Studies on the Toxicity of Smoke Containing Hydrogen Chloride

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ABSTRACT

Hydrogen chloride (HCl) is a relatively common component of fire ef-
fluents about which there has been much speculation and controversy.
The studies reported here represent a continuation of efforts to
clarify the role of HCl in combustion toxicology.

Studies with rodent exposures have shown that at low concentrations of
HCl, sensory irritation causes a decrease in respiratory minute vol-
ume, with somewhat slower loading of CO and a delay in toxicological
effects.   At much higher HCl concentrations, pulmonary irritant
effects are observed leading to postexposure lethality.   An empirical
analysis of data for mixtures of HCl and CO suggests that exposure
doses leading to lethality may be additive.

The lethal toxic potency (LC_{50}) of PVC smoke may be largely, but not
entirely, accounted for by the HCl produced. However, PVC smoke exhi-
bited a greater incidence of early postexposure deaths. The early
deaths, which may be partially attributable to a combined effect of CO
and HCl, may also be linked to the pattern of respiratory penetration
by the smoke.

EXPERIMENTAL METHODS AND MATERIALS

Exposure Of Animals

Apparatus. The exposure apparatus used in these studies, illustrated
in Figure 1, is similar in size and shape to that commonly used in the
NBS smoke toxicity test [1].   However, it was modified to create a
"flow-through" system.   The air flow through the exposure chamber
ranged from about 30 L/min up to about 200 L/min.   This wide range of
air flows was due to modification of the exhaust system during the
course of the program in order to provide greater flexibility and
control in generating and maintaining specific gas atmospheres.   The
higher flow rates permitted more rapid equilibration of the test
atmospheres and more stability in the atmosphere once established.

The animal restraints and isolation system, used to protect the ani-
mals from the test atmosphere until equilibrium was established, was
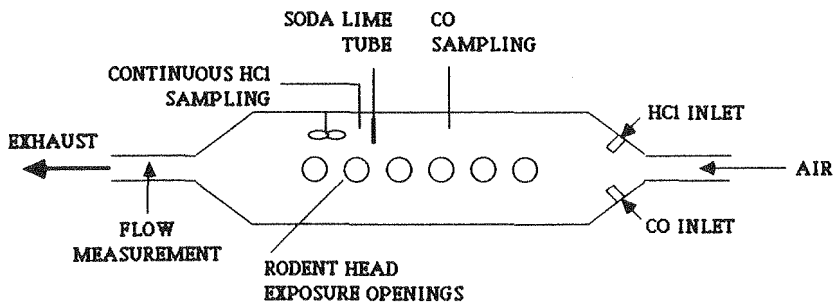the same as that used in a previous study [2].

Figure 1. Schematic of flow-through exposure apparatus

Exposure Protocol. Each animal exposure test involved the exposure of
six, young adult, male Sprague-Dawley rats positioned in tubular re-
strainers to provide for head-only exposure. Following insertion of
the tubed animals into position through the wall of the chamber, the
animal isolation system was closed and breathing air provided during
the establishment of the desired test atmosphere. Thirty-minute
exposures were initiated upon opening of the isolation system and ter-
mination of supplemental breathing air to the animals. The end point
recorded was lethality. Surviving animals were observed until either
postexposure death or 14 days. Animals surviving 14 days were subse-
quently sacrificed. Values for each LC_{50}, with 95-percent confidence
limits, were calculated from five to seven points of data using a
standard probit program.

Generation Of Test Atmospheres

Pure Gas Atmospheres. "Pure gas" atmospheres were generated by the
metering of the appropriate gases from cylinder sources into the expo-
sure chamber, with continuous analytical monitoring of concentrations.
Supplemental O_2 was provided as necessary to maintain the O_2
concentration at 20.5 ± 1.0%.

Sources were:

       Carbon Monoxide (99.9%):   Scientific Gas Products
       Hydrogen Chloride (99.5%): Scientific Gas Products

Polyvinyl Chloride (PVC) Fire Effluent Atmospheres. A continuous
combustion apparatus, developed at SwRI, was used for the studies
reported. Shown in Figure 2, it consists of a quartz tube 1 m long
and 7.6 cm in diameter, with two radiant heating devices positioned
exterior to the tube. One of several stainless steel combustion boats
(ranging from 50 to 110 cm in length), containing a weighed quantity
of PVC, was pulled at a constant rate of travel inside the tube past

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the radiant heater. The heat flux, sample weight and rate of travel of the combustion boat were predetermined to achieve the desired concentration of HCl in the fire effluent.
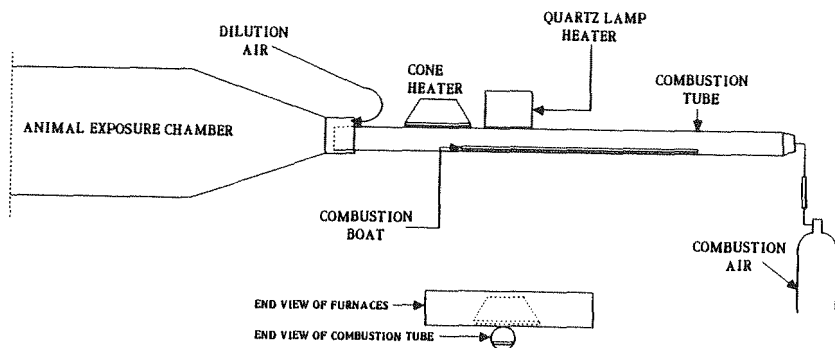

Figure 2. Continuous combustion apparatus

A constant flow of dry air (20 L/min) was metered into the combustion tube counter-current to flame propagation, with additional room air (from 30 L/min to approximately 200 L/min) being drawn into the system by an exhaust blower. The total flow of air through the apparatus was measured either by an orifice meter in the exhaust line or by calculation based on dilution of a carefully metered pure gas prior to the combustion experiments.

Different radiant heat furnaces were used for flaming and for nonflaming conditions. Nonflaming combustion was conducted at 3 W/cm^2, using a cone heater (the same as used in the NBS cone calorimeter). However, the cone heater was unable to produce the higher fluxes (6 W/cm^2) necessary for flaming PVC experiments. Therefore, a tungsten-quartz lamp heating device was used for the flaming mode. A small coil of resistance wire, connected to a variac and mounted inside the combustion tube, was the ignition source used to sustain flaming combustion.

Shown in Figure 3 is the relationship found between the HCl concentration produced and the quantity of PVC burned, expressed as $mg \cdot L^{-1}$. The latter values were estimated from the mass of PVC charged, sample travel and air flow rates.

The polyvinyl chloride (PVC) used was natural, unplasticized material in pellet form supplied by the B. F. Goodrich Chemical Company. It contained two parts lubricant and two parts stabilizer per hundred parts resin.
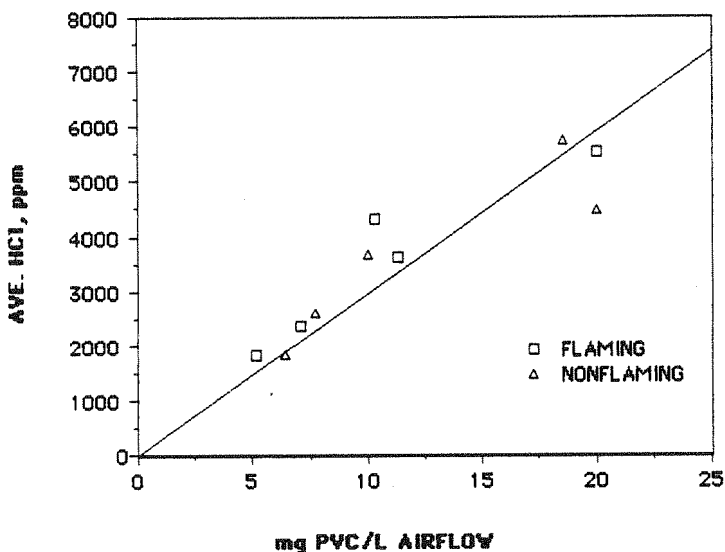
Figure 3. Plot of HCl concentration produced as a function of mass of PVC charged per liter of airflow

Analysis Of Test Atmospheres

Asphyxiant Toxicants. Analyses of exposure atmospheres for CO, CO_2 and O_2 were continuously conducted using a closed loop sampling system and the following instruments:

Carbon Monoxide:	Beckman 865
Carbon Dioxide:	Beckman 865
Oxygen:	Beckman OM-11

Hydrogen Chloride. The method used for continuous monitoring of hydrogen chloride (HCl) gas, both in a "pure gas" atmosphere and in smoke, was based on that reported in a French standard test method [3], with instrumentation and procedures modified in our laboratories. Complete verification of this method, including measurement of interferences, has not been done. Therefore, for most experiments, "back-up" analyses of HCl were also performed by soda-lime tube (SLT) sampling followed by aqueous extraction and titration [4].

A schematic drawing of the continuous HCl method is illustrated in Figure 4. A sample of an atmosphere containing HCl is drawn continuously by a pump into a gas-solution impinger containing 0.1 N HNO_3 aqueous solution. A silver/silver chloride electrode (or electrode pair) and a pipette for introduction of silver nitrate ($AgNO_3$) titrant are positioned in the cell. The basic principle is to maintain a pre-determined electrical potential (emf) in the test solution by automatically metering in $AgNO_3$ to react with chloride ion. The rate of addition of titrant is directly proportional to the concentration of HCl in the sample gas stream.
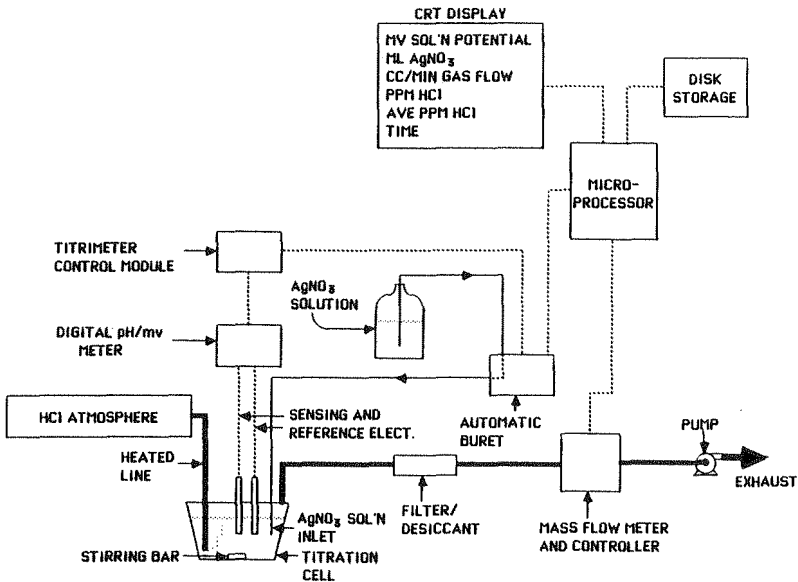
Figure 4. Continuous analysis of HCl

In operation, any increase in HCl is detected as a change in the emf of the solution. This value (mv) is monitored by a digital pH/mv meter connected to a "stat titrator" control module, which controls the dispensing of silver nitrate titrant solution through an automatic buret. When the emf of the solution deviates from the set point due to addition of chloride, the buret dispenses $AgNO_3$ in order to return the emf to the set point. This process continues as needed to maintain the solution at the set point, which is near the equivalence point of a silver-chloride titration.

The higher the concentration of HCl in the test atmosphere (or the higher the gas flow rate), the faster the silver nitrate is run into the titration cell. The output of the automatic burette (mL of titrant) is linked directly to an Apple IIe microcomputer for computation of HCl concentration. A mass flowmeter is used to monitor (and control) the gas flow, its output also going to the computer. Calculations are performed every 10 seconds in order to time-average the quantity of $AgNO_3$ being used. Due to fluctuations in the quantity of HCl introduced into the impinger during any given 10-second increment, an additional time average is performed over three successive readings. This final averaging "smoothes out" the curve of HCl vs time. The increment of time for each calculation and the interval for determining the "average" HCl are both under the control of the operator. The following data are displayed on the computer monitor every 10 seconds (or any other increment selected):

1. emf of the solution (mV);
2. Total volume of $AgNO_3$ consumed (mL);
3. Sample gas flow rate (cc/min);

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4. Concentration of HCl (ppm);
5. "Average" HCl concentration (ppm) over the selected
   time interval; and
6. Current run time (minutes and seconds).

Immediately following each experimental run, a plot of HCl concentration vs. time may be constructed from the stored data.

RESULTS

A total of nine LC_{50} (30-minute exposure plus 14-day observation) values were determined. Data obtained are summarized in Tables 1 and 2.

Table 1. Carbon monoxide LC_{50} values* (30-minute exposure + 14 days)

Atmosphere	LC_{50} (ppm)	95% Confidence Limits (ppm)
CO	6400	5400-7600
CO (600 ppm HCl)	5700	4800-7100
CO (1000 ppm HCl)	5300	4300-6500
CO (1000 ppm HCl/PVC smoke, nonflaming)	7100	6300-8000

*Values are rounded to the nearest 100 ppm

Table 2. Hydrogen chloride LC_{50} values* (30-minute exposure + 14 days)

Atmosphere	LC_{50} (ppm)	95% Confidence Limits (ppm)
HCl	3800	3100-4800
HCl (3000 ppm CO)	2100	1500-3000
HCl (4150 ppm CO)	1900	1600-2300
HCl/PVC (Nonflaming—no CO)	2900	2200-3700
HCl/PVC (Flaming—avg. CO ca. 700 ppm)	2100	1600-2500

*Values are rounded to the nearest 100 ppm

DISCUSSION

Hydrogen chloride, when present at high concentrations, is thought to penetrate into the lower respiratory tract of a subject, exerting its lethal toxic effect as a pulmonary irritant [5]. Pulmonary edema and subsequent death often follow exposure to HCl at high concentrations. Postexposure lethality results from exposure doses much lower than those required for either incapacitation or within-exposure lethality [6].

Concentration-response relationships for postexposure lethality of rats exposed to HCl have been studied over a range of exposure times from 5 minutes to 60 minutes [2]. Exposure doses (LCt_{50}'s) ranged from about 80,000 ppm-min to about 170,000 ppm-min, respectively. Higher exposure doses can be tolerated if the HCl concentration is relatively low. Conversely, progressively higher concentrations of

HCl result in tolerance to decreasing exposure doses. The 30-minute LC_{50} (postexposure lethality) for HCl was determined to be about 3700 ppm within a static system [2] and about 3800 ppm for a flow-through system. Considering the 95-percent confidence limits, the difference between these two values is not significant.

Very limited experience with baboons has indicated that 150,000 ppm-min (5- to 15-minute exposures) is probably on the threshold of postexposure lethality [2]. Although there has been no experience with human exposures under controlled conditions, somewhat conservative estimates based on the nonhuman primate experience would indicate that perhaps 100,000 ppm-min would likely result in very severe complications and even death. Exposure doses as low as about 20,000 ppm-min may be quite dangerous, however.

The 30-minute (plus 14-day observation) LC_{50} of HCl as contained in smoke from the nonflaming decomposition of PVC (little or no CO present) was found to be 2900 ppm. Although somewhat lower than the value of 3800 ppm for HCl, itself, it would be most reasonable to conclude that the postexposure lethal toxicity (LC_{50}) of nonflaming PVC smoke can largely be accounted for by the HCl content. Further support for this statement can be obtained from the data plotted in Figure 3, in which an HCl concentration of 2900 ppm corresponds to a PVC concentration (mass charged) of about 10 $mg \cdot L^{-1}$. Although this value is somewhat lower than that reported from the NBS cup furnace test [1], a greater observed toxicity of PVC smoke would be expected from the combustion method used in this study due to the absence of any HCl generation delay time and also the absence of HCl decay.

The mechanism of action of HCl is so very different physiologically from that of CO, that it would be anticipated that these two toxicants should be considered separately in predicting hazardous exposure conditions through the use of the Fractional Effective Dose model [7]. Fractional doses would not be expected to be additive, as in the case of CO and HCN. However, the LC_{50} data on mixtures of CO and HCl tempt one to consider additivity on an empirical basis. In Table 3 are shown data for some limited mixtures of CO and HCl in which the summation of fractional lethal doses approximates unity for 50-percent lethality with 30-minute exposures.

Table 3. Summation of fractional effective (lethal) doses for 30-minute exposure of rats to mixtures of CO and HCl

CO		HCl		FED
ppm	Fractional Lethal Dose	ppm	Fractional Lethal Dose	(50% Lethality)
6400	1.0	--	--	1.0
5700	0.89	600	0.16	1.05
5300	0.83	1000	0.26	1.09
4150	0.65	1900	0.50	1.15
3000	0.49	2100	0.55	1.04
--	--	3800	1.0	1.0

A comparable treatment of data using PVC as the source of HCl is shown in Table 4. It would first appear that the toxicity of smoke from nonflaming PVC is somewhat greater than expected from summation of HCl

FED's. However, in view of the 95-percent confidence limits, the significance is questionable. Summation of CO and HCl FED's for smoke from the flaming combustion of PVC does not adequately account for its greater than expected toxicity, a difference which is suggested to be significant. The full explanation may be quite complex, since the gas/aerosol/particulate nature of the real smoke may result in a different pattern of respiratory penetration than for HCl, alone. For example, particulate deposition in the upper respiratory tract may obstruct breathing of rodents and further stress an already compromised oxygen transport system. In the case of smoke from the nonflaming combustion of PVC to which has been added sufficient CO such that the CO is the major toxicant, the summation of FED's indicates the mixture to be less toxic than expected. This may be due to the HCl being present in such a low concentration that only sensory irritation is exhibited. This would decrease the apparent toxicity of CO through decreased respiration and slower loading of the CO.

Table 4. Summation of fractional effective (lethal) doses for 30-minute exposure of rats to mixtures of CO and HCl as produced from PVC

CO		HCl		FED
	Fractional Lethal		Fractional Lethal	
ppm	Dose	ppm	Dose	(50% Lethality)
--	--	2900 (nonflaming)	0.76	0.76
ca. 700	ca. 0.11	2100 (flaming)	0.55	ca. 0.66
7100	1.11	1000 (nonflaming)	0.26	1.37

Particularly striking, both in the case of the flaming combustion of PVC (with which up to 1680 ppm CO was produced) and in the case of HCl in the presence of 3000 ppm CO supplied from a cylinder source, was the incidence of postexposure deaths the same day as the exposure, usually within an hour. This is rare, except at high concentrations, for HCl, alone. Data showing the incidence of these early postexposure deaths are shown in Table 5.

Table 5. Composite lethality of rats exposed to atmospheres containing hydrogen chloride*

	Animals	Number of Deaths				LC_{50}
Atmosphere	Exposed	Exposure	Day 0	Days 1-4	Days 5-14	HCl in ppm
HCl	60	0	0	21	9	3800
PVC Smoke-Nonflaming	36	0	0	10	8	2900
PVC Smoke-Flaming	30	1	4	5	19	2100
HCl + 3000 ppm CO	30	1	2	8	17	2100

*At nominal approximate HCl concentrations of 1800, 2600, 3500, 4300, 5500 and 6500 ppm

Attempts to elucidate the effect of CO on the postexposure lethality of HCl were inconclusive, but did suggest somewhat impaired ability of rats to return to homeostasis following exposure. Exposure of rats to a mixture of 5300 ppm HCl and 3000 ppm CO was characterized by a relatively rapid initial drop in blood pH and slower than normal postexposure unloading of COHb. Even with these data (compared with those for CO alone), it is difficult to speculate as to the cause of the in-

cidence of same day postexposure lethality. The observations reported with rodents may pose some significance in the case of immediate postexposure complications following human exposures to mixtures of CO and HCl (e.g., prolonged hypoxemic conditions after rescue or escape).

In summary, it would seem that the lethal toxicity of combinations of CO and HCl can be predicted from an FED model. However, only limited success was obtained when applied to real smoke from PVC. This may be due to complications in respiratory penetration patterns involved with the complex gas/aerosol/particulate mixtures found in smoke.

ACKNOWLEDGEMENT

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