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REPORT OF INVESTIGATIONS

BUREAU OF MINES - - - DEPARTMENT OF THE INTERIOR

CARBON TETRACHLORIDE EXTINGUISHER ON ELECTRIC FIRES

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Introduction.

The Interior Department, Bureau of Mines, has received many inquiries regarding the extent and nature of the hazards to firefighters from gases and smoke resulting from the application of carbon tetrachloride extinguisher to electric arcs, burning insulation or fires such as may occur in electrical apparatus and machinery. The experiments described below were made for the purpose of determining the nature of such gases and smoke and ascertaining their toxic properties.

Description of Experiments.

Eleven tests were conducted in the gas chamber of the Bureau of Mines; this chamber is of metal construction throughout, painted, set with glass windows and has refrigerator clamp doors, making it nearly gas tight; it is 10 by 12-1/2 by 8 feet high, and holds 1000 cubic feet; a fan for mixing the gases is within the inclosure. Two tests were conducted in Gallery 5 of the electrical section of the Bureau, a cheese-box-like inclosure of painted boiler plate, 10 feet in diameter by 5 feet high and containing about 385 cubic feet; the lid may be lifted from a water seal setting with an electric crane; windows are in the sides; the inner atmosphere can be mixed by means of a centrifugal fan connected through 6-inch pipes.

In producing the fires, electric arcs, carrying from 40 to 65 amperes, were drawn between electrodes in a 220 volt direct current circuit. The electrodes were manipulated so as to keep the arc burning with interruptions as short as possible by the fire fighters in the chamber or by mechanical controls extending through the chamber wall. The current was regulated by means of a water-barrel rheostat. Table 2 gives details as to the material used for electrodes and the amount of current used.

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After gases had been evolved from the fires, the atmospheres in the chambers were thoroughly mixed and samples taken for analysis. Rats were exposed for 15 minute periods to the smoke and gases and the effects noted. Canaries were exposed in some tests to the chamber air from which all the poisonous gases excepting carbon monoxide had been removed by means of an army gas mask canister*. The tests were divided into three series as follows:

Carbon Tetrachloride on Electric Arcs.

Electric arcs were formed between carbon electrodes, between copper electrodes, or between carbon electrodes in close juxtaposition to copper wire strips loosely piled: a commercial carbon-tetrachloride fire-extinguisher liquid was played upon the fires from a 1-qt. hand extinguisher or from a separatory funnel and copper pipe that directed the liquid steadily upon the arc. In using the hand extinguisher, operators wearing universal gas masks** entered the chamber and thus were enabled to observe at close range the effect of extinguisher on the fires and to note the effect of the evolved gases upon their skin. Whenever the arcs were extinguished, which frequently happened, the flow of extinguisher was stopped until the arcs were started again, in order to obtain maximum decomposition of the liquid applied.

Burning Insulation and Electric Arcs.

Electric insulation was ignited by an arc between carbon electrodes. The weights of insulation bundled together for test were:

Summary of materials burned

	Avoirdupois pounds
1. Asphaltic impregnated cotton braid...=	.23
2. Asphaltic cotton braid partly impregnated.....=	.03
3. Vulcanized rubber.....=	.91
4. Unsaturated cotton wrapping.....=	.02
5. Tape - adhesive.....=	.09
6. Paper wrapping.....=	.04
7. Jute.....=	.04
8. Silk braid, colored.....=	.02
9. Cotton cord.....=	.10
10. Gray fibre switch handles.....=	.06
	1.54

The bundles were formed to straddle the arc carbons, which lay horizontally. No carbon tetrachloride was applied in this series, the gases evolved coming solely from the insulation. A single test was made using insulation taken from a

* Fieldner, A. C., Katz, S. H., and Kinney, S. P., Gas masks for gases met in fighting fires; Bureau of Mines Technical Paper 248, August, 1921, p. 31.
** Katz, S. H., Bloomfield, J. J., and Fieldner, A. C., The universal and fireman's gas masks: Bureau of Mines Technical Paper 300, 1923, 22 pp.

number 0000 stranded cable used at the Bureau's laboratory. It consisted of rubber about 1/10 inch thick covered by an asphaltic tape, and that by a braid impregnated with bituminous moisture-proof compound: this insulation contained 40 per cent ash. The bundle was wrapped with copper wire and hung close above the arc.

Carbon Tetrachloride on Burning Insulation and Electric Arcs.

This set of tests was similar to the preceding except that carbon tetrachloride extinguisher was applied to the fires. Table 1 following presents details of all the fires and the appearance of the smoke.

TABLE 1. - Details of the tests

Tests 1 and 2 were in 385 cu. ft. gallery, others in 1000 cu. ft. chamber. Rats were exposed to gases in all but first test.

Series	Test No.	Electrodes	Arc amperes. (a)	Material burned: Description	Material burned: Original weight, pounds	Material burned: Consumed pounds	Carbon tetrachloride: Method of application	Carbon tetrachloride: Volume cc (b)	Carbon tetrachloride: Duration of application, minutes	Description of smoke	Remarks (a) Current was 220 volts, D.C. (b) 946 cc equals 1 quart.
A	1	Copper	40 to 60	None used	-	-	Funnel & tube	800	7	Dense yellow and black fumes evolved. In 3/4 minute dark yellow smoke made the arc invisible at window 5 feet away. Odor of smoke indicated carbon tetrachloride, phosgene and hydrogen chloride, it was sweetish and acrid and very distasteful.	Arc was intermittent but with delays of only few seconds.
A	2	do.	40 to 60	do.	-	-	do.	320	5	Like preceding test.	do.
A	3	Carbon	50	do.	-	-	do.	800	17	No smoke formed, at end of test only a very light haze was visible. Odor was that of CCl_4, HCl and $COCl_2$. Gases were irritating to skin of man who entered wearing gas mask.	Arc was intermittent, the 17 minutes time of application of the CCl_4 was spread over 27 minutes start to finish.
A	8	1 copper,	40	do.	-	-	One quart extinguisher used.	936	6-1/2	Yellow smoke was formed, it rose with the hot gases to the top of chamber.	Arc was intermittent, the force of the extinguisher would stop it very quickly, whereas the slow stream from a funnel did not.
A	9	Carbon	.60	do.	-	-	Funnel & tube	900	8	Dense yellow gray, rose from arc to top of chamber, slowly descended and mixed with air below.	Strips of copper wire were piled closely around the arc and covered by a 1/16 inch steel plate, a hole quickly burned through the plate and CCl_4 was run through the hole.
B	4	do.	40	Insulation from Bureau 2 of Mines cable, wrapped into a bundle with copper wire, hung just above arc.	7/8		-	none	-	Started with smoky flame, globules of soot and much smoke evolved rose to top of chamber and descended in level layer as more smoke and hot air displaced it. Flame 15" long.	Arc was burned 17 minutes, flame on insulation lasted 22-1/2 minutes.

TABLE 1. - (cont'd)

Series	Test No.	Electrodes	Arc amperes, (a)	Material burned: Description	Original weight, pounds	Consumed pounds	Carbon tetrachloride: Method of application	Volume cc (b)	Duration of application, minutes	Description of smoke	Remarks (a) Current was 220 volts, D. C. (b) 946 cc equals 1 quart.
B	6	Carbon	40	Wire and insulation shaped to straddle arc.	3-5/8	7/8	-	none	-	Flame rose 18" and gave gray smoke, growing denser, rubber melted, and very dense black smoke was evolved, smoke rose to top of chamber and descended in level strata as displaced by fresh smoke and gas. Big globs of soot covered floor of chamber. After stirring the air in chamber looked black, could see arc dimly 2 feet through smoke.	Arc and flame lasted 15 minutes.
B	10	do.	60	do.	3-3/4	1-1/16	-	none	-	Appearance same as test 6.	Arc and flame lasted 8 minutes.
B	12	do.	60	Same as test 10 but loosely inclosed in asbestos paper case to prevent access of air.	3-5/8	1	-	none	-	A gray smoke slowly issued soon developing into thick rolls and becoming yellow. Smoke rose and slowly mixed with air. At end of 15 minutes burning it was impossible to see 1 foot through smoke which looked like light yellow gray paint on back of window panes.	Arc was continued 15 minutes.
B	13	do.	65	Cable, 7 strands No. 20 wire, rubber covered, and weather proofed with cotton braid filled with bituminous matter.	1-7/16	9/16	-	none	-	Burned with long flame giving dense black, sooty smoke. Smoke rose to ceiling and descended in strata chamber filled with black smoke in 5-1/2 minutes. Smoke was denser in appearance than previous black smokes.	Arc was burned 15 minutes.
C	5	do.	40	Same as test 4.	2-7/8	5/8	One quart extinguisher used.	1000	8	Dense black and yellow smoke was formed, yellow being soon lost in the black, smoke was denser than test 4, due to smoke added by pyrene and less complete combustion.	Application of CCl_4 was intermittent, fire was allowed to blaze up and was extinguished repeatedly.
C	7	do.	40	Same as test 6.	3-3/4	7/8	do.	900	5-1/2	Formation same as test 5 above. Very dense black smoke.	Flame at start was 24" long, it was repeatedly allowed to blaze and then extinguished.
C	11	do.	60	Same as test 6.	3-7/8	3/4	do.	946	6	Very dense black smoke, same appearance as test 5.	Flame was repeatedly extinguished.

Results of Experiments.

Composition of the atmospheres. The gases produced were analyzed for carbon tetrachloride (CCl_4), phosgene ($COCl_2$), chlorine (Cl_2), hydrogen chloride (HCl) also called muriatic acid gas, sulphur dioxide (SO_2), oxides of nitrogen (NO_2 & N_2O_4), carbon monoxide (CO), carbon dioxide (CO_2), oxygen (O_2) and methane (CH_4). The methods of analysis for most constituents have been described before*. Oxides of nitrogen and sulphur dioxide have not been determined previously in this connection; the former were analyzed by the method of Allison, Parker and Jones** that adapts the phenol sulphonic acid process as used in water analysis, to gases: sulphur dioxide was determined by aspirating a 5-liter sample through caustic soda solution and finally precipitating and weighing the sulphur as barium sulphate; in a few special tests where smoke was absent sulphur dioxide was determined by absorbing in caustic soda solution, acidifying and titrating with a standard iodine solution.

Table 2 gives the composition of the atmospheres as determined for the constituents essential to this discussion; oxygen which is omitted was in no case lower than 18.24 per cent and carbon dioxide did not exceed 2.15 per cent; oxides of nitrogen are omitted because they were found not to exceed 4 p.p.m. (parts per million), an inconsequential amount. Two sets of analyses were made in each test, first one complete set of samples being taken, then another. The time interval between samples of the same constituent ranged from about 30 to 40 minutes. The second analysis is almost always the lower, due to absorption of gas by the chamber walls and of those constituents showing large differences both determinations are reported; the single test figures are averages.

Table 2 shows that carbon tetrachloride was found in concentrations as high as 6673 p.p.m., one quart of liquid should give a theoretical maximum of 8310 p.p.m. Hydrogen chloride showed a maximum of 972 p.p.m. in test 9, but none was indicated by analysis in some of the tests, probably because of its very rapid disappearance. Chlorine shows a maximum of 174 p.p.m., and the amounts found in different tests were very variable, some tests showing none by analysis. In tests 7 and 11 in which sulphur dioxide was found, no chlorine was indicated because if both were formed they would react with water to form sulphuric acid and hydrogen chloride, either in the gaseous phase or when absorbed in solution. The sulphur dioxide was generated from the sulphur in the rubber insulation. Carbon monoxide in each instance depends upon the completeness of combustion. Test 12 in which admission of air to insulation was prevented during the heating shows the maximum of 0.51 per cent. The other tests show carbon monoxide not exceeding 0.26 per cent.

Comparing the effects of the simple arcs in decomposing carbon tetrachloride, with the burning insulation and arcs, no especial differences are disclosed. The chemical action that produces the poisonous gases is due to intimate contact of the carbon tetrachloride, oxygen and water vapor in the air with matter of sufficient temperatures and heat capacity to promote decomposition and reaction, 600° to 800° C. have been proved sufficient for this***. Thus the temperatures of

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* Fieldner, A. C., Katz, S. H., Kinney, S. P., and Longfellow, E. S., Poisonous gases from carbon tetrachloride fire extinguishers; Jour. Franklin Inst., vol. 190, Oct., 1920, pp. 543-65.

** Allison, V. C., Parker, W. L., and Jones, G. W., The determination of oxides of nitrogen: Bureau of Mines Technical Paper 249, Sept. 1921, 13 pp.

*** Work cited Fieldner, A. C., Kinney, S. P., Katz, S. H. and Longfellow, E. S.

TABLE 2. - Noxious gases found in the atmospheres

Series A was carbon tetrachloride applied to electric arcs, series B was burning insulation without application of carbon tetrachloride, series C was carbon tetrachloride applied to burning insulation and electric arcs.

Series	Test No.	Results of analyses: Carbon tetrachloride (CCl_4) P.P.M.	Hydrogen chloride (HCl) P.P.M.	Phosgene, ($COCl_2$) P.P.M.	Chlorine, (Cl_2) P.P.M.	Sulfur dioxide, (SO_2) P.P.M.	Carbon monoxide (CO) Per cent	Remarks: P.P.M. is parts per million by volume
A	1	5963	(28. (27.	64.	(15.)17.	-	.15	
A	2	2671	)0. (0.	32.	(13.)13.	-	.09	
A	3	2716	(385. (0.	23.	(174. (167.	-	-	
A	8	6673	(95. (35.	19.	(9. (9.	-	.05	
A 2	9	6103	(972. (366.	33.	(0. (0.	-	.01	
B	4	-	-	-	-	(13. (5.	.06	
B	6	-	-	-	-	(67. (25.	.11	
B	10	-	-	-	-	(8. (0.	.17	
B	12	-	-	-	-	-	.51	
B	13	-	-	-	-	(0. (0.	.15	
C	5	6349	(493. (0.	28.	(142. (43.	-	.05	

TABLE 2. - (cont'd)

Series	Test No.	Results of analyses: Carbon tetrachloride (CCl_4) P.P.M.	Hydrogen chloride (HCl) P.P.M.	Phosgene, ($COCl_2$) P.P.M.	Chlorine (Cl_2) P.P.M.	Sulfur dioxide, (SO_2) P.P.M.	Carbon monoxide (CO) Per cent	Remarks P.P.M. is parts per million by volume
C	7	6209	(59. (40.	27	(0. (0.	(214. (183.	.26	
C	11	6169	(0. (0.	43.	(0. (0.	(99. (99.	.16	

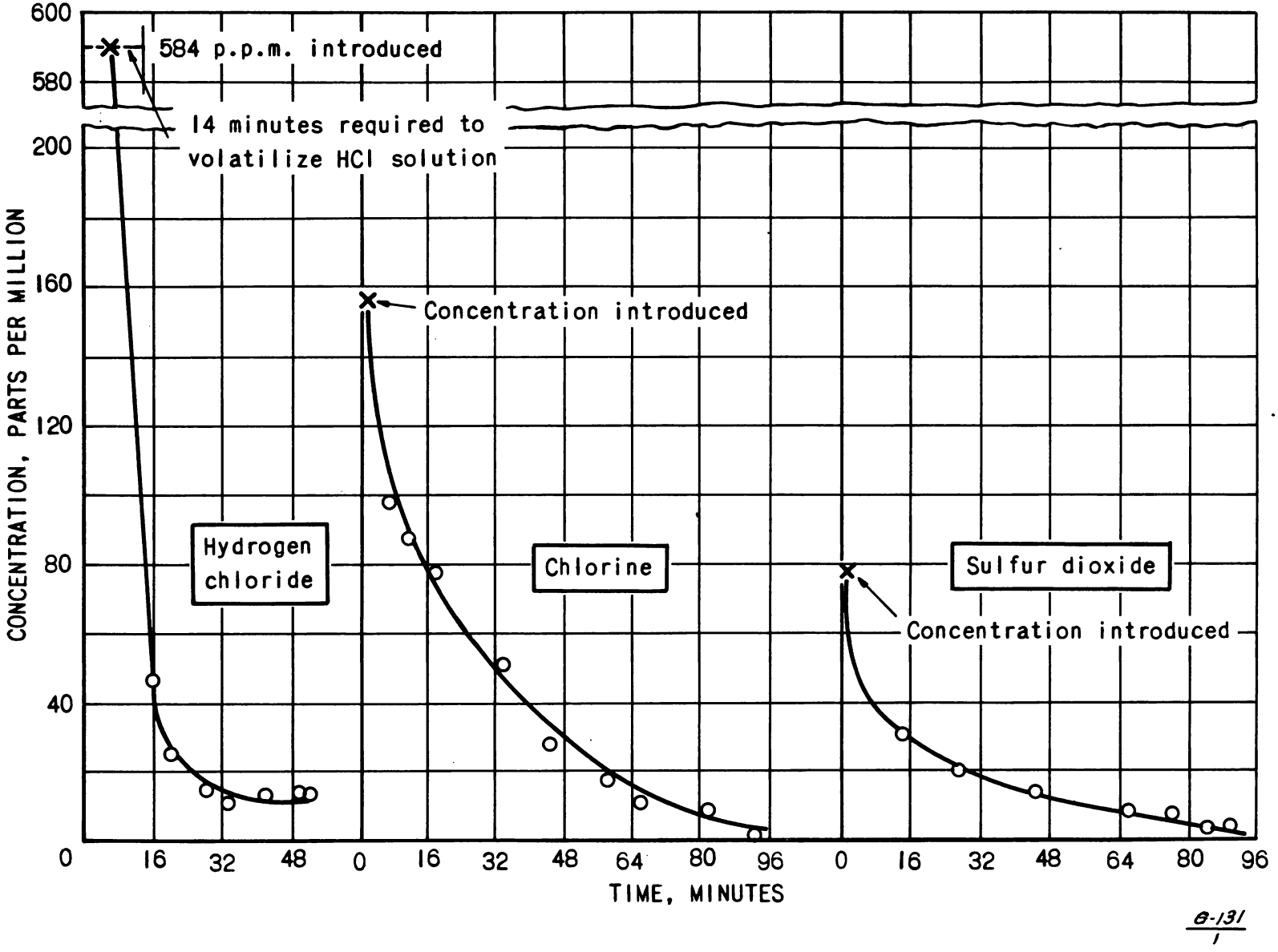

Figure 1.—Curves showing disappearance of HCl, Cl_2 and SO_2 from atmosphere in gas chamber.

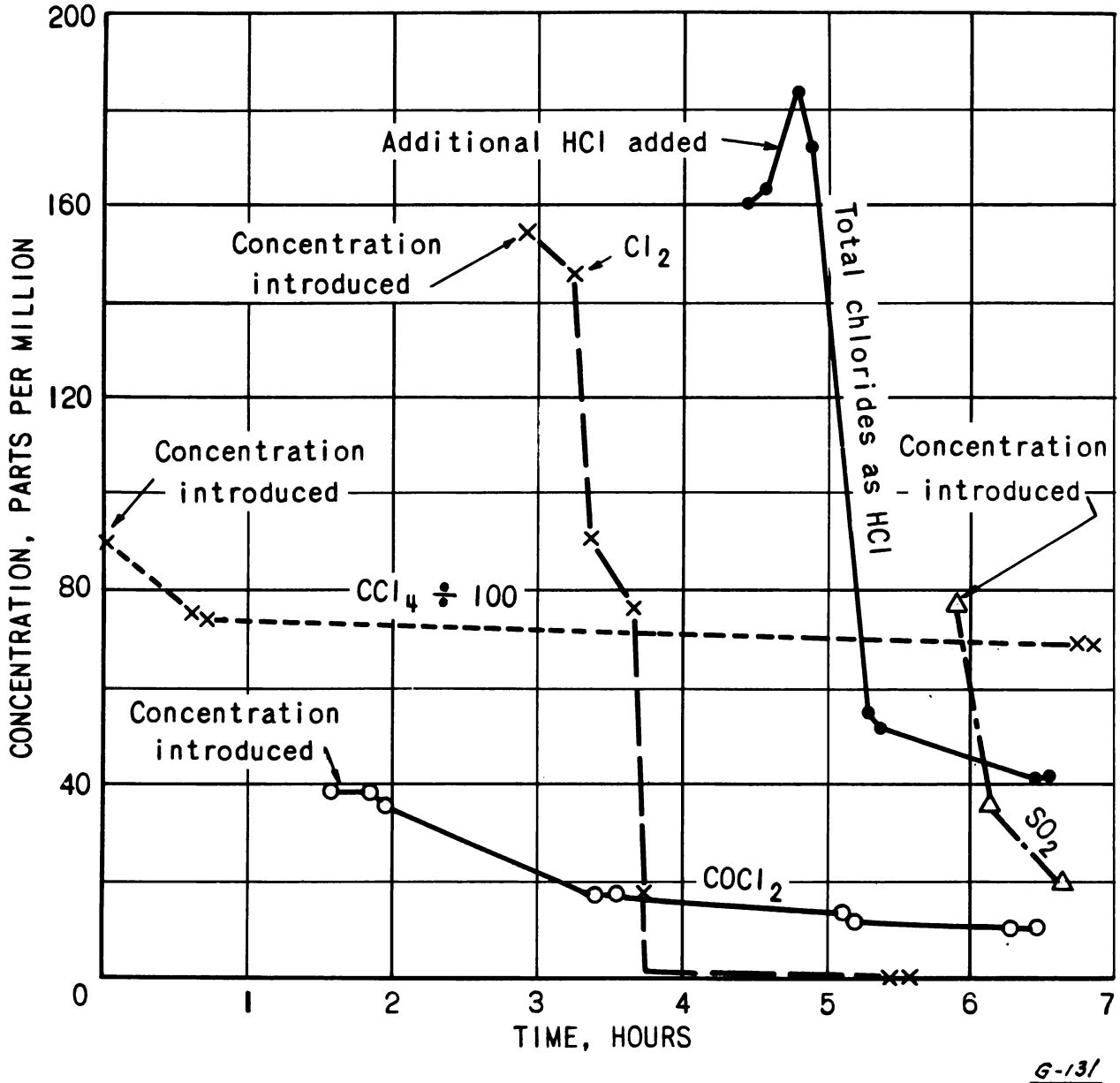

Figure 2.--Curves showing simultaneous disappearance of CCl_4, $COCl_2$, HCl and SO_2 from atmosphere in gas chamber.

the flames, the electric arcs and the incandescent carbon of burning material all promote formation of poisonous gases, lack of distinct differences no doubt are due to the poor control of the test conditions, provided by the methods employed.

Absorption of Gases by Chamber Walls.

The low concentrations determined in the second analysis for HCl, Cl_2, and SO_2, were due principally to absorption of these constituents by the chamber walls. The second samples were taken 30 to 40 minutes after the first. In the meantime only natural slow circulation of the air and diffusion brought the gases in contact with the walls.

In order to determine the magnitude of the absorption, special tests were made by introducing known amounts of gases into the chamber, running the fan continuously and noting the time of decrease. Figure 1 shows the absorption of HCl, Cl_2, and SO_2 each tested separately. The disappearance of HCl is very rapid; when a quantity that was calculated to give 584 p.p.m. was volatilized by boiling a hydrochloric acid solution for 14 minutes, the first sample, taken 16 minutes from the start, showed only 46 p.p.m. 154 p.p.m. of chlorine and 77 p.p.m. of SO_2 disappeared almost entirely in 1-1/2 hours. The SO_2 was determined in this case by an iodine titration since no gases to interfere were present. Figure 2 shows the disappearance of mixed gases. Duplicate analyses of CCl_4 and $COCl_2$ which were absorbed slowly, show close agreement. Checking results were not secured on consecutive samples of Cl_2, HCl and SO_2. The HCl in this case represents total chlorides (excepting CCl_4) figured as HCl.

Character of the Smokes.

Table 1 describes the appearance of the smokes produced. Visible smokes consist of particles of solid or liquid generated by fire, or arising from the burning material itself, particles so small in size that they float in air and are carried by the currents. That carbon tetrachloride may be decomposed without production of smoke was shown in test 3 when it was applied to an arc between carbon electrodes; Cl_2, $COCl_2$, and HCl were formed but no visible smoke. When copper or iron metal was present in the fires or was used for arc electrodes, dense yellow smokes were formed on application of the carbon tetrachloride. The yellow smokes consist of particles of copper chloride and iron chloride. The smokes from the fires themselves consist of free carbon particles and particles of tarry matter that escape combustion. Density of the smokes from burning insulation increased when carbon tetrachloride was applied so as partially to extinguish the fires; this is due principally to reduced burning of smoke forming constituents evolved by the material, partly to the addition of the metal chlorides, and possibly to some carbon released from the carbon tetrachloride as the metal chlorides are formed.

All the smokes are very irritating to breathe, but not corrosive to the tissues of the respiratory passages, nor especially poisonous. The harmful effects of breathing the atmospheres are due mostly to the gases and vapors.

Effect of breathing the Atmospheres.

After each test the gases in the chamber were mixed and a rat held in a wooden box screened on one side, was placed in the atmosphere to indicate the toxic effects. Men entered some of the less toxic atmospheres. Canaries were

exposed to the air which had been deprived of all noxious gas except carbon monoxide by drawing through an army gas mask canister. Table 3 gives the results.

The rats exposed for 15-minute periods to smoke from fires on which no carbon tetrachloride had been used, suffered no noticeable ill effects. The same was true of rats exposed to undecomposed vapor of carbon-tetrachloride fire-extinguisher, 3300 p.p.m. Four rats were subjected to the gases produced by the action of electric arcs on carbon tetrachloride, three for 15 minutes and one for 60 minutes. The latter and one other died within a day. The two that lived were very weak, they breathed laboriously, spasmodically, and irregularly for two to three days, refused food for one and two days, then finally recovered. Three rats were exposed for 15-minute periods to the gases and smoke from carbon tetrachloride on burning insulation and electric arcs, one died and two lived. The latter appeared about to die for four days after the tests, but in a week they were convalescing.

Autopsies on the dead rats showed hemorrhage and oedema of the lungs, which confirms the highly dangerous character shown by the chemical analysis of the gases from carbon tetrachloride on fires.

Canaries exposed to the chamber gases from which all toxic gases except carbon monoxide were removed were overcome in two instances, test 11, in which carbon tetrachloride was used, and test 12, in which carbon tetrachloride was not used. They recovered completely within an hour after removal. This verifies the presence of carbon monoxide which is produced by all fires in carbonaceous matter, which do not burn freely.

A man who without respiratory protection entered the 385 cubic foot gallery to remove the rat, breathed for a period not over one-half minute the atmosphere which had been diluted with fresh air. The gases were very distasteful, as described in table 3, and the sensation persisted after he came out. That night one of his nostrils was congested until he arose the following morning. His throat was then examined by a physician who stated that it was inflamed, but his condition was not due to a cold. All irritation disappeared the second morning. When men wearing gas masks entered the chamber containing gases arising from carbon tetrachloride applied to fires, they usually experienced severe skin irritation on the exposed parts of the face and neck, especially when perspiring. This fact emphasizes the corrosive action of the gases on the delicate mucous membranes of the respiratory system.

Discussion of Results.

The death of some rats following exposure for 15 minutes to the gases from carbon tetrachloride extinguisher on electrical fires and the precarious condition of those that did not die, mark these gases as decidedly poisonous. The effects are probably not due to one gas alone, but to additive effects of all. However, the gases from burning insulation or from carbon tetrachloride vapor 3300 p.p.m., each taken by itself, had no noticeable effects on rats, so the serious consequences must be attributed mostly to phosgene, chlorine and hydrogen chloride.

Irregularities in the apparent effects of gases on rats compared to the concentrations determined by chemical analysis are due in part to differences in resistance of individual rats. Difference in susceptibility of individuals is illustrated by the canaries subjected to the carbon monoxide. One canary exposed to 0.15 per cent carbon monoxide in air for 30 minutes showed no noticeable effects;

TABLE 3. - Physiological effects of the atmospheres.

Series A was carbon tetrachloride applied to electric arcs, series B was burning insulation without application of carbon tetrachloride, series C was carbon tetrachloride applied to burning insulation and electric arcs.

Series	Test No.	Effects of carbon monoxide on canary (a)		Effects of atmospheres on man		Effects of atmospheres on rats		Remarks
		Duration of exposure, minutes.	Results of exposure.	Duration of exposure, minutes.	Results of exposure	Duration of exposure,	Results of exposure. (Observations by Drs. F. Flynn and W. J. McConnell).	(a) All the noxious gases excepting carbon monoxide were removed from the air by drawing it through a canister of an army gas mask.
A	1	-	-	Smelled gases cautiously	Odor was carbon tetrachloride, hydrogen chloride and phosgene though latter was uncertain, it was sweetish, acrid, irritating to nasal passages and very distasteful.	None	-	
A	2	-	-	About 1/2 but gas was diluted with fresh air.	A man entered gallery without respiratory protection to remove rat as soon as lid was removed from gallery. The sensation was like that above but a foul sensation or taste in throat persisted for about an hour. That night one nostril was congested till arising. Physician's examination next morning showed inflamed throat not due to cold. All irritation had disappeared on second morning.	60	Rat dies 25 hours after the test.	This rat was exposed during the entire test and the time afterward while gases were being sampled.
A	3	-	-	Smelled gases cautiously.	Odor was that of carbon tetrachloride, hydrogen chloride and slightly phosgene, one man claimed he could distinguish odor of chlorine. Gases were sweetish, acrid, irritating and very distasteful. Man entering chamber wearing gas mask found gases very irritating to skin.	15	Rat died 1-1/2 hours after removal.	Another rat exposed 25 minutes during the test period and before mixing the gases appeared very sick and likely to die for four days after, then it recovered.
A	8	-	-	-	Odor like that above.	15	Rat weakened, staggered when he attempted to move, eyes dull and partly closed, respiration jerky and rapid. Rat very ill for 24 hours, refusing food and water, did not move except when stimulated. Recovered.	

TABLE 3. - (Cont'd)

Series A was carbon tetrachloride applied to electric arcs, series B was burning insulation without application of carbon tetrachloride, series C was carbon tetrachloride applied to burning insulation and electric arcs.

Series	Test No.	Effects of carbon monoxide on canary (a) Duration of exposure, minutes.	Effects of carbon monoxide on canary (a) Results of exposure	Effects of atmospheres on man Duration of exposure, minutes.	Effects of atmospheres on man Results of exposure	Effects of atmospheres on rats Duration of exposure, minutes.	Effects of atmospheres on rats Results of exposure. (Observations by Drs. F. Flynn and W.J. McConnell).	Remarks
A	9	45	Showed no effects.	-	Odor like that above.	15	Rat very weak when removed, appeared as though death might occur any time, but recovered slowly, refusing food for 48 hours.	(a) All the noxious gases excepting carbon monoxide were removed from the air by drawing it through a canister of an army gas mask.
B	4	-	-	3	Felt no lung irritation with deep breaths, slight cough due to throat irritation, eye irritation strong. Odor empyreumatic, like smoke from paper, wood, or cellulosic material, no odor of rubber present.	-	-	
B	6	-	-	3	Eyes and nose irritated, slight tendency to cough, no chest sensations. Odor like wood smoke, no odor of rubber.	15	Apparently searched around cage for fresh air, no other objective symptoms.	
B	10	47	Canary remained on perch, became quiet and showed marked signs of carbon monoxide, by gasping and unsteadiness, but was not overcome.	1	Three men could endure smoke no longer, eyes lachrymated profusely, came out coughing and gasping for breath, no lung irritation.	15	Same as above.	
B	12	11	Canary overcome and dropped from perch in 11 minutes, was then removed.	1	Very distasteful to breathe, irritating to nose, throat and eyes, no lung irritation. Could endure it 1 minute. Odor like burned rubber and wood smoke.	15	Same as above.	
B	13	30	Not overcome, showed no distress.	1	Very irritating to breathe, could endure atmosphere 1 minute, eyes lachrymated. No odor of rubber, empyreumatic like wood smoke.	15	Same as above.	

TABLE 3. - (cont'd)

Series A was carbon tetrachloride applied to electric arcs. Series B was burning insulation without application of carbon tetrachloride, series C was carbon tetrachloride applied to burning insulation and electric arcs.

Series	Test No.	Effects of carbon monoxide on canary (a) Duration of exposure, minutes.	Results of exposure	Effects of atmospheres on man Duration of exposure, minutes.	Results of exposure	Effects of atmospheres on rats Duration of exposure, minutes.	Results of exposure. (Observations by Drs. F. Flynn and W. J. McConnell)	Remarks. (a) All the noxious gases excepting carbon monoxide were removed from the air by drawing it through a canister of an army gas mask.
C	5	-	-	Smelled gases cautiously	Odor was that of wood smoke, carbon tetrachloride, hydrogen chloride and possibly phosgene. Gases very irritating and distasteful. A person would not endure the atmosphere unless forced to do so. Man wearing gas mask in gases found the gases very irritating to the skin.	15	Rat died about 12 to 15 hours after exposure. Autopsy showed right lung slightly collapsed exudes bloody froth on section, left lung crepitates, shows large hemorrhagic areas, exudes bloody serum and froth on section, showing oedema of lungs.	
C	7	-	-	Smelled gases cautiously	Same as above.	15	Rat lived, but was greatly weakened and appeared about to die for 24 hours. It then recovered and was apparently fully so after 7 days.	
C	11	10	Canary overcome and dropped. from perch in 10 minutes. It was then removed.	Smelled gases cautiously.	Same as above.	15	Rat lived but was very weak when removed. It appeared about to die for 4 days, refusing food, grew thin, then recovered, in one week it was well on road to recovery.	

another exposed to .17 per cent for 47 minutes showed some effects, but was not overcome; a third exposed to .16 per cent was overcome in 10 minutes. Such differences in canaries breathing carbon monoxide have been noted before* and similar differences should be true of rats.

Another reason for apparent irregularity lays in the fact, that the concentrations determined by analysis only existed at the time of sampling, for the walls of the chambers continually absorbing some of the gases decrease their concentrations. The concentration of gases throughout the chamber was less uniform when the second sample was taken than the first, because more time had elapsed since the gases were mixed. Thus the second sample represents a grab taken from a gas of non-uniform concentration. The results on the components undergoing absorption indicate decreases in concentration, but may not represent the average concentration of the constituent in the chamber atmosphere. Because of absorption it is impossible to determine from the chamber experiments the actual amount of poisonous gases generated, this certainly is true for HCl and Cl_2. The concentrations of gases determined, however, are probably representative of most confined spaces because absorption would occur in most situations.

Taking the maximum figures obtained as the most dangerous condition from 1 quart of extinguisher on a fire in a 1000 cubic foot space, and comparing the figures with the concentration of gases that can kill a man by exposure for 30 minutes, give the following:

Gas	Maximum concentration found in 1000 cu. ft. chamber, p.p.m.	Kills a man after** 30 minutes exposure- p.p.m.
CCl_4	6673	48000-63000 (4.8-6.3%)
$COCl_2$ ***	43	25
Cl_2	174	860 (kills dogs)
HCl	972	1000
SO_2 ***	214	-
CO	.51 (per cent)	.4 (per cent)

The maximum figures represent very dangerous atmospheres for a person exposed 30 minutes, and undoubtedly exposures of 5 or 10 minutes might produce effects decidedly unpleasant and lasting, not to say serious. The results confirm previous tests made with carbon tetrachloride extinguishers on fires in small confined spaces, and point anew to the danger of gassing should persons be unable to escape from the gases, or should the gases not be removed by ventilation.

* Burrel, G. A., Seibert, F. M., and Robertson, I. W., Relative effects of carbon monoxide on small animals, Bureau of Mines Tech. Paper 62, Dec. 1913, 23 pp.
** Taken from Fieldner, A. C., Katz, S. H., and Kinney, S. P., Gas masks for gases met in fighting fires: Bureau of Mines Tech. Paper 248, Aug. 1921, 61 pp.
*** Cl_2 and SO_2 can not exist together.

Protection from Gases and Smoke arising from Carbon Tetrachloride.

The fireman's gas mask was developed by the Bureau of Mines to protect from all poisonous gases, vapors and smokes not exceeding 1 or 2 per cent in air*. This type of mask protects from all or any of the products arising from carbon tetrachloride extinguishers. It is always necessary that the oxygen needed to support life be present in the air to the extent of 16% or more, which is easily indicated by a flame safety lamp, lantern or torch, which are extinguished when oxygen at lesser concentrations is encountered.

Extinction of Electrical Fires by Carbon Tetrachloride.

Electric arcs of 60 amperes direct current and 220 volts were easily extinguished with a one quart carbon tetrachloride extinguisher when the stream struck the arc fairly. The density of the smoke or the position of the electrodes in the testing apparatus sometimes made it difficult to hit the arc with the liquid, in such cases the vapor of carbon tetrachloride had no apparent effect. Sometimes the arcs restarted after extinguishing because the potential across the electrodes was not removed and hot material near or in contact with the electrodes allowed sufficient current to start the arc again. Burning insulating material was easily extinguished when not subject to the heat of a continuous arc, proving carbon tetrachloride an excellent extinguisher for small fires in electrical equipment when the power is off.

Arcs of 35 amperes direct current and 500 volts between No. 12 insulated copper wire mounted in parallel lines, were readily extinguished with a one quart extinguisher in special tests when no interfering substances intervened and the wires were separated by 1/2 inch distance or more.

Carbon tetrachloride extinguishers, so far as known, are the most effective and satisfactory of any which can be applied to electrical fires with freedom from shock to the operator. Also, because of its non-conductance, the presence of carbon tetrachloride does not interfere with electrical properties of apparatus after a fire is extinguished.

Conclusions.

1. Application of one quart of CCl_4 fire extinguisher to electric arcs and burning insulation in a chamber of 1000 cubic feet capacity developed the poisonous gases $COCl_2$ in concentrations up to 43 p.p.m., Cl_2, 17¼ p.p.m., and HCl, 972 p.p.m. CCl_4 vapors, SO_2 and CO were also formed in less dangerous concentrations.

2. Of 7 rats exposed for 15 minute periods to the gases evolved from the use of CCl_4 on the arcs, 3 died and the remainder were seriously affected, but recovered.

3. These tests confirm conclusions drawn from previous tests by the Bureau of Mines that it is dangerous to breathe the gases that may be generated from one quart of CCl_4 extinguisher applied to a fire in a confined space (say 1000 cubic feet) from which escape is difficult or impossible, and from which the

* Katz, S. H., Bloomfield, J. J., and Fieldner, A. C., The Universal and the fireman's gas masks. Bureau of Mines Tech. Paper 300, 1923.

gases would not be removed by ventilation.

4. So far as is known, carbon tetrachloride extinguishers are the most effective and satisfactory of any that can be applied to electrical fires with safety from shock to the operator.

5. Arcs of 60 amperes direct current and 220 volts and 35 amperes and 500 volts were easily extinguished with a 1 quart carbon tetrachloride fire extinguisher.

The purpose of these experiments has been to determine the extent of the danger from poisonous gases arising from use of carbon tetrachloride extinguisher on electrical fires to promote safety of fire-fighters through their knowledge of those conditions. It is not the purpose to discourage the use of carbon tetrachloride extinguishers which are safe under all conditions excepting those of close confinement of fire gases in absence of ventilation and lack of ready escape for the operator from the gases. Such conditions may occur in unventilated parts of mines, vaults and cellars. They do not usually exist in buildings or the entries of mines where electric locomotives are used for hauling, since these customarily are well ventilated.
