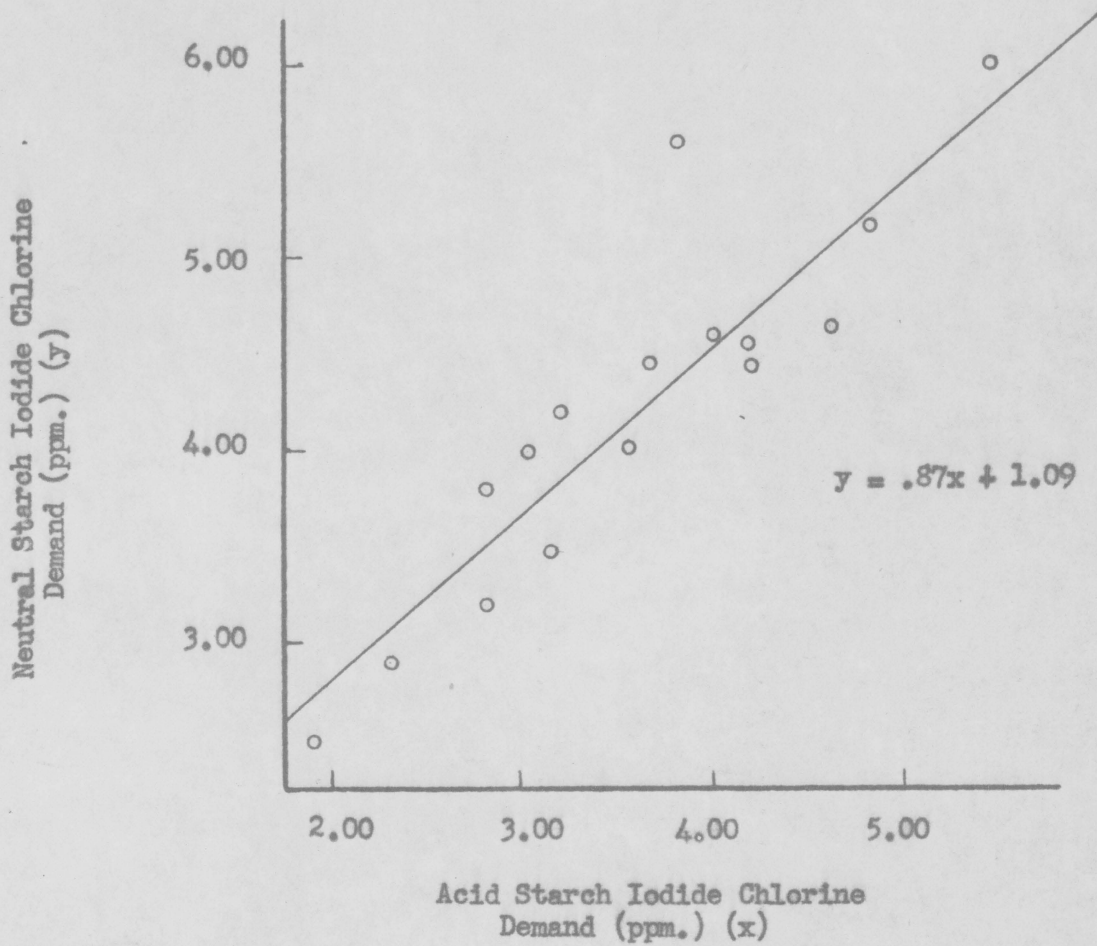


Figure 3
Neutral and Acid Starch Iodide
Chlorine Demand

Table 3
Neutral Starch Iodide and Neutral
Amperometric Chlorine Demands

Date	Time	Chlorine Demand by Neutral Amperometric (ppm.)	Chlorine Demand by Neutral Starch Iodide (ppm.)
August 21	10:00	4.00	3.84
August 21	12:00	4.40	4.44
August 21	1:00	4.44	4.64
August 21	2:00	4.36	4.02
August 22	9:05	3.98	3.48
August 22	10:05	3.82	3.10
August 22	11:30	4.40	4.56
August 22	12:30	4.20	4.00
August 28	10:15	4.36	4.02
August 28	11:40	4.88	5.16
August 28	12:40	4.60	4.46
August 29	11:40	4.56	4.40
August 29	12:40	5.56	6.00
August 29	1:45	5.22	5.60
August 29	3:00	4.30	4.20
August 30	9:30	4.02	3.80
August 30	11:30	4.56	4.60

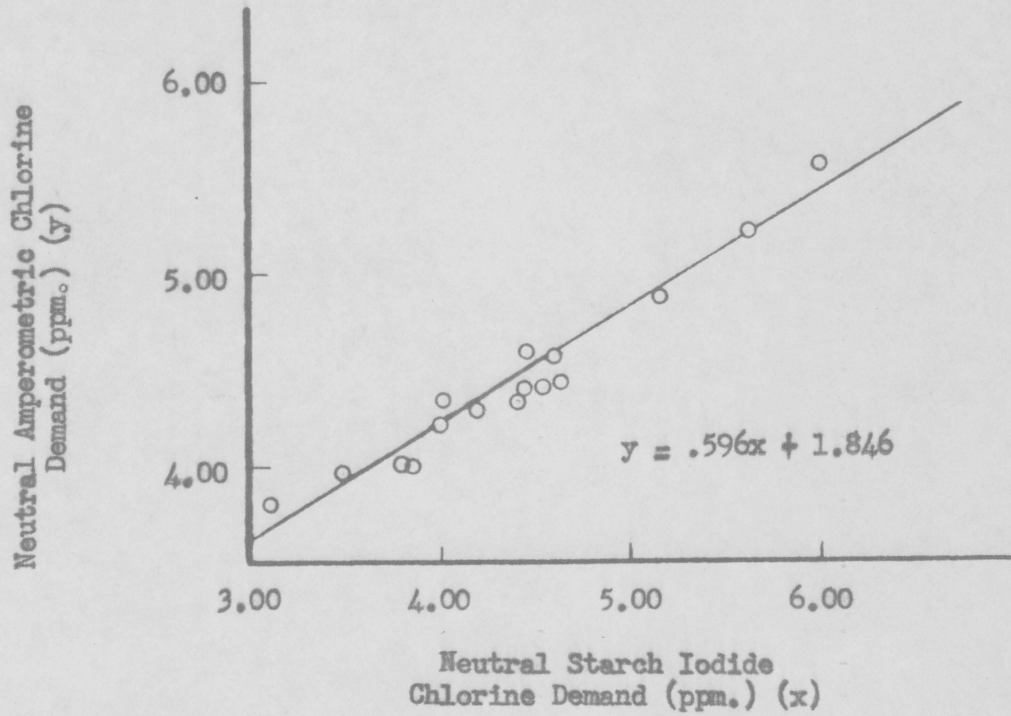


Figure 4

Neutral Starch Iodide and Neutral Amperometric
Chlorine Demands

Table 4
Acid Starch Iodide and Neutral Amperometric
Chlorine Demands

Date	Time	Chlorine Demand by Neutral Amperometric (ppm.)	Chlorine Demand by Acid Starch Iodide (ppm.)
August 21	12:00	4.40	4.20
August 21	1:00	4.44	4.62
August 22	9:05	3.98	3.14
August 22	11:30	4.40	4.18
August 22	12:30	4.20	3.05
August 28	10:15	4.36	3.54
August 28	11:40	4.88	4.82
August 28	12:40	4.60	3.66
August 29	11:40	4.56	4.20
August 29	12:40	5.56	5.45
August 29	1:45	5.22	3.80
August 29	3:00	4.30	3.20
August 30	9:30	4.02	2.80
August 30	11:30	4.56	4.00

Table 5
Correlation of Acid Starch Iodide and Neutral
Amperometric Chlorine Demands

Neutral amperometric and neutral starch iodide titration
equation of best fit:

$$y = 0.596x_2 + 1.846 \quad (1)$$

Neutral and acid starch iodide titration equation of best
fit:

$$y_2 = 0.87x + 1.09 \quad (2)$$

$$y_2 = x_2$$

Substitute y_2 for x_2 in equation (1)

$$y = 0.596(0.87x + 1.09) + 1.846$$

$$y = 0.518x + 0.650 + 1.846$$

Equation of best fit:

$$y = 0.52x + 2.49$$

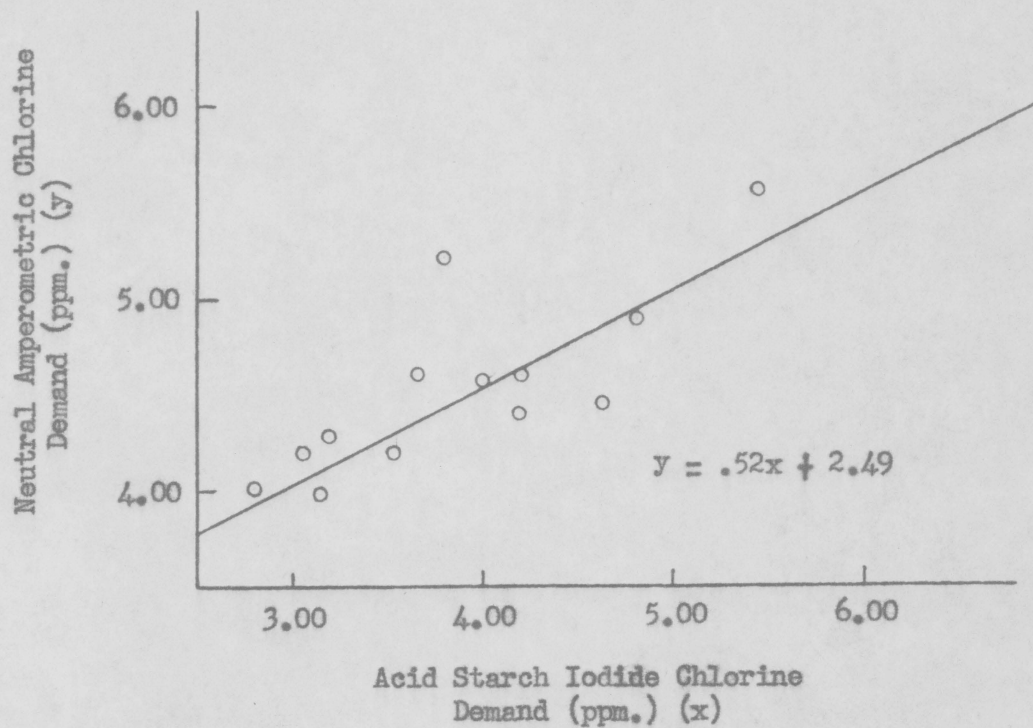


Figure 5

Acid Starch Iodide and Neutral Amperometric
Chlorine Demands

Table 6

Acid Ortho Tolidine and Neutral Amperometric

Chlorine Demands

Date	Time	Chlorine Demand by Neutral Amperometric (ppm.)	Chlorine Demand by Acid Ortho Tolidine (ppm.)
July 26	11:15	4.80	5.76
July 26	1:45	4.45	5.80
July 27	8:15	4.18	5.56
July 27	11:00	4.90	6.04
July 31	9:35	4.14	5.12
August 2	11:30	5.18	6.20
August 8	9:30	4.16	5.10
August 8	1:05	4.10	4.85
August 8	2:55	4.30	5.05
August 10	10:00	4.50	5.66
August 15	9:20	4.40	5.50
August 19	1:30	4.14	5.55
August 19	3:15	3.20	3.90
August 20	1:25	4.46	5.70
August 20	3:00	3.84	5.10
August 20	4:15	3.55	4.24
August 21	10:00	4.00	4.96

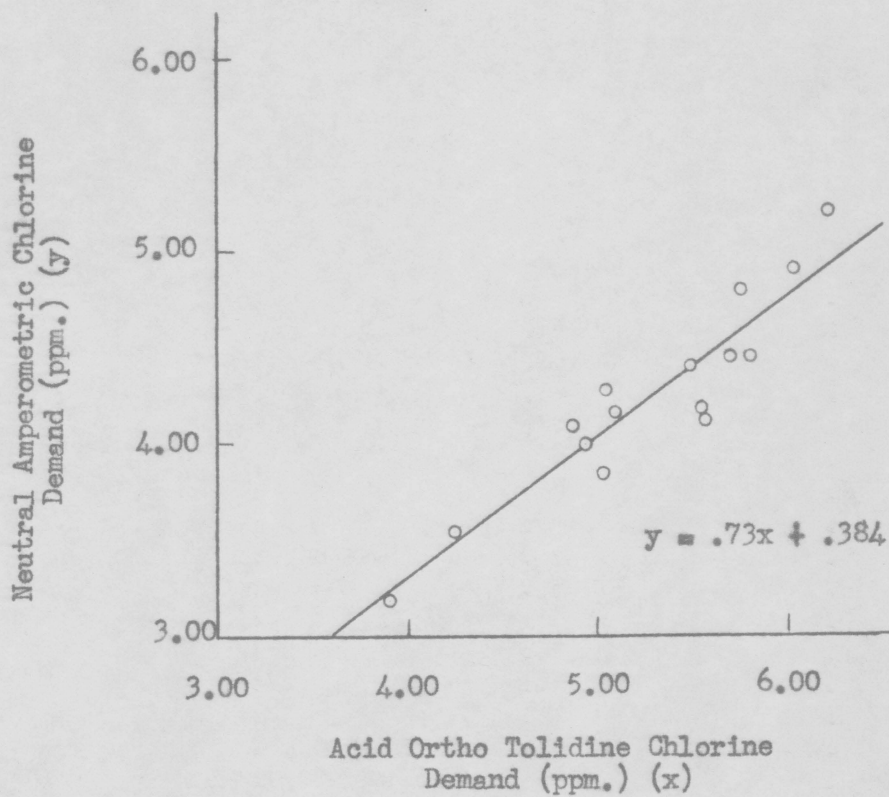


Figure 6

Acid Ortho Tolidine and Neutral
Amperometric Chlorine Demands

Table 7
Acid Ortho Tolidine and Acid Amperometric
Chlorine Demands

Date	Time	Chlorine Demand by Acid Amperometric (ppm.)	Chlorine Demand by Acid Ortho Tolidine (ppm.)
July 26	11:15	5.98	5.76
July 26	1:45	5.80	5.80
July 27	8:15	5.20	5.56
July 27	11:00	5.94	6.04
July 31	9:35	5.24	5.12
August 2	11:30	6.25	6.20
August 8	9:30	5.20	5.10
August 8	2:55	5.30	5.05
August 10	10:00	5.70	5.66
August 15	9:20	5.58	5.50
August 19	1:30	5.60	5.55
August 19	3:15	4.00	3.90
August 20	1:25	5.92	5.70
August 20	3:00	5.28	5.10
August 20	4:15	4.32	4.24
August 21	10:00	5.10	4.96

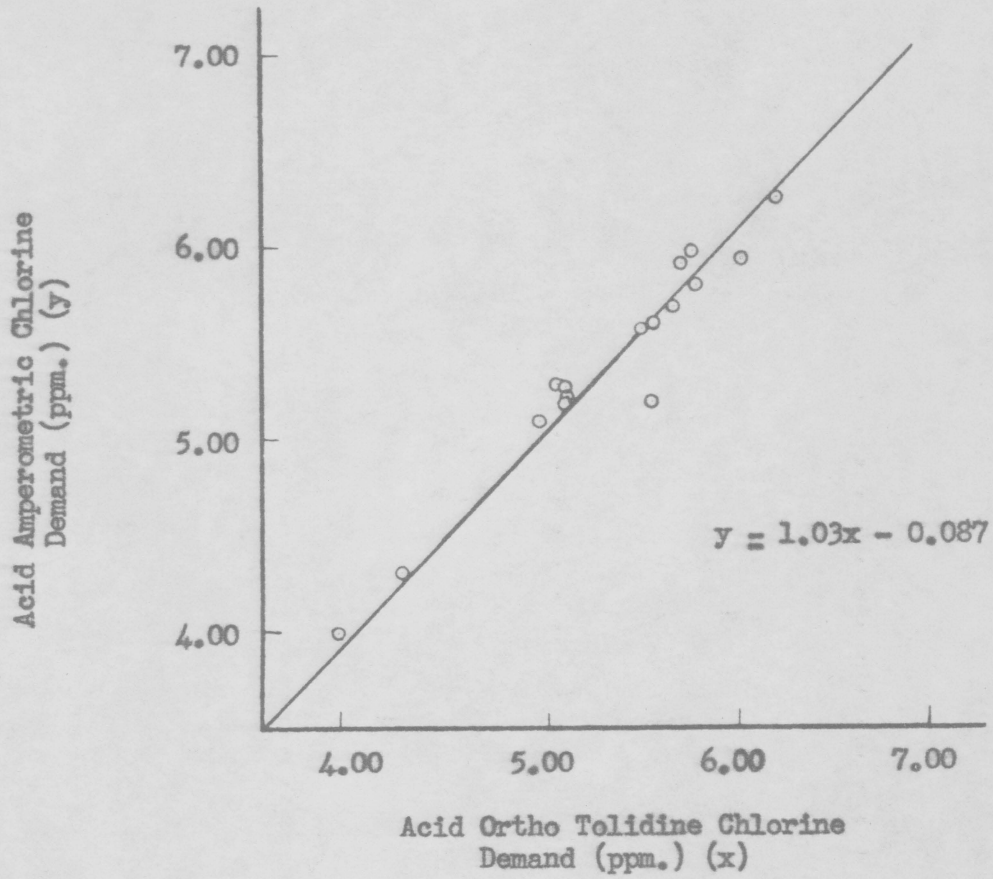


Figure 7

Acid Ortho Tolidine and Acid Amperometric
Chlorine Demands

Table 8

Neutral and Acid Amperometric Chlorine Demands

Date	Time	Chlorine Demand by Neutral Amperometric (ppm.)	Chlorine Demand by Acid Amper- ometric (ppm.)
July 7	9:30	4.00	4.85
July 10	9:05	4.00	5.36
July 11	9:15	4.00	4.96
July 12	9:00	4.37	5.60
July 26	8:50	4.32	5.16
July 26	11:15	4.80	5.98
July 26	1:45	4.45	5.80
July 27	8:15	4.18	5.20
July 27	11:00	4.90	5.94
July 31	9:35	4.14	5.24
August 2	8:45	4.17	5.20
August 2	11:30	5.18	6.25
August 6	9:00	4.06	4.98
August 8	9:30	4.16	5.20
August 8	2:55	4.30	5.30
August 9	8:55	3.30	3.46
August 10	10:00	4.50	5.70
August 13	9:10	3.56	4.30
August 15	9:20	4.40	5.58
August 19	1:30	4.14	5.60
August 19	3:15	3.20	4.00
August 20	1:25	4.46	5.92
August 20	3:00	3.84	5.28
August 20	4:15	3.55	4.32
August 21	10:00	4.00	5.10

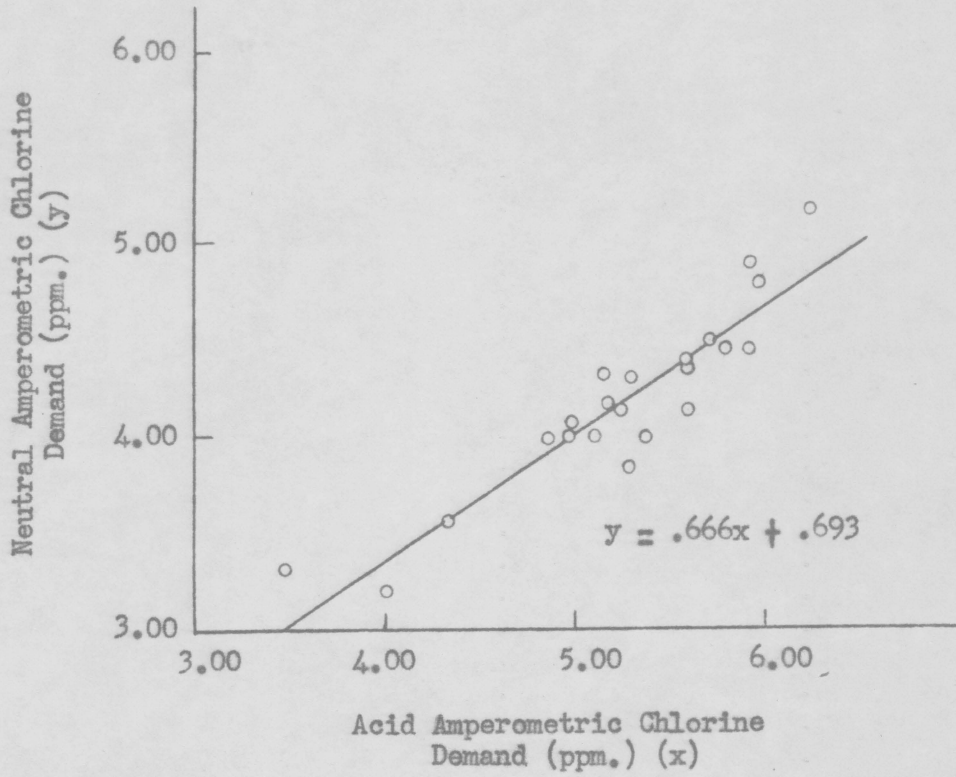


Figure 8

Neutral and Acid Amperometric
Chlorine Demands

Table 9
Neutral and Starch Amperometric
Chlorine Demands

Date	Time	Chlorine Demand by Neutral Amperometric (ppm.)	Chlorine Demand by Starch Amperometric (ppm.)
August 6	9:00	4.06	4.08
August 8	9:30	4.16	4.30
August 8	1:05	4.10	4.20
August 8	2:55	4.30	4.36
August 9	8:50	3.30	3.42
August 10	10:00	4.50	4.60
August 13	9:10	3.56	3.66

IV. DISCUSSION OF RESULTS

Figure 11 shows the graphical correlation which exists between the chlorine demand determination methods, based on the neutral amperometric chlorine demand. Marks, Joiner, and Strandskov (8), and Strandskov, Marks, and Horchler (10) found that the neutral amperometric method could be correlated with the bacterial reduction in sewage; whereas the other method, used in this study, could not be correlated; therefore, the results obtained are correlated with respect to the neutral amperometric method.

Neutral and Acid Starch Iodide Methods

The neutral starch iodide method end-point was not as definite as the acid starch iodide method end-point. Apparently, the addition of glacial acetic acid made the end-point in the acid starch iodide method more definite than the end-point in the neutral starch iodide end-point.

As can be seen from Table 1 and Figures 3 and 11, the chlorine demand by the neutral starch iodide method was greater than the acid starch iodide chlorine demand. When solving the equation of best fit, (Table 2) $y = .87x + 1.09$, the following correlation exists between the two methods:

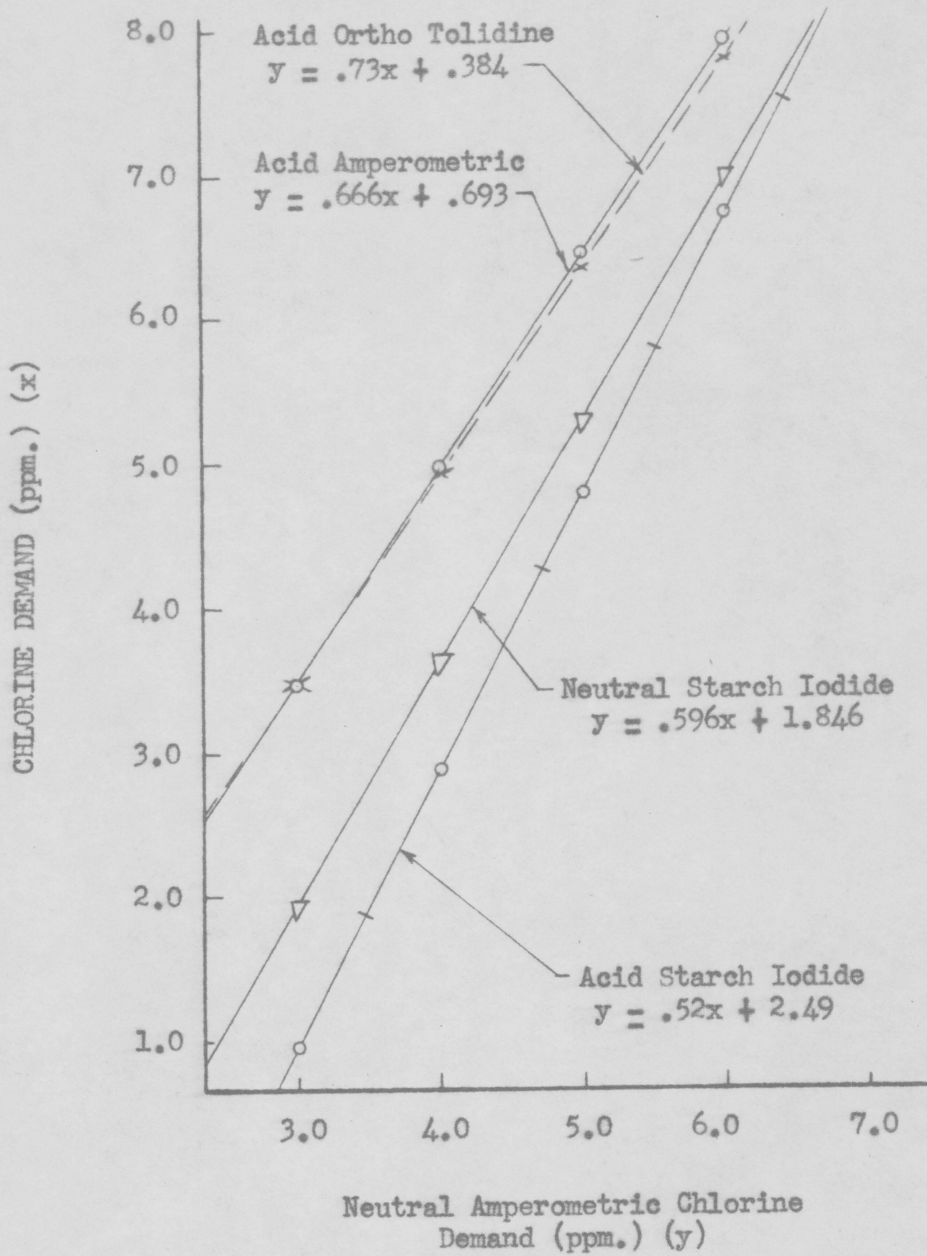


Figure 9

Correlation of Chlorine Demand Methods Based On
Neutral Amperometric Chlorine Demand

Chlorine Demand by Acid Starch Iodide (ppm.)	Chlorine Demand by Neutral Starch Iodide (ppm.)
2.00	2.83
3.00	3.70
4.00	4.57
5.00	5.44

As the strength of the sewage increased, the chlorine demand by the acid starch iodide method was progressively approaching the chlorine demand by the neutral starch iodide method.

The acid starch iodide method gave erratic results, at times as reported by Marks, Joiner, and Strandkov (8). The neutral starch iodide method had a chlorine demand of 3.10 ppm.; however, when 3.00 ppm. of chlorine were added, the acid starch iodide method had a chlorine residual content of 4.35 ppm.

Neutral Starch Iodide and Neutral Amperometric
Chlorine Demands

As can be seen from Table 3 and Figures 4 and 11, the chlorine demand by the neutral starch iodide method was sometimes lower than the neutral amperometric method and at other times the chlorine demand by the neutral starch iodide method was greater than the neutral amperometric chlorine demand. When solving the equation of best fit, (Table 10), $y = .596x + 1.846$, the following correlation exists between the two methods:

Chlorine Demand by Neutral Amperometric (ppm.)	Chlorine Demand by Neutral Starch Iodide (ppm.)
3.00	1.93
4.00	3.64
5.00	5.28
6.00	6.97

The chlorine demand of both the neutral starch iodide and neutral amperometric methods is identical at 4.57 ppm. At a chlorine demand greater than 4.57 ppm., the neutral starch iodide method increases more than the neutral amperometric chlorine demand. At a chlorine demand less than 4.57 ppm., the neutral starch iodide chlorine demand decreases more than the neutral amperometric chlorine demand.

Acid Starch Iodide and Neutral Amperometric
Chlorine Demands

As can be seen from Table 4 and Figures 5 and 11, the chlorine demand by the acid starch iodide method was sometimes lower than the neutral amperometric chlorine demand and at other times the chlorine demand by the acid starch iodide method was greater than the neutral amperometric chlorine demand. The required number of tests were not completed so that a correlation between the two methods could not be made using the method of least squares; however, the equation of best fit, (Table 5), was obtained by solving the equations for the neutral

amperometric and neutral starch iodide methods with the neutral and acid starch iodide methods. When solving the equation of best fit, $Y = .52x + 2.49$, the following correlation exists between the two methods:

Chlorine Demand by Neutral Amperometric (ppm.)	Chlorine Demand by Acid Starch Iodide (ppm.)
3.00	.98
4.00	2.90
5.00	4.82
6.00	6.74

The chlorine demand of both the neutral amperometric and acid starch iodide methods are identical at 5.18 ppm. At a chlorine demand greater than 5.18 ppm., the acid starch iodide method increases more than the neutral amperometric method. At a chlorine demand less than 5.18 ppm., the acid starch iodide method decreases more than the neutral amperometric method.

Acid Ortho Tolidine and Neutral Amperometric
Chlorine Demands

Nitrite interference was noted in the acid ortho tolidine methods during the morning hours; however, the nitrates did not interfere in the neutral amperometric method.

As can be seen from Table 6 and Figures 6 and 11, the chlorine demand by the acid ortho tolidine method was more than the neutral

amperometric chlorine demand. When solving the equation of best fit, (Table 11) $y = .73x + .384$, the following correlation exists between the two methods:

Chlorine Demand by Neutral Amperometric (ppm.)	Chlorine Demand by Acid Ortho Tolidine (ppm.)
3.00	3.44
4.00	4.89
5.00	6.35
6.00	7.80

As the strength of the sewage increased, the acid ortho tolidine method chlorine demand was progressively more than the neutral amperometric chlorine demand.

Acid Ortho Tolidine and Acid Amperometric
Chlorine Demands

Nitrites did not interfere with the acid amperometric method; however, the acid ortho tolidine method could not be run during the morning hours because of nitrite interference.

As can be seen from Table 7 and Figures 7 and 11, the chlorine demand by both of these methods are approximately the same. When solving the equation of best fit, (Table 12) $y = 1.03 - 0.087x$, the following correlation exists between the two methods:

Chlorine Demand by Acid Ortho Tolidine (ppm.)	Chlorine Demand by Acid Amperometric (ppm.)
4.00	4.03
5.00	5.06
6.00	6.09

Therefore, it can be said that these two methods indicate the same chlorine demand in settled domestic sewage.

It is significant to notice that both of these methods, which are acidified with hydrochloric acid, indicate a chlorine demand equally greater than that of the neutral amperometric chlorine demand; therefore, it is assumed that the hydrochloric acid must cause this discrepancy in these chlorine demand determinations.

Neutral and Acid Amperometric Chlorine Demands

These two methods required the same reagents but in the neutral amperometric method, phenylarseneoxide solution was added followed by the hydrochloric acid solution, and, in the acid amperometric method, hydrochloric acid solution was added followed by the phenylarseneoxide solution. In the neutral amperometric method, the residual chlorine present combined with the phenylarseneoxide plus potassium iodide at a neutral pH and the back titration with the iodine was made at a pH of 2.5. In the acid amperometric method, the solution was acidified and the chlorine residual present combined with the phenylarseneoxide plus potassium iodide at a pH of 2.5. The back

titration with the iodine solution was made at a pH of 2.5; therefore, the time of acidifying the chlorinated sewage sample was the difference between the two methods.

As can be seen from Table 8 and Figures 8 and 11, the chlorine demand by the acid amperometric method was more than the neutral amperometric chlorine demand. When solving the equation of best fit, (Table 13) $y = .666x + .693$, the following correlation exists between the two methods:

Chlorine Demand by Neutral Amperometric (ppm.)	Chlorine Demand by Acid Amperometric (ppm.)
3.00	3.45
4.00	4.95
5.00	6.45
6.00	7.95

As the strength of the sewage increased, the acid amperometric method chlorine demand was progressively more than the chlorine demand by the neutral amperometric method.

Neutral and Starch Amperometric Methods

The starch amperometric method was made in conjunction with the neutral amperometric method to determine if the same relation as obtained by Marks, Joiner, and Strandkov (7) was found.

As can be seen from Table 9, the chlorine demand of the starch amperometric method was approximately 0.10 ppm. greater than the

neutral amperometric method. The neutral amperometric end-point was more sensitive than the starch amperometric end-point.

V. CONCLUSIONS

1. The chlorine demand correlations, which exist in the settled domestic sewage at the V. P. I. Sewage Treatment Plant between the limits of one and seven ppm. of applied chlorine dosage, are as follows:
 - (a) Neutral starch iodide (x) and neutral amperometric (y) relationship -- $y = .596x + 1.846$.
 - (b) Acid starch iodide (x) and neutral amperometric (y) relationship -- $y = .52x + 2.49$.
 - (c) Acid ortho tolidine (x) and neutral amperometric (y) relationship -- $y = .73x + .384$.
 - (d) Acid amperometric (x) and neutral amperometric (y) relationship -- $y = .666x + .693$.
 - (e) Acid starch iodide (x) and neutral starch iodide (y) relationship -- $y = 0.87x + 1.09$.
 - (f) Acid ortho tolidine (x) and acid amperometric (y) relationship -- $y = 1.03x - 0.087$.
2. The acid amperometric and acid ortho tolidine methods indicate approximately the same chlorine demand in settled domestic sewage.
3. Nitrites do not interfere with the acid or neutral amperometric methods.

4. The end-point in the acid starch iodide method is more definite than the neutral starch iodide method.
5. The visible starch amperometric method is not as sensitive as the neutral amperometric method for determining the chlorine demand.

VI. ACKNOWLEDGEMENTS

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IX. APPENDICES

Preparation of Reagent

Starch Iodide Methods

Potassium Iodide Solution:

- (1) Dissolve 75 gms. cp. KI (free from iodine and iodate) in one liter freshly boiled and cooled distilled water.

Acid Solution:

- (1) Dilute 500 mls. of Glacial Acetic Acid with 500 mls. of distilled water.

Starch Solution:

- (1) Make a thin paste of about 2 gms. of starch in cold water. Pour into 200 mls. of boiling distilled water. When cool add a few drops of chloroform.

Thiosulfate Solution:

- (1) Make up 0.10 N sodium thiosulfate solution by dissolving 25 grams of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in one liter of freshly boiled water and allow to stand for at least two weeks. As needed standardize with 0.10 N $\text{K}_2\text{Cr}_2\text{O}_7$ and dilute to 0.01 N. Standardize frequently to insure strength of 0.01 N sodium thiosulfate.

Ortho Tolidine Method

Ortho Tolidine Reagent:

- (1) Dissolve 1.35 gms. of ortho tolidine dihydrochloride in 500 mls. of distilled water. Add this solution,

with constant stirring, to 500 mls. of dilute HCl (mix 350 mls. of distilled water and 150 mls. of concentrated HCl).

Amperometric Methods

Phenylarseneoxide Solution:

- (1) Dissolve approximately 0.8 gms. of phenylarseneoxide in 150 mls. of 0.30 N NaOH. This solution is unstable and should be used immediately by adding 110 mls. of it to 800 mls. of distilled water containing 7.5 gms. of KI and mix thoroughly.
- (2) Bring to a pH of 6 to 7 with dilute HCl and finally dilute to one liter.
- (3) A 50 ml. sample is titrated with freshly standardized 0.0282 N iodine solution using starch as the indicator.
- (4) Dilute with distilled water until 0.00564 N is reached and titrated again.

Iodine Solution:

- (1) Dissolve 2 gms. of KI crystals in small quantity of hot boiled distilled water.
- (2) When cool, add 3.173 gms. of iodine and make up to one liter with distilled water.
- (3) Titrate against 0.025 N sodium thiosulfate until 0.0282 N iodine solution is obtained

Starch Indicator:

- (1) Make a thin paste of about 2 gms. of starch in cold water. Pour into 200 mls. of boiling water and stir. When cool add a few drops of chloroform.

Chlorine Solution

The chlorine solution was made up daily using 95 mls. of distilled water and five mls. of "zonite"; each ml. of this solution was equivalent to two ppm. of free available chlorine per 250 mls. of sewage.

Table 10

Correlation of Neutral Starch Iodide and Neutral
Amperometric Chlorine Demands

Number of Runs (n)	Neutral Starch Iodide (x)	Neutral Amperometric (y)	(x) ²	(x)(y)
1	3.84	4.00	14.7456	15.3600
1	4.44	4.40	19.7136	19.5360
1	4.64	4.44	21.5296	20.6016
1	4.02	4.36	16.1604	17.5272
1	3.48	3.98	12.1104	13.8504
1	3.10	3.82	9.6100	11.8420
1	4.56	4.40	20.7936	20.0640
1	4.00	4.20	16.0000	16.8000
1	4.02	4.36	16.1604	17.5272
1	5.16	4.88	19.8916	20.5160
1	4.46	4.60	26.6256	25.1808
1	4.40	4.56	19.3600	20.0640
1	6.00	5.56	36.0000	33.3600
1	5.60	5.22	31.3600	29.2320
1	4.20	4.30	17.6400	18.0600
1	3.80	4.02	14.4400	15.2760
1	4.60	4.56	21.1600	20.9760
17	74.32	75.66	333.3008	335.7732

$$74.32 a + 17.00b - 75.66 = 0 \quad (1)$$

$$333.3008a + 74.32b - 335.7732 = 0 \quad (2)$$

Solve simultaneously for a

$$a = + 0.596$$

Substitute 0.596 for a in equation (1)

$$b = + 1.846$$

Equation of best fit ————— $y = .596x + 1.846$

Table 11

Correlation of Acid Ortho Tolidine and Neutral
Amperometric Chlorine Demands

Number of Runs (n)	Acid Ortho Tolidine (x)	Neutral Amperometric (y)	(x) ²	(x)(y)
1	5.76	4.80	33.1776	27.6480
1	5.80	4.45	33.6400	25.8100
1	5.56	4.18	30.9136	23.2408
1	6.04	4.90	36.4816	29.5960
1	5.12	4.14	26.2144	21.1968
1	6.20	5.18	38.4400	32.1160
1	5.10	4.16	26.0100	21.2160
1	4.85	4.10	23.5225	19.8850
1	5.05	4.30	25.5025	21.7150
1	5.66	4.50	32.0356	25.4700
1	5.50	4.40	30.2500	24.2000
1	5.55	4.14	30.8025	22.9770
1	3.90	3.20	15.2100	12.4800
1	5.70	4.46	32.4900	25.4220
1	5.10	3.84	26.0100	19.5840
1	4.24	3.55	17.9776	15.0520
1	4.96	4.00	24.6016	19.8400
17	96.09	72.30	483.2795	387.4486

$$96.09 a + 17.00b = 72.30 = 0 \quad (1)$$

$$483.2795a + 96.09b = 387.4486 = 0 \quad (2)$$

Solve simultaneously for a

$$a = + 0.73$$

Substitute 0.73 for a in equation (1)

$$b = + 0.384$$

Equation of best fit _____ $y = 0.73x + 0.384$

Table 12

Correlation of Acid Ortho Tolidine and Acid
Amperometric Chlorine Demands

Number of Runs (n)	Acid Ortho Tolidine (x)	Acid Amperometric (y)	(x) ²	(x) (y)
1	5.76	5.98	33.1776	34.4448
1	5.80	5.80	33.6400	33.6400
1	6.04	5.94	36.4816	35.8776
1	5.12	5.24	26.2144	27.3408
1	6.20	6.25	38.4400	38.7500
1	5.10	5.20	26.0100	26.5200
1	5.05	5.30	25.5025	26.7650
1	5.66	5.70	32.0356	32.2620
1	5.50	5.58	30.2500	30.6900
1	5.55	5.60	30.8025	31.0800
1	3.90	4.00	15.2100	15.6000
1	5.70	5.92	32.4900	33.7440
1	5.10	5.28	26.0100	26.9280
1	4.24	4.32	17.9776	18.3168
1	4.96	5.10	24.6016	25.2960
1	5.56	5.20	30.9136	28.9120
16	85.24	86.41	459.7570	466.1670

$$85.24 a + 16.00b - 86.41 = 0 \quad (1)$$

$$459.7570a + 85.24b - 466.1670 = 0 \quad (2)$$

Solve simultaneously for a

$$a = + 1.03$$

Substitute 1.03 for a in equation (1)

$$b = - 0.087$$

Equation of best fit _____ $y = 1.03x - 0.087$

Table 13

Correlation of Neutral and Acid Amperometric
Chlorine Demands

Number of Runs (n)	Acid Amperometric (x)	Neutral Amperometric (y)	(x) ²	(x) (y)
1	4.85	4.00	23.5225	19.4000
1	5.36	4.00	28.7296	21.4400
1	4.96	4.00	24.6016	19.8400
1	5.60	4.37	31.3600	24.4720
1	5.16	4.32	26.6256	22.2912
1	5.98	4.80	35.7604	28.7040
1	5.80	4.45	33.6400	25.8100
1	5.20	4.18	27.0400	21.7360
1	5.94	4.90	35.2836	29.1060
1	5.24	4.14	27.9816	22.1076
1	5.20	4.17	27.0400	21.6840
1	6.25	5.18	39.0625	32.3750
1	4.98	4.06	24.8004	20.2188
1	5.20	4.16	27.0400	21.6320
1	5.30	4.30	28.0900	22.7900
1	3.46	3.30	11.9716	11.4180
1	5.70	4.50	32.4900	25.6500
1	4.30	4.56	18.4900	15.3080
1	5.58	4.40	31.1364	24.5520
1	5.60	4.14	31.3600	23.1840
1	4.00	3.20	16.0000	12.8000
1	5.92	4.46	35.0464	26.4032
1	5.10	3.84	26.0100	19.5840
1	4.32	3.55	18.6624	15.3360
1	5.10	4.00	26.0100	20.4000
25	130.10	103.98	687.7546	548.2418

$$130.10 a + 25.00b - 103.98 = 0 \quad (1)$$

$$687.7546a + 130.10b - 548.2418 = 0 \quad (2)$$

Solve simultaneously for a

$$a = \dagger 0.666$$

Substitute 0.666 for a in equation (1)

$$b = \dagger 0.693$$

Equation of best fit ~~_____~~ $y = 0.666x + 0.693$