

FORMATION OF CYANOGEN CHLORIDE DURING CHLORINATION OF CERTAIN LIQUIDS TOXICITY OF SUCH LIQUIDS TO FISH

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(With 3 Figures in the Text)

Certain sewage effluents have been found (Allen, Blezard, and Wheatland, 1946) to become highly toxic when treated with doses of chlorine much smaller than are required to give residual chlorine detectable by the ortho-tolidine test. Evidence from laboratory tests suggested that this toxicity was mainly due to a compound formed by interaction of the chlorine with small quantities of thiocyanate derived initially from gas liquor admitted to the sewage and surviving treatment at the sewage works. Key & Etheridge (1934) has shown that oxidation of the thiocyanate in a percolating filter or an activated-sludge plant, depends on the establishment of the necessary bacterial flora, and that a sudden increase in the concentration of thiocyanate in the sewage may result in a proportion of it being discharged in the effluent. Admission of gas liquor to sewage is common practice, and chlorination of such effluents would have serious effects on the living organisms, including fish, in surface waters to which they were discharged. Further work has revealed the nature of the compound responsible for toxicity, and has established the relation between toxicity and concentration of the substance in solution. An experimental study has been made of conditions affecting its formation during chlorination and of means of removing it from solution.

EXPERIMENTAL PROCEDURE IN TESTING TOXICITY

Rainbow trout (*Salmo gairdneri* Richardson) were used for testing toxicity. In the first series of experiments, in which the toxicity of various liquids on treatment with chlorine was tested, the chlorine demand of the liquid was first determined,* and the appropriate doses of chlorine to be added for the purpose of the test were decided. The requisite dose

* In most cases the ortho-tolidine method was used. Occasionally samples of effluent were encountered which contained substances interfering with this test. In such cases the starch-iodide method was used.

was applied by adding to 80 l. of the liquid, contained in carboys, the calculated quantity of a solution of chlorine of known strength (usually 3000–6000 p.p.m.), the carboy being shaken thoroughly to ensure mixing. After a period of contact of 15 min. the chlorinated liquid was added to a bath containing 80 l. of tap water, thus giving a dilution of 1:1. Ten rainbow trout were immersed in the bath and the time was recorded at which each individual fish lost its balance and turned over. The toxicity for each fish was expressed as 100 times the reciprocal of the period of immersion (in minutes) up to the point at which the fish lost its balance. The average toxicity of the liquid was taken as the average of the values for toxicity obtained for the ten fish and the 'mean period of survival' was taken as 100 times the reciprocal of the average toxicity.

Determinations were also made of the pH value and temperature of the liquid in the bath in each experiment. The content of dissolved oxygen was determined at sufficiently frequent intervals during the course of each test to ensure that the toxicity observed was not due to lack of oxygen.

Any modifications in this procedure which were made in subsequent experiments are indicated in the text, but the general method of testing was the same throughout.

TOXICITY OF CHLORINATED SEWAGE EFFLUENTS

The final effluents from certain sewage works were found to be highly toxic when treated with doses of chlorine well below the demand so that there was no trace of residual chlorine present. Examples of results obtained with effluents of this character, taken from sewage works in different parts of the country, are shown in Table 1. At each of these works the sewage received treatment in sedimentation tanks, percolating filters, and humus tanks. Samples taken from other works, in which the treatment included either alternating double filtration, filtra-

tion with recirculation of effluent, or aeration with activated sludge, were also found to be toxic when chlorinated.

Tests with a large number of sewage effluents revealed the fact that those which became toxic when treated with a dose of chlorine below the demand were derived from sewage to which gas liquor had been admitted. That gas liquor contains constituents which yield extremely toxic substances on chlorination is shown by the results in Table 2.

number of samples of sewage effluent by Aldridge's method (1945) revealed the fact that, in effluents which were highly toxic on treatment with doses of chlorine below the demand, thiocyanate was present in amounts ranging from 2 to 8 p.p.m. Examples of the toxicity resulting from treatment of thiocyanate solutions with different doses of chlorine (each of which was much smaller than the amount required to satisfy the chlorine demand) are shown in Table 3. Results of a series of tests with a solution of ammonium

Table 1. *Toxicity of effluents from different sewage works when treated with doses of chlorine below the demand*

Effluent			Diluted liquid in which fish were immersed				
Source of sample (sewage works)	Chlorine demand (p.p.m.)	Amount of chlorine added (p.p.m.)	pH value	Temperature (° C.)	Content of dissolved oxygen during test (% of saturation value)	Average toxicity	Mean period of survival
B	9-10	0 6	7.2 7.0	4.0 4.0	49-58 60	<0.07 3.7	> 24 hr. 27 min.
C	15-16	0 12	7.2 6.9	10.0 10.0	42-47 44	<0.26 32	> 6½ hr. 3.2 min.
D	22-23	0 10	7.2 7.1	8.5 8.5	41-44 51	<0.3 7.3	> 6 hr. 14 min.

Table 2. *Effect of chlorination on toxicity of dilute gas liquor from three different towns*

Proportion of gas liquor in solution %	Chlorine demand of solution (p.p.m.)	Amount of chlorine added (p.p.m.)	pH value	Temperature (° C.)	Content of dissolved oxygen during test (% of saturation value)	Average toxicity	Mean period of survival
0.05	5-6	0 4	7.2 7.3	13.5 13	— 67.5	<0.06 13	> 30 hr. for 9 out of 10 fish 7.7 min.
0.1	12-14	0 5	7.2 7.2	13 13	66-84 84	<0.06 15	> 28 hr. 6.5 min.

In each test the gas liquor was diluted with water, the dose of chlorine was added directly to 160 l. of the dilute liquid in a bath, and the mixture was well stirred and allowed to stand for 15 min. before immersing the fish.

Investigations showed that, of the various constituents of gas liquor, thiocyanate in solution reacted instantaneously with comparatively large amounts of chlorine (a solution of ammonium thiocyanate containing 2 p.p.m. CNS had a chlorine demand of 10.6-10.7 p.p.m.) and yielded an exceedingly toxic liquid. Moreover, tests on a large

thiocyanate at a temperature of 12° C., expressed graphically in Fig. 1, showed that the toxicity of such solutions was approximately proportional to the dose of chlorine added.

NATURE OF THE COMPOUND RESPONSIBLE FOR TOXICITY

Reaction between chlorine or bromine and either cyanide or thiocyanate is known to result in formation of the cyanogen halide. Aldridge's method (1945) for estimating small quantities of thiocyanate, for example, depends upon the fact that, in neutral

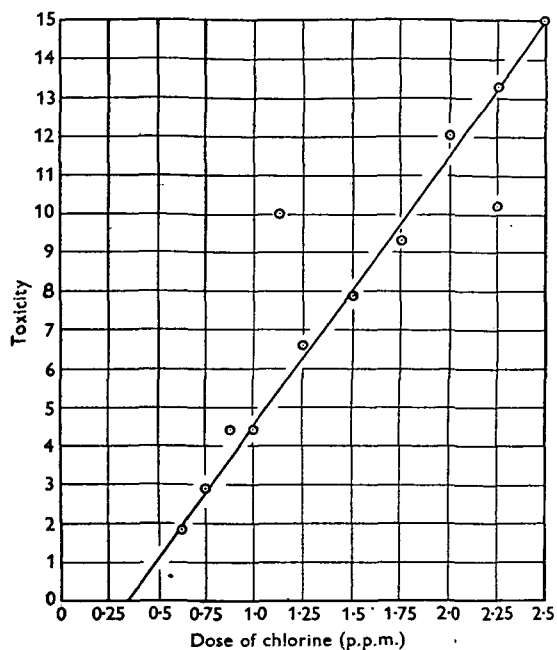
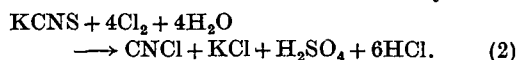


Fig. 1. Toxicity of a solution of ammonium thiocyanate treated with different doses of chlorine. Strength of thiocyanate varied from 0.5–1.5 parts per million of – CNS. Each dose of chlorine was much smaller than the chlorine demand. Temperature of solutions 12° C.

measured in a Spekker absorptiometer, using a green filter.

Tests showed that when chlorine was used in place of bromine, a colour of comparable intensity was produced. Moreover, on titrating an acidified solution of potassium thiocyanate with a solution of sodium hypochlorite, using starch-iodide as external indicator, it was found that four molecules of chlorine reacted with one molecule of thiocyanate:



Cyanogen chloride has long been known to be exceedingly toxic (cf. Blyth & Blyth, 1920; Reed, 1920*a*). Thus according to Sartori (1939) a concentration of 2.5 mg./cu.m. of air produces abundant lachrymation in man in a few minutes; and a concentration of 400 mg./cu.m. is lethal in 10 min.

It was concluded, therefore, that the toxicity of the chlorinated effluents described earlier in this paper was due to cyanogen chloride, formed by reaction of the chlorine with thiocyanate in accordance with equation (2).

FACTORS AFFECTING THE QUANTITY OF CYANOGEN CHLORIDE FORMED

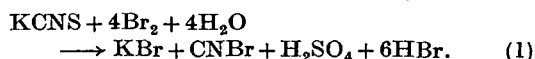
The properties of cyanogen chloride suggest that the quantity formed by reaction of chlorine and thiocyanate will be greatly influenced by a number of

Table 3. *Toxicity of chlorinated solutions of thiocyanate*

Solutions diluted with an equal volume of tap water before immersing fish.

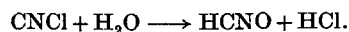
Solution of thiocyanate		Amount of chlorine added (p.p.m.)	Diluted liquid in which fish were immersed				
Content of thiocyanate (p.p.m.)	Chlorine demand (p.p.m.)		pH value	Temperature (° C.)	Content of dissolved oxygen during test (% of saturation value)	Average toxicity	Mean period of survival
1.0 (NH ₄ CNS)	3–4	1.25	7.2	12	69–73	1.8	55 min.
2.0 (NH ₄ CNS)	7–8	2.5	7.2	12	71	6.6	15 min.
3.0 (NH ₄ CNS)	11–12	0	7.3	15	—	< 0.07	> 24 hr.
		4.0	7.2	15	74	14	7.0 min.
3.0 (KCNS)	9–10	3.0	7.2	12	73	9.7	10 min.

or acidic solution, addition of bromine water results in the following reaction:



After removal of excess bromine with arsenious acid the cyanogen bromide reacts with a solution of benzidine in dilute pyridine to give an orange-red colour, the intensity of which is proportional to the concentration of cyanogen bromide and may be

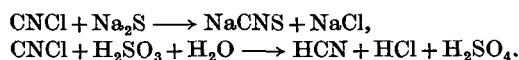
factors. Thus, although relatively stable in neutral solution, cyanogen chloride is hydrolysed in alkaline solution according to the following equation:



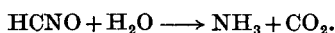
Price, Larson, Beck, Harrington, Smith & Stephenoff (1947) found that this change occurred slowly at pH 8 and much more rapidly at pH 10, and that it was accelerated by phosphate. At pH 7–8, cyanogen chloride reacted readily with

hypochlorite, this reaction being much more rapid than hydrolysis under the same conditions. Although in more concentrated solutions, cyanogen chloride reacts with ammonia to form cyanamide, these authors found that in dilute solutions (20 p.p.m. CNCl and 3–6 p.p.m. NH_3) there was no measurable reaction.

Cyanogen chloride reacts with alkali sulphides to form thiocyanates, and with sulphites to form cyanides:



It is slowly hydrolysed by acids, the cyanate formed being then rapidly converted to ammonia and carbon dioxide:



The quantities of cyanogen halide resulting from the interaction in dilute solution of different proportions of thiocyanate and either chlorine or bromine were determined as follows:

To a series of bottles, each containing 100 ml. of a solution of potassium thiocyanate (3 p.p.m. CNS) in $\text{M}/30$ phosphate buffer, measured quantities of a solution of the halogen (chlorine, bromine, and sodium hypochlorite in different experiments) were added so as to provide concentrations of halogen ranging from 0 to 36 p.p.m. chlorine or 0 to 81 p.p.m. bromine. Differences in volume were compensated by addition of appropriate quantities of distilled water, so that the final concentration of phosphate was about 0.031 M . Immediately after mixing, and again after standing for 15 and for 90 min., a sample of 1 ml. was abstracted from each bottle and transferred to a 10 ml. graduated flask containing 2 drops of dilute arsenious acid (2%) and the benzidine-pyridine reagent (3.6 ml.) was then added. After standing for 30 min. the volume of liquid in the flask was made up to the mark with distilled water, and the content of cyanogen chloride was estimated by a modification of Aldridge's method, intensity of colour being determined exactly 35 min. after sampling. Data were obtained for solutions buffered to initial pH values of approximately 5.5, 6.5, and 7.5. The pH value in any one series varied slightly according to the concentration of halogen. The results of these experiments are expressed graphically in Fig. 2. Each graph shows also the theoretical yield of the cyanogen halide which would result from the dose of halogen added. The following conclusions may be drawn:

(1) Treatment of a dilute solution of thiocyanate with an amount of halogen less than the total quantity capable of reacting with the thiocyanate present, resulted in the formation of less than the theoretical quantity of cyanogen halide. The pro-

portion of the theoretical amount which was formed increased as the quantity of halogen added approached the maximum capable of reacting with the thiocyanate present. At pH values of 6.5 and 7.5 there was only a slight decrease in the amount of cyanogen halide on standing for 90 min., suggesting slow hydrolysis.

(2) There was a marked loss of cyanogen halides when they were allowed to stand in contact with excess halogen. This tendency was greater with the chloride than with the bromide, and with both compounds the loss was greater with increasing concentration of halogen and with increasing pH value. At pH 7.6–7.7 the reaction between cyanogen chloride and chlorine was so rapid* that with an excess of 21 p.p.m. of chlorine there was a loss of 25% of cyanogen chloride even when the sample was taken immediately after mixing.

These findings show that, when solutions containing thiocyanate are treated with quantities of chlorine lower than the chlorine demand, the cyanogen chloride formed may be expected, in the absence of interfering substances, to amount to 40–90% (depending on the relative proportions of thiocyanate and chlorine) of the theoretical yield calculated on the basis of equation (2).

Effect of interfering substances

The concentration of cyanogen chloride formed, and therefore the resulting toxicity, when solutions containing thiocyanate were chlorinated, was found to depend not only on the concentrations of thiocyanate and of chlorine, but on the presence or absence of other substances which competed for the chlorine.

A solution containing 2 p.p.m. CNS as ammonium thiocyanate was treated with different doses of chlorine, and the amounts of cyanogen chloride formed were compared with the amounts formed in a similar solution in the presence of measured quantities of the test substance. Glucose, phenol, and acetic acid had little effect; the amount of cyanogen chloride formed was reduced slightly by peptone, and more markedly by catechol. Sodium sulphide, cystine, and cysteine reacted so readily with added chlorine that comparatively little cyanogen chloride was formed. Results of experiments with these latter substances are shown in Table 4.

* The rate at which cyanogen chloride is lost by hydrolysis is accelerated by the presence of phosphate buffer. Data obtained by Price *et al.* (1947) show that, with a concentration of 0.031 M phosphate the 'half life' of a solution of cyanogen chloride would be changed from approximately 44 to approximately 8 hr. These rates are, however, much slower than those obtaining in the presence of chlorine.

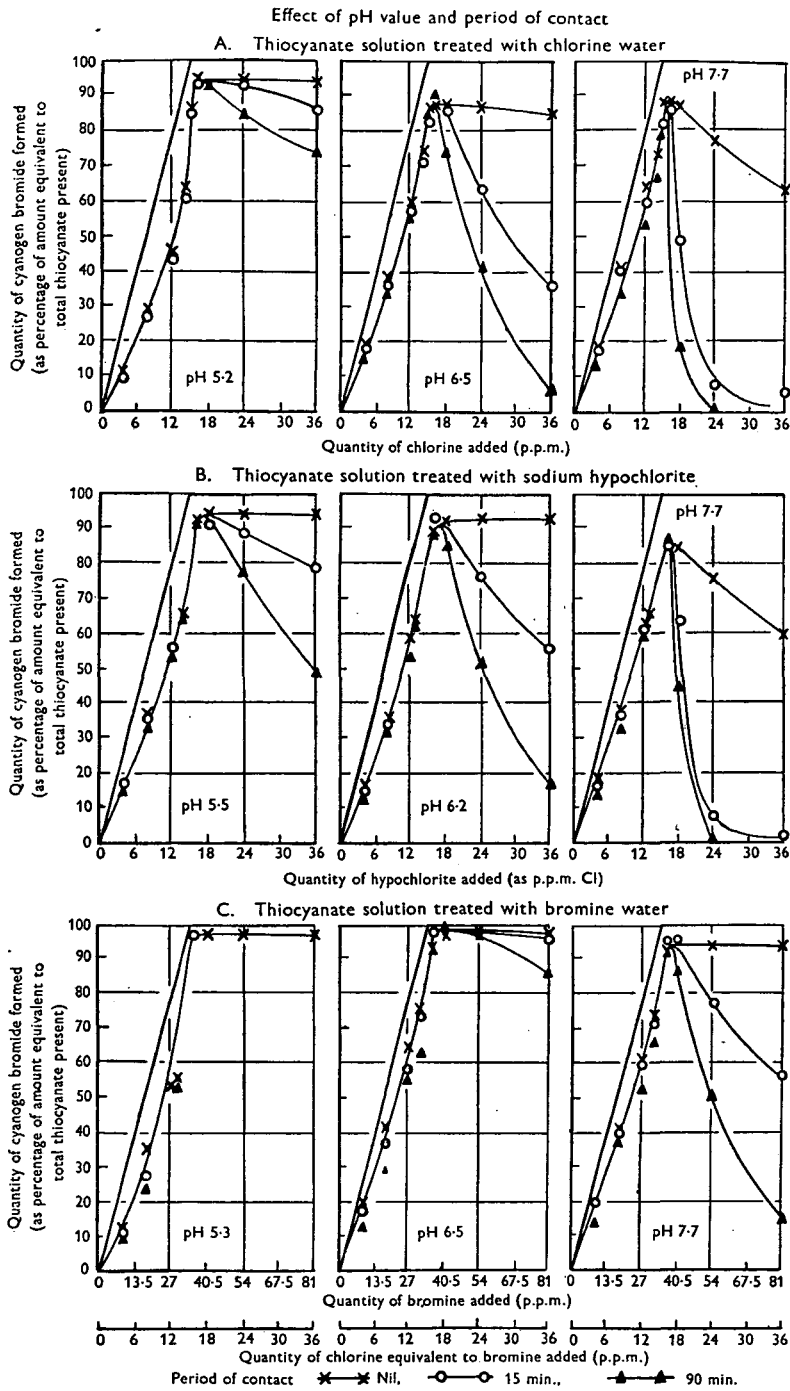


Fig. 2. Relation between dose of halogen and quantity of cyanogen chloride formed from a solution of thiocyanate.

Table 4. *Effect of presence of different substances on proportion of thiocyanate reacting with added chlorine*

Aqueous solution containing 2 p.p.m. CNS as NH₄CNS
Percentage of initial thiocyanate converted to cyanogen chloride*

Dose of chlorine added (p.p.m.)	Percentage of initial thiocyanate converted to cyanogen chloride*					
	Test 1			Test 2		
	Substance added			Substance added		
	None	Sodium sulphide (20 p.p.m.)	None	Cystine (40 p.p.m.)	Cysteine (40 p.p.m.)	
2	5	0	—	—	—	
4	10	Trace	6	5.5	2	
9	75	Trace	—	—	—	
20	100	25	83	26	3	

Determined in test 1 by comparing colours in test-tubes, in test 2 by means of the Spekker instrument.

Table 5. *Effect of aeration on toxicity of chlorinated solutions of thiocyanate*

Samples diluted with equal volumes of tap water before immersing fish

Diluted liquid in which fish were immersed

Test no.	Solution of thiocyanate		Amount of chlorine added (p.p.m.)	Period of aeration (hr.)	pH value	Temperature (°C.)	Content of dissolved oxygen during test (% of saturation value)	Average toxicity	Mean period of survival
	Content of thiocyanate (as p.p.m. NH ₄ CNS)	Chlorine demand (p.p.m.)							
1	0.75	2.9-3.0	2.0	0	7.3	11	71	6.9	14 min.
				4	7.3	11	—	<0.07	> 25 hr.
2	2.0	7-8	4.0	0	7.3	11	—	8.9	11 min.
				1	7.3	11	—	7.6	13 min.
				2	7.3	11	—	3.2	31 min.
				3	7.3	11	—	0.6	167 min.
				4	7.3	11	—	0.07	> 22 hr.
3	3.0	11-12	6.0	0	—	11	—	15	6.6 min.
				1	—	10.5	—	11	9.2 min.
				2	—	10	—	5.6	18 min.
				3	—	8	—	2.5	40 min.
				4	—	10	—	<0.12	> 18 hr. for 8 out of 10 fish

EFFECT OF AERATION ON SOLUTIONS CONTAINING CYANOGEN CHLORIDE

When considering possible means of reducing the toxicity of chlorinated effluents it was found that aeration had a marked effect. Experiments were, therefore, designed to find the effect of aeration on the toxicity of chlorinated solutions of thiocyanate and on the toxicity of chlorinated sewage effluents. The fate of the cyanogen chloride during aeration was also investigated.

Effect of aeration on toxicity of chlorinated thiocyanate solutions

The toxicity of chlorinated solutions of thiocyanate was compared with the toxicity of similar solutions after aeration with diffused air at a rate

of 12.5 l. of air per 160 l. of liquid per minute. It was found that the toxicity progressively decreased as aeration proceeded, and was eventually eliminated. Results of three such tests (Table 5) show that highly toxic solutions were rendered harmless after aeration for about 4 hr.

Effect of aeration on toxicity of chlorinated sewage effluents

The effect of aeration on the toxicity of chlorinated sewage effluents was tested on a number of effluents taken from sewage works when gas liquor was being admitted to the sewage. Tests for toxicity were made on the untreated effluent, on the effluent after treatment with a dose of chlorine below the demand, and on the chlorinated effluent after 160 l. had been aerated at a rate of 12.5 l. of air per minute

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until tests for cyanogen chloride were negative. In several of the tests aeration was continued for several hours longer than was necessary to effect this condition. Aeration greatly reduced the toxicity of all the chlorinated effluents tested, but in no case was toxicity entirely removed. Residual toxicity appeared to be most marked with effluents of high chlorine demand, and the evidence suggested that such effluents contained substances, other than thiocyanate, which reacted with chlorine to form a toxic compound. This compound differed in two ways from cyanogen chloride: (1) it was not removed by prolonged aeration, and (2) fish exposed to its action for sufficiently long to lose their balance did not recover when transferred to fresh water. It was found, over a prolonged period of investigation, that in all solutions in which cyanogen chloride was the toxic agent the fish recovered when transferred to fresh

the aeration was momentarily stopped, the bubblers were replaced by four similar bubblers and the current of air was restarted. On each occasion the quantity of cyanogen chloride in each of the bubblers was determined.

Results obtained in two experiments (Table 7) showed that most of the cyanogen chloride was displaced by the current of air and was recovered in the bubblers. During a prolonged period of aeration, however, about 20% of the cyanogen chloride was lost, possibly by hydrolysis. In the second experiment the pH value in the aerated bottle was 2.4 and in the bubblers 6.5-6.7; the temperature of the liquid in the bottle was 25° C. and that in the bubblers ranged from 4 to 6° C.; the rate of aeration was ¼ l. of air per litre of liquid per minute. In the first experiment the rate of aeration was 0.15 l. of air per litre of liquid per minute.

Table 6. *Effect of aeration on toxicity of chlorinated sewage effluents from three different sewage works*

Samples diluted with equal volumes of tap water before immersing fish

Chlorine demand of effluent (p.p.m.)	Amount of chlorine added (p.p.m.)	Diluted liquid in which fish were immersed			Content of dissolved oxygen during test (% of saturation value)	Average toxicity	Mean period of survival
		Period of aeration (hours)	pH value	Temperature (° C.)			
5-6	0	0	7.2	10.5	52-54	<0.07	> 24 hr.
	4	0	7.2	10.5	53-56	0.91	110 min.
	4	3½	7.2	10.5	—	<0.18	> 24 hr. for 7 out of 10 fish
12-13	0	0	7.1	10	44-48	<0.3	> 6½ hr.
	10	0	7.0	10	46	18	5.7 min.
	10	19	7.8	9	77	0.7	145 min.
22-23	0	0	7.2	8.5	41-44	<0.3	> 6 hr.
	10	0	7.1	8.5	51	7.3	14 min.
	10	17	7.6	5.5	72	0.7	143 min.

water. Seven effluents were subjected to test to discover the effect of aeration. Representative results are shown in Table 6.

Displacement of cyanogen chloride during aeration

Laboratory experiments proved that aeration resulted mainly in physical displacement of the cyanogen chloride from solution. A solution of cyanogen chloride, obtained by treating a solution of ammonium thiocyanate with excess chlorine and discharging the excess with arsenious acid, was aerated in a bottle fitted with a sintered glass diffuser. Issuing gases were passed through a train of four bubblers (three of which contained distilled water and one of which contained benzidine-pyridine reagent) immersed in a mixture of ice and water. When the benzidine-pyridine reagent developed an appreciable colour due to absorption of cyanogen chloride,

Table 7. *Displacement of cyanogen chloride from solution by aeration. Quantity recovered in bubblers*

Experiment	Period of aeration (hr.)	Quantity of cyanogen chloride (mg. CNCl)		
		Retained in bottle	Recovered in bubblers and tube	Total in apparatus
1	0	0.36	—	0.36
	1	0.26	0.10	0.36
	2	0.18	0.15	0.33
2	0	1.67	—	1.67
	1	1.17	0.54	1.71
	2	0.78	0.87	1.65
	3	0.50	1.02	1.52
	4	0.33	1.11	1.44
	5	0.22	1.18	1.40
	6	0.14	1.20	1.34

EFFECT OF TREATMENT WITH
THIOSULPHATE ON TOXICITY OF
SOLUTIONS CONTAINING CYANOGEN
CHLORIDE

Chlorinated solutions, in which the toxicity is due to free chlorine, may be rendered non-toxic by treatment with sufficient thiosulphate to discharge residual chlorine. Preliminary experiments with chlorinated sewage effluents, which were toxic when treated with doses of chlorine below the demand, showed that the toxicity was not appreciably affected by the addition of small amounts of sodium thiosulphate equivalent to the whole of the chlorine added.

Previous workers have found that, *in vivo*, thiosulphate exerts a protective action against both cyanide and cyanogen chlorides. Thus Lang (1895), quoted by Heymans & Masoin, 1896-7) showed that injection of animals with sodium thiosulphate protected them against lethal doses of potassium cyanide. Hunt (1904) found that mice were similarly protected by thiosulphate against a number of cyanogen compounds. Heymans & Masoin (1896-7) concluded, as a result of a series of experiments with rabbits, that thiosulphate exerted a preventive action against cyanide subsequently administered, but had no power to counteract the poisoning once the symptoms had begun. They suggested that thiosulphate reacted with cyanide in the animal body to form thiocyanate, which was non-toxic. Reed (1920b) in experiments with mice, dogs and cats, found that previous injection with thiosulphate afforded similar protection against subsequent exposure to, or injection with, cyanogen chloride. In view of these observations a further investigation was made.

Toxicity tests with fish showed that previous immersion for a period of 5 hr. in a 1% solution of sodium thiosulphate did not protect the fish against subsequent exposure to a solution of cyanogen chloride. Neither was the toxicity appreciably affected by addition of small quantities of thiosulphate to the solution in which the fish were immersed. On the other hand, relatively large quantities reduced the toxicity considerably and, if sufficiently large, gave complete protection. For example, addition to a chlorinated solution of thiocyanate (3 p.p.m. KCNS, 5 p.p.m. Cl, temperature 17° C.) of 500 p.p.m. sodium thiosulphate reduced the toxicity from 10.3 to 5.8, and addition of 0.5% rendered the solution non-toxic.

That reaction between cyanogen chloride and thiosulphate does take place was shown by adding different quantities of thiosulphate to a chlorinated solution of thiocyanate, and determining the concentration of cyanogen chloride in each mixture after standing for 5 min. The results, given in

Table 8, indicate that cyanogen chloride is destroyed by a large excess* of thiosulphate.

Table 8. *Effect of addition of sodium thiosulphate on concentration of cyanogen chloride in a chlorinated solution of thiocyanate*

Concentration of added thiosulphate (p.p.m. Na ₂ S ₂ O ₃)	5 p.p.m. chlorine added to a solution containing 3 p.p.m. KCNS in tap water			
	Exp. I (solution in tap water)		Exp. II (solution in distilled water)	
	p.p.m. CNCl	pH value	p.p.m. CNCl	pH value
Nil	0.93	7.2	0.50	—
5	0.89	7.2	0.47	3.7
50	0.87	7.2	0.46	3.6
500	0.64	7.2	0.32	3.7
5000	0.07	7.3	0.02	3.9
10000	Nil	7.2	Nil	4.2

RELATION BETWEEN CONCENTRATION OF
CYANOGEN CHLORIDE AND TOXICITY

In view of the effect of the different factors discussed above on the quantity of cyanogen chloride formed and on the stability of its solutions, considerable caution had to be exercised in assessing the effect of concentration on toxicity.

Preliminary tests showed that, if a relatively strong solution of cyanogen chloride was prepared by chlorinating a solution of potassium thiocyanate in a carboy, a portion of the liquid could be transferred to a bath of water to give the concentration required for a toxicity test without incurring appreciable loss in the course of transfer. The length of time for which solutions of cyanogen chloride in tap water at different pH values are stable in a bath is shown by the results in Table 9. Each bath contained 160 l. of a solution of potassium thiocyanate (4 p.p.m. CNS in tap water) to which 8 p.p.m. chlorine were added, the pH value of the tap water having been adjusted by addition of suitable quantities of sulphuric acid. It was concluded that during tests with fish lasting for less than 3 hr. the amount of cyanogen chloride lost from the solution would probably not be appreciable.

The relation between concentration and toxicity was therefore investigated as follows: A strong solution of cyanogen chloride was prepared by adding to 40 l. of a solution of potassium thiocyanate (15 p.p.m. KCNS in tap water) in a carboy, sufficient

* Although thiosulphate of 'AnalaR' grade was used, the relatively large amounts required suggested that the effect might possibly have been due to presence of traces of an impurity which reacted readily with cyanogen chloride. Investigation showed that the maximum amounts of sulphide or sulphite which might have been present could not have accounted for the effects observed.

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Table 9. *Stability of solutions of cyanogen chlorine in open baths*

Period of exposure (hr.)	Concentration of cyanogen chloride (p.p.m. CNCl)							
	Exp. I				Exp. II			
	Bath 1, pH 6.0	Bath 2, pH 6.5	Bath 3, pH 7.0	Bath 4, pH 7.5	Bath 1, pH 6.0	Bath 2, pH 6.5	Bath 3, pH 7.0	Bath 4, pH 7.5
0	0.92	1.06	1.11	0.92	0.90	0.95	0.93	1.15
1	0.99	1.06	1.09	0.85	0.92	0.95	0.92	1.13
2	0.95	1.13	1.00	0.81	0.90	0.99	0.95	1.09
3	0.91	1.18	1.06	0.81	—	—	—	—
19	—	—	—	—	0.73	0.65	0.69	0.78
20	1.00	1.00	0.85	0.65	—	—	—	—
67	—	—	—	—	0.38	0.32	0.27	0.30

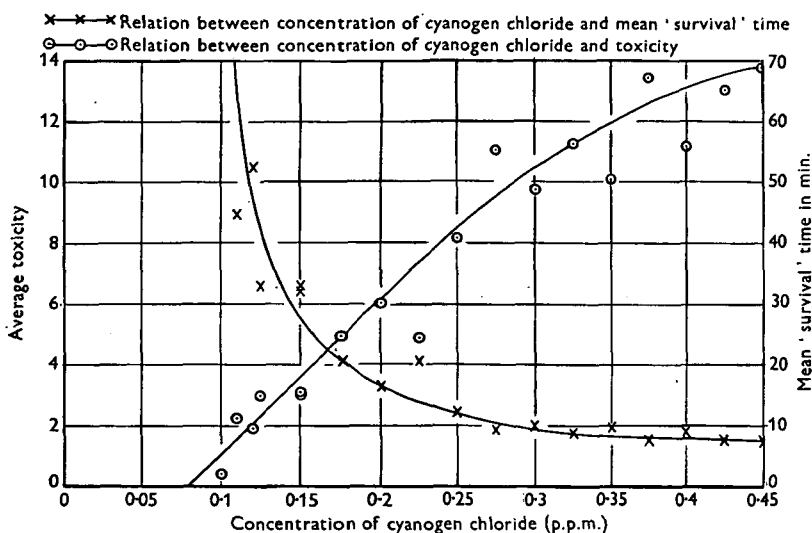


Fig. 3. Toxicity to fish of a solution containing different concentrations of cyanogen chloride.

of a strong solution of chlorine to give a concentration of 15 p.p.m. Cl. After thorough mixing, the concentration of cyanogen chloride was determined. Sufficient of the solution was transferred by means of a graduated vessel to quantities of 160 l. of tap water in a series of baths to give the concentrations required for the tests. Results are expressed graphically in Fig. 3. The temperature of the solutions in different tests ranged from 17 to 20° C. It appears that for cyanogen chloride the theoretical 'threshold of toxicity' as defined by Powers (1917, quoted by Gersdorff, 1930), is under the conditions of these tests, about 0.08 p.p.m. CNCl.

CONCLUSIONS

Effluents from certain sewage works were found to be highly toxic to fish when treated with doses of chlorine much smaller than were required to give residual chlorine detectable by the ortho-tolidine

test. These effluents were derived from sewage to which gas liquor had been admitted. The compound responsible for toxicity was cyanogen chloride, formed by interaction of the chlorine with thiocyanate which had originated in the gas liquor and had survived the process of treatment at the sewage works.

Fish exposed to the action of cyanogen chloride sufficiently long to lose their balance recovered after transfer to fresh water.

The quantity of cyanogen chloride formed when a solution of thiocyanate was treated with a quantity of chlorine lower than the demand was found to depend not only on the dose of chlorine, but also on the relative proportions of thiocyanate and chlorine. When excess of chlorine was added, interaction between cyanogen chloride and chlorine resulted in a loss of cyanogen chloride on standing which was more rapid the higher the pH value. The presence in the solution being chlorinated of substances which

react readily with chlorine, such as sulphide, cystine, cysteine, and to a less extent peptone and catechol, considerably reduced the proportion of chlorine which reacted with thiocyanate to form cyanogen chloride.

Aeration of solutions containing cyanogen chloride resulted in physical displacement of the cyanogen chloride by the current of air, toxicity progressively diminished and, if the aeration was sufficiently prolonged, was eliminated. Aeration greatly reduced, but did not entirely remove, the toxicity of chlorinated effluents derived from sewage to which gas liquor had been admitted.

The toxicity of a solution of cyanogen chloride was not appreciably affected by small doses, but was greatly reduced and even eliminated by com-

paratively large doses, of thiosulphate. Previous immersion for several hours in a solution of thiosulphate did not protect fish against subsequent exposure to cyanogen chloride.

Curves showing the relation between concentration and toxicity indicated that under the condition of test (temperature 17–22° C., dissolved oxygen 72–87 % of saturation value) the theoretical threshold of toxicity for cyanogen chloride is about 0.08 p.p.m.

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