

# Health Effects of Cyanogen Chloride and Methods of Controlling its Percentages in Water

REEM N. DABAIBEH

Faculty of Engineering Technologie, Al-Balqa Applied University, Amman, 11134,

E-Mail: reem.dabaibeh@bau.edu.jo

## *Abstract*

*Cyanogen chloride is a toxic chemical compound with the formula  $\text{NCCl}$ . This linear, triatomic pseudo-halogen is an easily condensed colorless gas. More commonly encountered in the laboratory is the related compound cyanogen bromide, a room-temperature solid that is widely used in biochemical analysis and preparation. This paper presents a description for Cyanogen chloride formation and creations, its effects on animals and human bodies, and finally methods to control its percentages in drinking water under the acceptable levels. The method of controlling its concentration in water is summarized by using suitable chemical additives and noting the time for settlement and then removed from the samples. A comparison between 4 additives in removing Cyanogen chloride is performed for the same sample of water. It is found that as the concentration of  $\text{NCCl}$  increases the  $\text{pOH}$  of the sample increases while  $\text{pH}$  decreases. Also, for the four additives  $\text{NH}_4^+$ ,  $\text{CN}^-$ ,  $\text{Cl}_2$  and  $\text{SO}_2$  for the water samples, it was found that  $\text{SO}_2$  is the most efficient chemical additive in removing  $\text{CNCl}$  since it needs the lowest time of removing  $\text{CNCl}$ .*

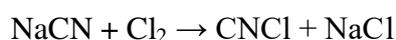
*Keywords: Cyanogen chloride, water, analytical chemistry, additives, hydrolyzation.*

## **Introduction**

Cyanogen chloride is a toxic chemical compound, if it is found in water it will harm both animals and human. It was found that a degree of a  $100 \text{ mg/m}^3$  is fatal to cats at intervals of time of eighteen min, also, a  $120 \text{ mg/m}^3$  for six hours was fatal to dogs,

while  $5 \text{ mg/m}^3$  for two minutes was fatal to goats. About human, a degree of  $2.5 \text{ mg/m}^3$  causes irritation. Gas chloride was used in wars within the 1<sup>st</sup> war. A degree of a  $120 \text{ mg/m}^3$  was deadly [14-17]. So it is very important to remove or decrease high concentrations of Cyanogen chloride from water, which is the main purpose of this paper, but firstly, we should know more about Cyanogen chloride chemical properties, its reactions, its resources and its effects on environment. Different samples of water were collected from different locations of Amman-Jordan, and then analyzed as shown in Appendix A.

Cyanogen chloride is a chemical compound with the chemical composition given as ClCN. Carbon and halogen are joined by one bond, and carbon and chloride gas by a triple bond. It's a linear molecule, as the other connected gas halides (NCF, NCB<sub>r</sub>, and NCI). Cyanogen chloride is created by the chemical reaction of cyanide with halogen. This reaction issue via the intermediate gas ((CN)<sub>2</sub>)[1].



The compound is divided in the presence of acid to the heterocycle called cyanuric chloride. Cyanogen chloride is slowly hydrolyzed by water to release cyanate and chloride ions at neutral pH



### **Cyanogen Chloride Applications in synthesis and Weapons**

Cyanogen chloride is considered as the base of to the sulfonyl cyanides [2] and chlorosulfonyl iso-cyanate, and as a helpful chemical agent in organic synthesis [3]. Chloride gas could be an extremely deadly blood agent, and was once projected to be used in chemical operations. It causes immediate injury upon contact with the eyes or metabolic process organs. Symptoms of exposure might embody sleepiness, symptom (runny nose), raw throat, coughing, confusion, nausea, vomiting, and edema, loss of consciousness, convulsions, paralysis, and death [4]. It's particularly dangerous as a

result of it's capable of penetrating the filters in gas masks, per U.S. analysts. CK is unstable because of polymerization, generally with explosive violence [5].

Cyanogen chloride is listed in schedule three of the Chemical Weapons Convention: all production should be reportable to the international organization [6]. By 1945, the U.S. Army's war Service developed war rockets meant for the new M9 and M9A1 Bazookas. Associate in Nursing M26 Gas Rocket was custom-made to fire gas chloride-filled warheads for these rocket launchers [7]. Because it was capable of penetrating the protecting filter barriers in some gas masks [8]. It had been seen as an efficient agent against Japanese forces (particularly those concealment in caves or bunkers) as a result of their normal issue gas masks lacked the barriers that will offer protection against gas chloride.[7][9][10]. The North American country more the weapon to its arsenal however the CK rocket was ne'er deployed or issued to combat personnel.

The reaction of gas chloride is that the rate determinant and most significant step within the chlorination method for the destruction of cyanide in industrial effluents, and a few studies of the processes concerned are created [8-10]. A number of the sooner work has been recurrent to determine a basis for chemical change investigations, to increase the variation of conditions examined and to penetrate additional deeply into the reaction mechanisms and their dominant parameters. The reaction is sometimes developed as:



Upon this reaction the acid can be ionized according to the pH of the solution. The order with relevance hydroxide ion was initial examined by polishing off a series of hydrolyses at constant temperature over a variety of fastened radical concentrations maintained by mineral buffers, the pH being endlessly monitored to verify constancy. A closed system is important to stop loss of gas chloride by volatilization.

### **Cyanogen chloride Percentages in drinking water**

Cyanogen chloride is employed in tear gas, in chemical gases, and as a chemical agent within the synthesis of alternative compounds [11] gas chloride is also fashioned as a by-product of chloramination or chlorination of water. It's additionally fashioned by the chlorination of cyanide particle in raw water gas chloride is unstable within the presence of free chlorine; for instance, its halflife in chlorinated water containing a free atomic number 17 concentration of 0.5 mg/l was about one hour [12]. At high pH, it's hydrolyzed to unleash cyanide ions [13]. Its calculable Henry's law constant of 2.48 kPa.m<sup>3</sup>/mol suggests a big potential for volatilization [14].

### **Effects on Laboratory Animals and humans**

Estimates of inhalation LC50s vary from a hundred mg/m<sup>3</sup> in cats to 7536 mg/m<sup>3</sup> in rabbits [15]. In different morbidity tests, a degree of a hundred mg/m<sup>3</sup> was fatal to cats at intervals eighteen min, a hundred and twenty mg/m<sup>3</sup> for six h was fatal to dogs, five mg/m<sup>3</sup> for two min was fatal to goats, and a body covering dose of twenty mg/kg of weight was fatal to rabbits [16]. An LD50 of half-dozen mg/kg of weight was rumored in rats following oral administration [17]. Virulent signs enclosed irritation of the tract, hemorrhagic exudate of the bronchi and trachea, and respiratory organ swelling. On inhalation, a degree of 2.5 mg/m<sup>3</sup> causes irritation. Gas chloride was used as a war gas within the 1st war. A degree of a hundred and twenty mg/m<sup>3</sup> was deadly [14].

Ogbuagu et al. (2019) mentioned the toxicity of CNCl, and declared that the management of cyanide toxicity involves air manner management, ventilation and 100 percent element, crystalloids and vasoconstrictor, as required for high blood pressure. conjointly carbonate/bicarbonate of {soda/sodium hydrogen carbonate/baking soda/saleratus/bicarbonate/hydrogen carbonate} is titrated per blood gas (ABG) and body fluid bicarbonate level; clean the patient with removal of consumer goods /skin flushing and/or atomic number 6 (1g/kg), as acceptable in alert patients or once

endotracheal canalization in Associate in Nursing unconscious patient through a nasogastric tube once lavage. Administer hydroxo-cobalamin or fixer and nitrite if the identification is powerfully suspected. Roberts and Liu (2019) studied the solubilities and also the first-order reaction rate of HNCO species for a spread of solutions employing a bubble flow reactor methodology with total reactive element (Nr) detection. The binary compound solubility of HNCO was measured as an operate of hydrogen ion concentration Associate in Nursingd had an intrinsic Henry's law solubility. The temperature dependence of HNCO solubility was terribly just like different little element containing compounds, like HCN, acetonitrile (CH<sub>3</sub>CN), and nitro-methane, and also the dependence on salt concentration exhibited the "salting out" development. the speed constant of reaction of HNCO with 0.45 M NHC+4 , as NH<sub>4</sub>Cl, was measured at pH D3 and located to be  $1.2 \times 10^{-3}/\text{m.s.}$ , quicker than the speed that might be calculable from rate measurements at a lot of higher pHs. The percentages of Cl-1 molecules and other elements are shown in Table A, Appendix A.

## Results and Discussion

### Determining the cyanogen chloride concentration spectrophotometrically

Initial concentrations of gas chloride were of the order of ten - four ~or half dozen p.p.m. glorious one-dimensional plots of the power of the gas chloride concentration against the clock were obtained, showing that the reaction is exactly initial order with regard to gas chloride, and first-order rate constants were calculated from the slope of those plots for every pH scale worth [19]. The connection between these pseudo first-order rate constants,  $k'$ , and pH scale over the range of 7.3 to 11.2 is set. At higher group concentrations the order closely approaches nine.2 with unity power, 0.96 at pOH = three to four, however at lower group concentrations the order of the power drops, to 0.80 at pOH = half dozen. Table one shows all values of concentrations and values of pOH and pH scale, the transition is sleek this implies that there are a unit 2 occurring

processes: direct reaction with anion that preponderates at high pH scale values, and reaction with water that will increase in importance because the pH scale falls the consequences of diverse additives are examined with a read each to help mechanistic interpretation and to get attainable accelerators or catalysts. Metal ions like iron (II) and mercury (II) area unit while not impact, however nickel (II) at a level of 10 p.p.m. magnified the speed by concerning ten per cent. Phosphate, which has been reportable to turn the chemical reaction has no impact, nor have chloride, salt, carbonate or hydrogen carbonate [8].

Table 1. Relation between pH, and pOH and HOCN concentrations

<b>K[Concentration of HOCN]</b>	<b>Log K</b>	<b>pOH (= pK<sub>w</sub> - pH), pK<sub>w</sub>=14 at 25 °C</b>	<b>pH</b>
19.9	1.298853076	2.5	11.5
13.2	1.120573931	3	11
9.2	0.963787827	3.5	10.5
9	0.954242509	4	10
8	0.903089987	5	9
7.5	0.875061263	5.5	8.5
7.3	0.86332286	6	8
7	0.84509804	6.7	7.3

Figure 1 shows the relation between PH and CNOH concentrations, it can be noticed that as the concentrations of CNOH increases the value of PH increases.

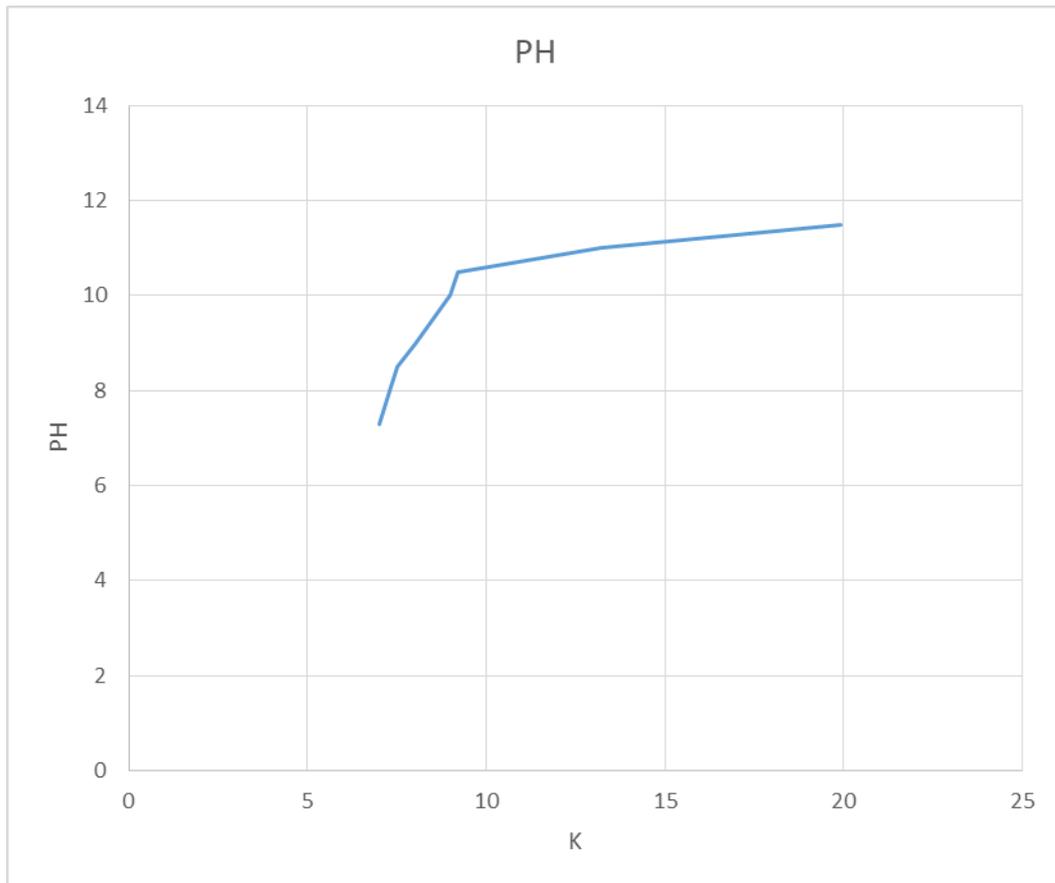


Figure 1. Relation between PH and the concentration of CNOH

### Control methods and technical achievability

There is little information available on the removal of cyanogen chloride, and information on its stability in the distribution system is ambiguous (i.e. its concentration can increase or decrease). However, it is known to be unstable in chlorinated water (Na & Olson, 2004). Cyanogen chloride can be removed by chemical reduction agents such as sodium sulfite, sodium disulfite and sodium thiosulfate [20].

The fast impact of another species on the speed of destruction of gas chloride at pH= 10.1 is shown in Table 2. Initial concentrations of each additive and gas chloride were 10.4 M; the plot shows the speed of reaction within the absence of any additives; the ordinate is  $(-\log_{10}A_t/A_0)$ , wherever  $A_t$  is that the absorbance at time t, and  $A_0$ , is that the absorbance at time zero, and is proportional to  $[NCCI]$  concentration. Ammonia (added as ammonia ion) shows the littlest effect; this is often undue to accelerated

reaction however to improvement of the speed of removal of gas chloride by a subsidiary chemical process to create cyanamide. A potential rationalization for the impact of cyanide may be the formation of a one: 1 adduct of cyanide and gas chloride, as according by Pungor [21]; it's not unlikely that Associate in Nursing adduct of this nature would change sooner than gas chloride. sulfur dioxide bleached the coloring material fashioned within the determination of gas chloride , however this interference may be quantitatively eliminated by precipitation and natural process of metal sulphite gas chloride disappears chop-chop within the presence of sulfur dioxide, the half-life at hydrogen ion concentration = 10.1 being four minutes. Determination of sulfur dioxide before and once the reaction showed that sulfur dioxide is consumed in one: one stoichiometry with the gas chloride. If the sulfur dioxide acts as a reductant, then the plain product would be cyanide, however tests by 3 freelance strategies for cyanide were negative, showing that 1% at the foremost, and doubtless none, of the gas chloride was born-again into cyanide.

Table 2. Time needed to remove CNCl with different additives

[CNCl]	t <sub>A</sub> (original sample w.o Additives)(min)	t <sub>B</sub> sample with NH <sub>4</sub> <sup>+</sup>	t <sub>C</sub> sample with CN <sup>-1</sup>	t <sub>D</sub> sample with Cl <sub>2</sub>	t <sub>E</sub> sample with SO <sub>2</sub>
1	0	0	0	0	0
1.58	12	10	9	5	4
2.51	22	21	20	8	6
3.16	30	26	23	9	7

Figure 1 shows the comparison between the four additives in removing CNCl with different concentrations of the CNCl.

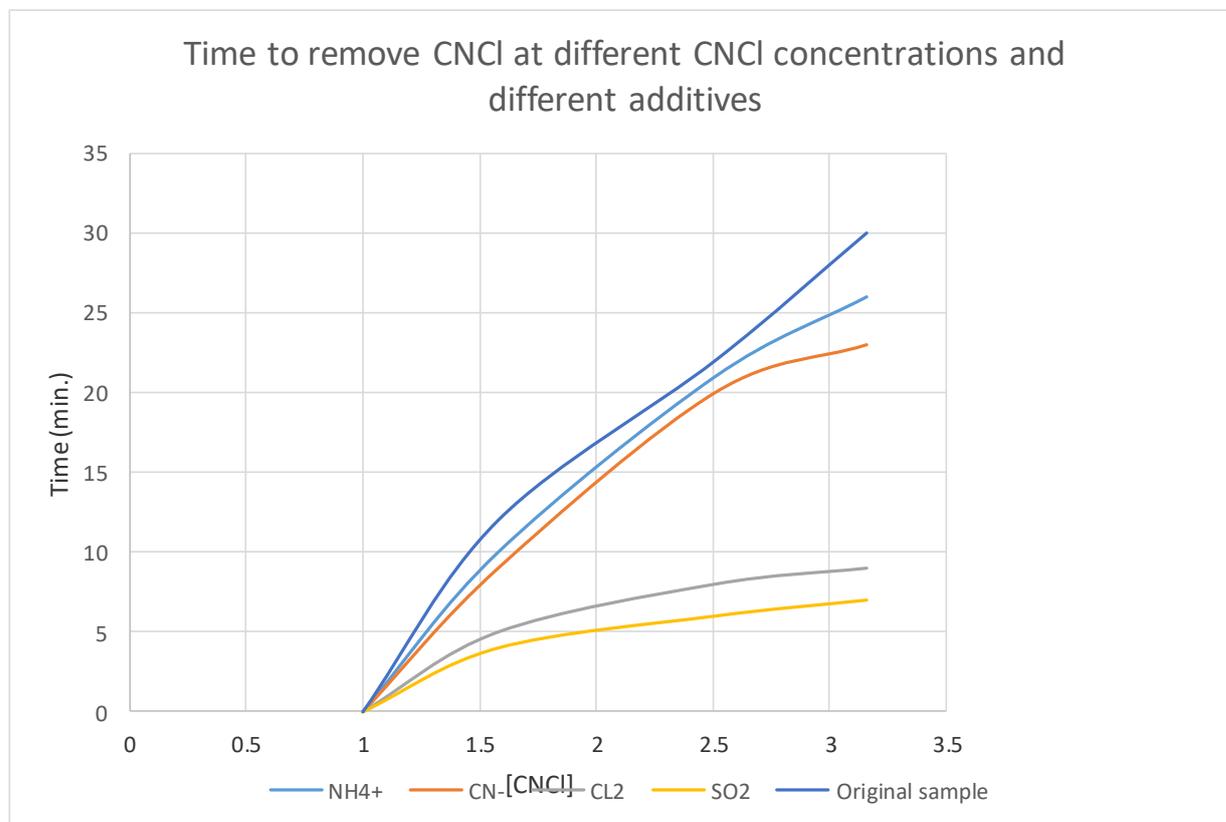


Figure 1. Time of removing CNCl with different additives

Catalysis by chlorine species poses substantial problems. In early experiments, the chlorine was added in the form of an aliquot of sodium hypochlorite solution, prepared by passing excess of chlorine into sodium hydroxide solutions: drastically varying hydrolysis rates were obtained. With freshly prepared hypochlorite the cyanogen chloride was destroyed extremely rapidly, but, as the hypochlorite solution aged, its catalytic power decreased until, after the lapse of 2 weeks, addition of an aliquot containing the same available chlorine content as the original fresh solution produced no acceleration of hydrolysis at all. The analysis shown in Table 2 is one of the faster hydrolyses at this pH, the half-life being about 5 minutes compared with 17 minutes for the control. At pH = 9.2 and with a fairly fresh hypochlorite solution a half-life of 1.5

minutes, compared with 90 minutes for the control, was obtained. In none of these reactions did analysis before and after indicate any consumption of chlorine. It was clearly necessary to discover which of the species present in such a hypochlorite solution was responsible for the catalysis. Additions of perchlorate, chlorate, chloride and chlorine dioxide produced no catalysis. Chlorite gave a rate constant 15 per cent higher than the control, but this is a relatively trifling effect and, furthermore, the amount of chlorite in the hypochlorite solution will be small. This left three species: molecular chlorine, hypochlorous acid and hypochlorite ion: but at pH= 10 little chlorine or unionized hypochlorous acid could be expected to remain, although all three will be in equilibrium in the presence of chloride. Chlorine (and chloride which has no catalytic effect) was removed from the stock hypochlorite by addition of mercury(II) oxide, and the resultant solution produced no catalysis in the pH range 9 to 10, but addition of fresh chlorine water to the reaction mixture again produced a great acceleration of hydrolysis. It is reasonable to conclude that molecular chlorine is the active catalyst, yet it is difficult to accept that any considerable amount of free chlorine remains unhydrolysed at pH=9 to 10. However, the catalysis becomes more marked as the pH decreases, which supports the conclusion; so does the loss of catalytic activity as the hypochlorite ages with gradual removal of excess of chlorine from the solution. If the pH is lowered too far, chlorine will react directly with the cyanate produced in the hydrolysis, and this will consume chlorine and mask its effect on the hydrolysis.

### Conclusions

In this paper the main idea was to use analytical chemistry principles in removing CNCl using some suitable agents and additives, the time of removal is very important and a comparison between different additives and cases is performed. Because of high toxicity of CNCl removing it or decreasing its levels to acceptable percentages is crucial, it is found that  $\text{NH}_4^+$ ,  $\text{CN}^-$ ,  $\text{Cl}_2$  and  $\text{SO}_2$  additives are efficient in removing

CNCl, also it was found that SO<sub>2</sub> is the most efficient chemical additive in removing CNCl since it needs the lowest time to do so.

### References

- [1] Coleman, G. H.; Leeper, R. W.; Schulze, C. C. (1946). "Cyanogen Chloride". *Inorganic Syntheses*. *Inorganic Syntheses*. 2. pp. 90–94. doi:10.1002/9780470132333.ch25. ISBN 9780470132333.
- [2] Vrijland, M. S. A. (1977). "Sulfonyl Cyanides: Methanesulfonyl Cyanide" (PDF). *Organic Syntheses*. 57: 88.; Collective Volume, 6, p. 727
- [3] Graf, R. (1966). "Chlorosulfonyl Isocyanate" (PDF). *Organic Syntheses*. 46: 23.; Collective Volume, 5, p. 226
- [4] "CYANOGEN CHLORIDE (CK)". The Emergency Response Safety and Health Database. NIOSH.
- [5] FM 3-8 Chemical Reference Handbook. US Army. 1967. "Schedule 3". [www.opcw.org](http://www.opcw.org). Retrieved 16 March 2018.
- [6] Smart, Jeffrey (1997), "2", *History of Chemical and Biological Warfare: An American Perspective*, Aberdeen, MD, USA: Army Chemical and Biological Defense Command, p. 32. [https://www.cdc.gov/niosh/ershdb/EmergencyResponseCard\\_29750039.html](https://www.cdc.gov/niosh/ershdb/EmergencyResponseCard_29750039.html)
- "Characteristics and Employment of Ground Chemical Munitions", *Field Manual 3-5*, Washington, DC: War Department, 1946, pp. 108–19.
- [7] Skates, John R (2000), *The Invasion of Japan: Alternative to the Bomb*, University of South Carolina Press, pp. 93–96, ISBN 978-1-57003-354-4.
- [8] Price, C. C., Larson, T. E., Beck, K. M., Harrington, F. C., Smith, L. C., and Stephanoff, I., J .
- [9] Eden, G. E., and Wheatland, A. B., *J. SOC. Chem. Ind.*, 1950, 69, 166.
- [10] Eden, G. E., Harnpson, B. L., and Wheatland, A. B., *Ibid.*, 1950, 69, 244.

- [11] Hawley GG (1981) The condensed chemical dictionary, 10th ed. New York, NY, Van Nostrand.
- [12] Na C, Olson TM (2004) Stability of cyanogen chloride in the presence of free chlorine and monochloramine. *Environmental Science and Technology*, 38(22): 6037–6043.
- [13] Xie Y, Reckhow DA (1992) Stability of cyanogen chloride in the presence of sulphite and chlorine. In: *Proceedings of the American Water Works Association Water Quality Technology Conference*, Toronto, Ontario, November. Denver, CO, American Water Works Association.
- [14] WHO. (2007). Cyanogen Chloride in Drinking-water. Geneva, Switzerland.
- [15] Tarken RL, Lewis RJ Sr, eds (1983) Registry of toxic effects of chemical substances, Vol. 2, 1981–82 ed. Cincinnati, OH, National Institute for Occupational Safety and Health (DHHS (NIOSH) Publication No. 83-107).
- [16] Flury F, Zernik F (1931). [Harmful gases.] Berlin, Springer [cited in NAS, 1977].
- [17] Leitch JL, Bauer VE (1945) Oral toxicity of cyanogen chloride in water to rats. Edgewood Arsenal, MD, United States Chemical Warfare Service (Medical Division Report No. 19) [cited in NAS, 1977].
- [18] NAS (1977) Drinking water and health. Washington, DC, National Academy of Sciences. NTP (1993) Sodium cyanide administered in drinking water to F344/N rats and B6C3F1 mice.
- [19] Bark, L. S., and Higson, H. G., *Talanta*, 1964, 11, 471 and 621.
- [20] Shang C et al. (2005) Kinetics of cyanogen chloride destruction by chemical reduction methods. *Water Research*, 39(10): 2114–2124.
- [21] Pungor, E., and Schulek, E., *Ann. Univ. Scient. Budapest Roland0 Eotvos Nomiuzatae, Sec. Chim., Anzer. Chew. SOC.*, 1947, 69, 1640. 1960, 2, 99.
- [22] Roberts J.M. and Liu Y. (2019). Solubility and solution-phase chemistry of

isocyanic acid, methyl isocyanate, and cyanogen halides. *Atmos. Chem. Phys.*, 19, 4419–4437, 2019.

[23] Emmanuel O. Ogbuagu, Augustine I. Airaodion, Victor N. Okoroukwu, Uloaku Ogbuagu and John A. Ekenjoku (2019). Cyanide Toxicity: The Good, the Bad and the Ugly. *International Journal of Bio-Science and Bio-Technology*. Vol-11-Issue-9-September-2019.

### APPENDIX A.

TABLE A.

number	Na <sup>+</sup>	CN <sup>+</sup>	Cl <sup>-</sup>
1	151.775	5.85	166.615
2	151.775	6.84	166.615
3	151.775	3.87	149.9535
4	151.775	5.85	166.615
5	176.575	6.84	166.615
6	176.575	6.84	216.5995
7	151.775	6.84	183.2765
8	176.575	6.84	166.615
9	126.975	3.87	199.938
10	151.775	5.85	166.615
11	176.575	6.84	166.615
12	126.975	3.87	166.615
13	151.775	3.87	199.938
14	176.575	3.87	183.2765
15	151.775	6.84	199.938
16	126.975	4.86	166.651

17			
18	102.175	3.87	166.651
19	126.975	4.86	216.59995
20	176.575	5.85	199.938
21	126.975	3.87	149.9535
22	126.975	3.87	183.2765
23	151.775	4.86	166.615
24	151.775	3.87	199.938
25	353.15	3.87	216.6
26	300.575	4.86	166.615
27	176.575	3.87	166.615
28	176.575	4.86	216.6
29	126.975	4.86	199.938
30	126.975	3.87	199.938
31	126.975	3.87	199.938
32	151.775	4.86	199.938
33	176.575	3.87	166.615
34	176.575	5.85	233.261
35	226.175	3.87	199.938
36	151.775	3.87	216.6
37	126.975	3.87	166.615
38	151.775	3.87	166.615
39	176.575	3.87	199.938
40	151.775	3.87	199.938
41	201.375	2.88	166.615

42	126.975	5.85	199.938
43	102.175	3.87	199.938
44	176.575	3.87	183.277
45	126.975	3.87	183.277
46	151.775	3.87	199.938
47	102.175	3.87	133.292
48	176.575	5.85	199.938
49	201.375	3.87	166.615
50	102.175	3.87	216.6
51	176.575	3.87	166.615
52	474.175	3.87	233.261
53	126.975	3.87	233.261
54	102.175	1.89	133.292
55	151.775	4.86	216.6
56	176.575	4.86	216.6
57	201.375	6.84	183.277
58	151.775	6.84	183.277
59	226.175	7.83	216.6
60	126.975	6.84	216.6
61	300.575	7.83	216.6
62	126.975	6.84	216.6
63	151.775	7.83	216.6
64	126.975	5.85	166.615
65	102.175	6.84	183.277
66	102.175	6.84	199.938

67	201.375	4.86	166.615
68	77.375	4.86	149.954
69	102.715	3.87	183.277
70	77.375	1.89	199.938
71	226.175	2.88	149.954
72	126.975	4.86	133.292
73	151.775	4.86	183.277
74	102.175	3.87	199.938
75	474.175	5.85	199.938
76	102.175	3.87	166.615
77	176.575	3.87	183.277
78	126.975	3.83	183.277
79	126.975	3.87	199.938
80	102.175	5.85	183.277
81	176.575	6.84	183.277
82	167.575	6.84	199.938
83	226.175	5.85	183.277
84	176.175	4.86	216.6
85	126.975	3.87	199.938
86	151.775	5.85	199.938
87	176.575	6.84	233.261
88	151.775	4.86	199.938
89	201.375	4.86	183.277
90	201.375	3.87	133.292
91	250.975	6.84	233.261

92	176.575	6.84	199.938
93	176.575	3.87	199.938
94	126.975	4.86	166.615
95	353.15	4.86	216.6
96	151.775	5.85	216.6
97	226.175	4.86	216.6
98	226.175	6.84	199.938
99	151.775	4.86	183.277
100	126.975	6.84	199.938

