

*If nerve gases, incidentally or accidentally, contaminate public water supplies, the choice of methods for detection and decontamination will be crucial. Satisfactory methods for Sarin and Tabun are assured.*

## Nerve Gas in Public Water

By JOSEPH EPSTEIN, M.S.

WATER WORKS ENGINEERS, alert to the hazards of radiological, biological, and chemical warfare agents, must be concerned primarily, among the chemicals, with the nerve gases.

Many other chemical agents, because of intrinsically low toxicity if admitted orally, or because of rapid hydrolysis to relatively nontoxic products, are unlikely to appear in hazardous concentrations in a large volume of water. For example, consider hydrogen cyanide and cyanogen chloride, extremely toxic if inhaled. It would take 1 ton of either, uniformly dissolved in a 10-million-gallon reservoir, to reach a concentration of 25 p.p.m. This concentration in water is considered physiologically tolerable for the average man if consumed in normal quantities for a 1-week period (1).

More specifically, it would take 1.66 tons of either chemical to reach a 25 p.p.m. concentration in Baltimore's 16-million-gallon capacity Montebello Reservoir; 43,200 tons in Boston's 415-billion-gallon Quabbin Reservoir; 13,500 tons in New York City's 130-billion-gallon Ashokan Reservoir.

In reservoirs of less than 1-million-gallon capacity, the margin of safety owing to dilution is, of course, reduced.

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Even the highly toxic and vesicant lewisite, when viewed in this light, presents little hazard as a water contaminant. Lewisite hydrolyzes almost instantaneously in water to the mildly vesicant oxide. The toxicity of the oxide is apparently due to its trivalent arsenic content, which may be oxidized with ease by chlorine or other oxidizing agents to the less toxic pentavalent state. In fact, trivalent arsenic becomes converted to the pentavalent state upon standing in water.

If water containing lewisite is chlorinated according to standard procedures for bacterial purification and is used for not more than 1 week to avoid possible cumulative effects, as much as 20 p.p.m. of lewisite can be tolerated in drinking water (1). Calculation of the quantities of lewisite required to produce concentrations of physiological significance in the bodies of water mentioned previously quickly reveal the improbability that significant contamination of large bodies of water by lewisite will occur as a result of general chemical warfare.

By similar reasoning, the danger of contamination of fairly large bodies of water during general warfare by agents such as phosgene, chloropicrin, chlorine, chloroacetophenone, diphenyl-chlorarsine, and the like is not particularly great.

Although it may appear that the danger of contamination of water supplies by most chemical agents will be small, nevertheless, the possibility of contamination to dangerous levels is a contingency which requires knowledge of the

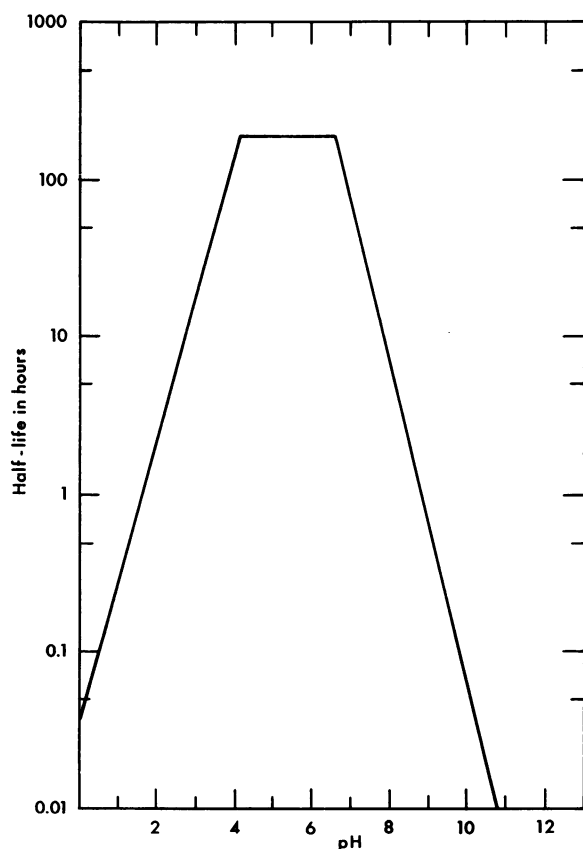


In the absence of large quantities of salts, the half-life ( $t_{1/2}$ ) of Sarin in water at 25° C. (77° F.) at constant pH in the pH range of 6.5 to 13.0 can be estimated from equation 2.

$$t_{1/2} = (5.4 \times 10^8) (10^{\text{pH}}) \quad [2]$$

Thus at pH 7, the half-life of Sarin in water at 77° F. is 54 hours; at pH 8, 5.4 hours; at pH 9, 0.54 hours, and so forth. Between pH 4.0 and 6.5, the hydrolysis rate of Sarin is at a minimum; its half-life in this range is approximately 175 hours. It is evident from equation 2 that above pH 6.5 the rate of hydrolysis increases 10 times per unit increase in pH. Below pH 4.0, the rate increases approximately 10 times per unit decrease in pH. At a given pH, the hydrolysis rate will vary by a factor of approximately 2 for each change of 10° C. The relationship between the half-life of Sarin in dilute aqueous solution at 25° C. and the pH of the water is shown graphically in figure 1.

**Figure 1. The relationship between the half-life of Sarin at 25° C. and the pH of water.**



The rates of hydrolysis which one might estimate from the use of equation 2 presupposes that the pH will remain constant during the time the Sarin is undergoing hydrolysis. For small concentrations of Sarin, that is, up to 5 p.p.m., in waters containing some buffer capacity, a constant pH will, in all probability, prevail. However, in the absence of significant buffer constituents in the water and at the higher concentrations of Sarin under discussion, the effect of the acidity produced by the hydrolysis may be very important to the stability of Sarin in water. In slightly alkaline water of low buffer capacity, the production of acids caused by a limited hydrolysis of Sarin can lower the pH to the range in which Sarin exhibits maximum stability. Thus, under certain conditions, the hydrolysis of Sarin may produce materials which retard subsequent hydrolysis. In effect, Sarin can stabilize itself.

The rate of hydrolysis of Sarin is accelerated by anions other than hydroxyl ions. The hydrolysis of Sarin is more rapid in the presence of such anions as trivalent phosphate or carbonate ions than might be predicted from the pH of the solution. On the other hand, the hydrolysis rate in the presence of rather large quantities of sulfate, chloride, or nitrate does not materially differ from the rate in water devoid of salts at the same pH. However, the quantities of the catalytic anions, for example, trivalent phosphate, needed to produce appreciable effects upon the hydrolysis rate, will not normally be encountered in water supplies.

Depending upon the pH of the water, some metal ions have strong catalytic effects upon the rate of hydrolysis of Sarin. Cupric, manganous, magnesium and calcium ions, to mention a few, are very effective catalysts, whereas sodium and potassium ions are virtually ineffective. Cupric and manganous salts are more effective in neutral or slightly acidic waters, whereas magnesium and calcium are more effective in alkaline waters.

At pH 6.5 and 25° C., where magnesium salts show practically no effect upon the hydrolysis rate of Sarin, the half-life of Sarin in water containing only 1 p.p.m. cupric ion is 2 hours as compared to a half-life of approximately 175 hours in the absence of the metallic ion. At pH 8.5 and 25° C., on the other hand, where

the cupric ion is ineffective (due presumably to its insolubility) the half-life of Sarin may be decreased from 1.7 hours to 0.5 hours by the addition of 100 p.p.m. magnesium ion. The proportional effectiveness of magnesium ion is greater at alkalinities above pH 8.5, but is less necessary because of the effectiveness of hydroxyl ion alone at a higher pH.

Thus, in waters of high magnesium or calcium ion content, or in waters containing even trace quantities of some heavy metal ions, the hydrolysis rate of Sarin may be much more rapid than that predicted by equation 2. In most natural waters, however, the quantity and type of dissolved solids are such that prediction of the hydrolysis rate may be made from equation 2, provided, of course, that the pH is maintained constant during the hydrolysis.

### Hydrolysis of Tabun

The hydrolysis of Tabun, like that of Sarin and DFP, is catalyzed by acids and bases, and bases are more effective than acids (10). Unlike Sarin and DFP, whose products of hydrolysis are independent of the catalyst used, Tabun is destroyed by attacks upon different parts of the molecule by acid and base, and the products of hydrolysis are different. In alkaline solution, the phosphorus to cyanide linkage is cleaved, resulting in the formation of a substituted phosphonate and sodium cyanide. In acid solution, the Tabun molecule is cleaved between the phosphorus and nitrogen. Both attacks result in destruction of the toxic properties of Tabun. (See below.)

In alkaline solution, the formation of acid tends to lower the pH of the solution; in slightly acid medium, the hydrolysis products are one acid and one base, and the pH remains constant.

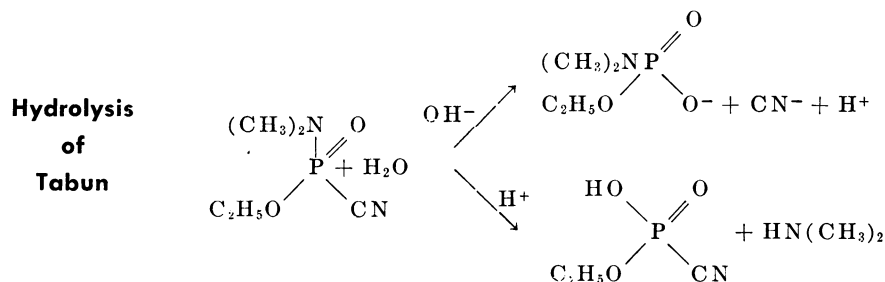
From the data of Larsson (10) and Holmstedt (11), it appears that the rate of hydrolysis of Tabun at the P—CN bond is for all practical purposes independent of the hydroxyl ion concentration between the pH range of 4.0 to approximately 8.5. The half-life of Tabun in this pH range at 20°–25° C. is 2–4 hours.

### Detection

Although a nerve gas attack would alert water works personnel, Sarin in water in concentrations of at least 35 p.p.m. is not detectable by odor or taste. Water containing concentrations of the hydrolysis products of Sarin as high as 200 p.p.m. was acceptable to rats. However, Tabun, which possesses a fruity odor, is detectable by smell in rather low concentrations. Furthermore, suspicion as to potability of water supply would be aroused by the odor of hydrocyanic acid which is formed by the hydrolysis of Tabun. Unlike Sarin, Tabun, through its released cyanide, will alter the "chlorine demand" of a water.

The uptake of chlorine in the reaction with Tabun will depend upon whether the chlorinating material is hypochlorite or chloramine. The chloramines will react only with cyanide ion which becomes available as a result of the hydrolysis of Tabun. The uptake of chlorine when hypochlorite is one of the reactants is also due to its reaction with cyanide, but apparently hypochlorite ion catalyzes the decomposition of Tabun to form cyanide so that, in effect, the uptake of chlorine is due to the Tabun as well as to the hydrolysis product.

If appreciable quantities of Sarin have hydrolyzed, and the contaminated water is of low buffer capacity, the low pH of the water, resulting from the acidic hydrolysis products,



may serve to warn that contamination has occurred. An abnormally high fluoride ion concentration in water should arouse the suspicion of the operator as to the potability of the water. However, since only 13 percent of the Sarin molecule after complete decomposition is fluoride ion, probably only when relatively high concentrations are in the water supply would the water be suspected because of fluoride ion concentrations.

The existence of fluoride ion and the low pH can only serve to point out that undecomposed Sarin may be present, not that it is. The same limitations apply to detection methods via the phosphorus moiety of the molecule.

It appears reasonable to conclude that dangerous concentrations of Sarin may remain undetected if only the nonspecific pH and chlorine demand tests and the tests for the fluoride ion and phosphorus are used. However, judicious choice of methods for estimation of fluoride ion concentrations and correlation of these tests with others such as pH and the alteration of the pH of the water observed at various time intervals may be helpful in the detection and estimation of Sarin.

Depending upon the method used for estimation of fluoride ion, one may obtain varying values for fluoride ion in waters containing both unhydrolyzed and hydrolyzed Sarin. If the methods recommended for fluoride in Standard Methods for the Examination of Water and Sewage, Ninth Edition, 1946, are used, then the total fluorine of the hydrolyzed and unhydrolyzed Sarin will be determined, since under the conditions of acidity required for this test, the bound fluorine in Sarin will be converted to ionic fluorine in a few minutes and thus will be determined as ionic fluorine. On the other hand, if fluoride ion is determined in neutral solution, and in the absence of hydrolytic catalysts, then only the fluoride ion present at the time of the test will be determined.

Both Sarin and Tabun in the presence of their hydrolysis products may be detected and estimated rapidly and in very low concentration by their reaction with benzidine or *o*-tolidine and alkaline peroxide solutions (12). By means of this reaction, the author and co-workers have been able to estimate quantitatively as little as 0.1 p.p.m. of Sarin in water, and the method

can probably be modified to increase the sensitivity.

The test has been adapted for field use and is included in two Chemical Corps water testing kits described in technical bulletins (13, 14).

The response of three small species of fish, the fathead minnow (*Pimephales promelas*), the green sunfish (*Lepomis cyanella*), and the goldfish (*Carassuis auratus*) to Sarin and Tabun are useful to the detection and, in some cases, estimation of small concentrations of nerve gases in water. The approximate LC<sub>50</sub> (concentration of agent required to kill 50 percent of the test animals) for exposures of 10, 15, and 20 minutes at 70°–75° F. for the three species are shown in table 1.

It is possible to decrease the concentration of the nerve gas necessary to produce an LC<sub>50</sub> by increasing the exposure time, but with increased exposure times, the effect of the pH of the water becomes very important due to hydrolysis rates of the agents. Thus, for a 24-hour period, the LC<sub>50</sub> of Sarin for the sunfish is 2 p.p.b. (.002 p.p.m.) if the water is kept at pH 6.5 (minimum hydrolysis), but 9.5 p.p.b. at pH 8.0. Similar data have been obtained with the other species for Sarin and Tabun.

The LC<sub>50</sub> values are increased if the temperature of the water is lowered. For a change of approximately 25° F., the LC<sub>50</sub> values for a 10-minute exposure should be multiplied by 6 to 8 for the three species.

**Table 1. Approximate LC<sub>50</sub> of Sarin and Tabun (p.p.m.) for fish at 70°–75° F., by various exposure times**

Fish species	Tabun			Sarin		
	Minutes of exposure			Minutes of exposure		
	10	15	20	10	15	20
Green sunfish.....	1.5	1.0	0.70	0.35	0.23	0.27
Fathead minnow.....	1.5	.9	.60	.63	.40	.3
Goldfish.....	2.4	1.7	1.3	.93	.6	.5

#### Decontamination

On the premise that decontamination procedures should reduce the level of Sarin and

Tabun concentration to 0.1 p.p.m., field tests have shown that coagulation with ammonium alum, followed by filtration through diatomite or sand filters is not an effective decontaminating procedure. A procedure involving the use of ferric chloride as coagulant and powdered limestone as coagulant aid, followed by filtration through diatomite filters is also ineffective. These materials are used in the Corps of Engineers Mobile Water Purification Unit (15).

Approximately 62 pounds of carbon would have to be added to each 1,000 gallons of water to reduce the concentration of 30 p.p.m. to 0.1 p.p.m. A smaller total dose of carbon can accomplish the same objective if a multiple treatment procedure is applied. However, the time involved and the multiplicity of operations make such a procedure objectionable.

Sarin in water is rapidly hydrolyzed by the catalytic action of strongly basic ion exchange resins, such as Amberlite IRA-400 and Nalcite SAR and strongly acidic cationic resins such as Dowex 50 and Amberlite IR-112. The anionic resins are more effective, and function not only as catalysts, but also remove the hydrolytic products. In doing so, however, the resins lose their available hydroxyl ion and ultimately their ability to catalyze the hydrolysis.

Furthermore, in water of appreciable dissolved solid content, the anions of the salts replace the hydroxyl groups in the resin (and cations, the hydrogen ions of the cationic resins) resulting in a decreased efficiency of the resin, since the efficiency is related to the number of available hydroxyl or hydrogen ions in the resin. The use of resins for large scale water decontamination is not economically feasible.

At least two feasible methods for the destruction of Tabun and Sarin in water supplies are available. Both methods are based upon an acceleration of the normal hydrolysis rate. The methods involve chlorination or alkalization.

Chlorine will not react with Sarin, but hypochlorite ion is a very effective catalyst for the hydrolysis of both Sarin and Tabun. Compounds containing combined chlorine, such as chloramine T, on the other hand, exert practically no catalytic action. Table 2 shows the half-life of Sarin in water at approximately

**Table 2. Half-life of Sarin ( $2 \times 10^{-4}$ M) in water in the presence of free chlorine**

Temperature	pH	p.p.m. Cl <sub>2</sub>	Half-life in minutes
77° F. -----	6	200	11
		25	13
		9	12
	8	4	15
		200	38
36°-37° F. -----	7	100	12
		100	3
	9	50	4

77° F. and 35° F. at various pH's and in the presence of free chlorine, added as high test hypochlorite (HTH).

The importance of pH in this reaction is seen from the figures shown in table 2 on experiments at 77° F. Only one-eighth of the chlorine concentration was required at pH 7.0 as was required at pH 6.0 to give approximately the same rate of destruction. Approximately one-third the concentration of chlorine was required at pH 8.0 to produce the same effect at pH 7.0, and so forth. It can also be seen by comparing the half-lives of Sarin in the presence of equal concentration of chlorine and at the same pH but at two different temperatures, for example, pH 6, that the rate of destruction is approximately doubled for each rise of 10° C.

Where time of treatment can be extended to several hours, much lower concentrations can be used to produce effective decontamination. For example, by maintaining the water at pH 8.0, addition of 5 p.p.m. chlorine will reduce the concentration of Sarin from 30 to 0.1 p.p.m. in approximately 3 hours. Figure 2 shows half-life of Sarin at 25° C. at pH ranges between 6 and 9 in the presence of different concentrations of free chlorine.

A dosage of chlorine to be added to a water supply may be calculated from the values given in figure 2, a knowledge of the concentration of Sarin in the water, the temperature and pH of the water. The action of hypochlorite may be completely inhibited, however, if amines or ammonium salts are present in the water because of the very rapid reaction of hypochlorite with the nitrogen compounds to form chloramines (16) which are catalytically inactive.

Chlorine as hypochlorite will destroy Tabun, and the cyanide produced upon hydrolysis of Tabun will consume the chlorine.

Satisfactory procedures for decontamination of Sarin have been developed, utilizing the catalytic properties of hypochlorite. In field trials, HTH was used as the source of hypochlorite and, because rapid decontamination was desired, 100 p.p.m. chlorine was used. Following decomposition, the hypochlorite concentration was reduced to less than 1 p.p.m. by treatment with activated carbon.

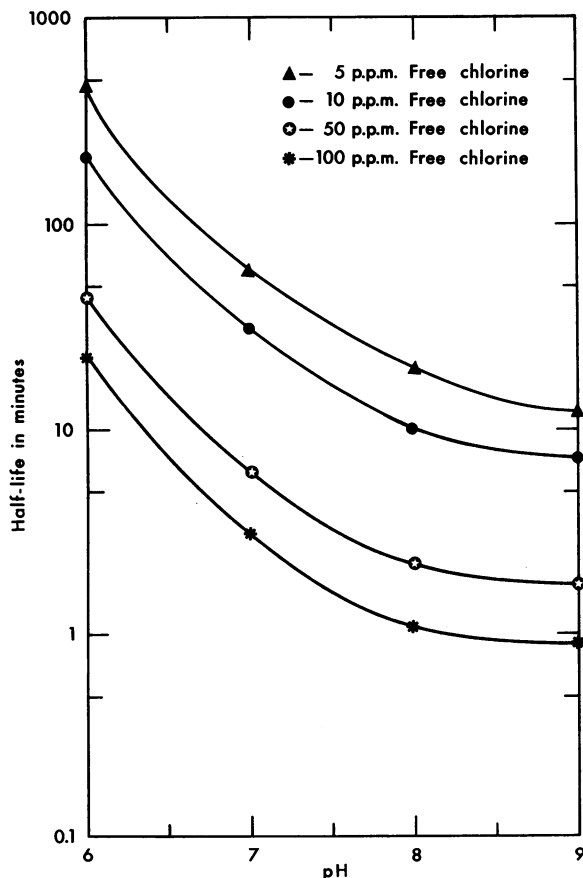
Another satisfactory procedure for decontamination proved by field trials is to raise the pH of water to approximately 10.0 with soda ash, slaked lime or magnesium hydroxide, allow the Sarin or Tabun to hydrolyze, and when tests indicate that the concentration of the nerve gas is 0.1 p.p.m. or less, use a coagulant such as ammonium alum or ferric chloride, filter and

chlorinate. The rate of hydrolysis is followed by the test methods described (14) and the quantity of alkaline material to be added is regulated by the rate of hydrolysis. The alum or ferric chloride function not only as coagulants but also to reduce the pH of the water to normal acidities. Water treated by either procedure is potable and palatable.

### Conclusion

From the preceding discussion, it appears reasonable to conclude that, in the event of general chemical warfare, the nerve gases Tabun and Sarin must be considered potential water contaminants because of the very small quantities of these agents required to produce toxic symptoms from ingestion. The hazard due to Tabun, however, is lessened somewhat because of its ease of detection in water by taste, odor, and chlorine demand test. Sarin presents a more difficult problem inasmuch as specific detection methods are necessary. Once detected, both Sarin and Tabun can be rapidly destroyed by simple decontamination procedures.

**Figure 2. The relationship between the half-life of Sarin at 25° C. and the pH of water for different concentrations of free chlorine.**



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## The Mayo Memorial

Forming the heart of what is virtually a complete medical center on the University of Minnesota campus is the recently completed Mayo Memorial. The university's School of Public Health occupies 2½ floors of the new building's 14-story tower section.

The Mayo Memorial, which was dedicated on October 21, 1954, is the fulfillment of an idea begun more than a decade ago. In 1939, shortly after Doctors Charles H. and William J. Mayo had died, the Governor of Minnesota appointed a Mayo Memorial Commission to propose an appropriate monument. After considering many projects, the commission agreed that a center for teaching and research as a building of the University of Minnesota Medical Center would be the most fitting memorial. During their lifetime, the Mayo brothers had devoted much time, interest, and aid to the work of this institution.

A Committee of Founders started the project on its way. Funds were raised by legislative appropriation, public subscription, and grants from public and private agencies.

Construction was started in 1951 and completed in the early autumn of 1954.

The new building brings together the facilities of the School of Public Health formerly scattered in several university buildings. On the 11th floor are laboratories, offices, and classrooms for work in environmental sanitation and epidemiology. The 12th floor houses facilities for biostatistics, health education, and the course in hospital administration. The public health nursing unit, offices for the non-professional health and hygiene courses, and other offices are located on the 13th floor, which the school shares with the medical school administration. Conference and reading rooms are provided on each of the three floors used by the School of Public Health.

In addition to the tower section, the Mayo Memorial has three 6-story wings that connect with existing hospital and medical school buildings. The building has facilities for education, research, and service in connection with various departments of the medical school.