Production of Carbon Monoxide During Fire Suppression Using Halon Replacements

Joseph Z. Su* and Andrew K. Kim
Fire Risk Management Program, Institute for Research in Construction,
National Research Council of Canada, Ottawa, Canada K1A 0R6

ABSTRACT

During full-scale fire suppression tests, halon replacement agents (HFC-227ea and HCFC Blend A) were observed to produce an increased quantity of carbon monoxide (CO), in addition to the production of halogenated compounds. Agent-flame interaction resulted in the increased CO production in the fire tests. CO inhalation has been considered as an important cause of incapacitation in many fire incidents. Therefore, future risk assessment of potential exposure to toxic gases generated during fire suppression using halon replacements should include not only the toxic effect of halogenated compounds but also the toxic effect of CO and their combination.

KEYWORDS: halon replacement, fire suppression, carbon monoxide, and toxic hazard

1   INTRODUCTION

Carbon monoxide (CO) has been known as an important cause of incapacitation and death in many fire incidents [1]. However, its production during fire suppression using halon replacements and its safety implications are yet to be addressed. Up to now, the safety concerns for fire gas products from halon replacements have been limited to halogenated compounds, such as hydrogen halides and carbonyl halides, produced during fire suppression.

During full-scale fire-suppression tests conducted by the National Research Council of Canada [2-4], HFC-227ea (1,1,1,2,3,3,3-heptafluoropropane C_3HF_7) and HCFC Blend A were found to produce not only the halogenated compounds but also an increased quantity of CO. (HCFC Blend A is a mixture of 82% chlorodifluoromethane $CHClF_2$,

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* Author to whom correspondence should be addressed.

9.5% 2-chloro-1,1,1,2-tetrafluoroethane C_2HClF_4, 4.75% 2,2-dichloro-1,1,1-trifluoroethane $C_2HCl_2F_3$ and 3.75% D-limonene $C_{10}H_{16}$ by weight.) This paper analyzes the results of CO measurement during the fire suppression tests and examines the contribution of the interaction between the halon replacements and fires to the increased production of CO.

2   EXPERIMENT

2.1   Fire Scenarios

Fire suppression tests were conducted in a 121 m^3 test compartment. Simulated electronic-cabinet fires, wood-crib (WC) fires and heptane-pool fires were used as test fires.

The heptane-pool fires included a round-pan (RP, 0.7 m diameter) fire, three square-pan (SP, 0.3 m × 0.3 m) fires and eight tell-tale (TT, 75 mm diameter can) fires. The TT fires, placed strategically throughout the room, had an estimated total heat output of 50 kW. The heat release rates were estimated to be 400 kW for the RP fire and 50 kW for each SP fire.

The wood crib (0.6 m × 0.6 m × 0.24 m) was made of pine sticks (40 mm × 40 mm × 600 mm) arranged in 6 layers.

Three mock-up electronic cabinets (MC-1, MC-2 and MC-3) were used. Each mock-up cabinet was 0.81 m in length, 0.81 m in width and 1 m in height. MC-1 and MC-2 had a 5% opening area in the sides and MC-3 had a 2% opening area. A tell-tale fire was placed inside each mock-up cabinet. An electronic switching-gear cabinet (SGC, 0.75 m × 0.61 m × 2.13 m) with 10% grill openings was used in some tests. A cable bundle fire (with diesel-soaked hemp rope as an ignitor) and a tell-tale fire were placed inside SGC at the upper and lower levels, respectively.

These test fires were used to form three fire scenarios as shown in Figure 1. A pre-burn of 30 s was allowed for the heptane pool fires and a pre-burn of 2 min was allowed for the wood crib fire. The compartment door was kept open during the pre-burn to prevent oxygen depletion and was then closed. Fuel was sufficient for at least 3 min of burning. The suppression agent was discharged into the compartment and the door was closed at the same time.

Fire tests without suppression were also conducted in order to compare gas product generation. The tests without suppression are hereafter referred to as the free burn tests. In the free burn tests, the door was also closed after the same pre-burn but the test fires were left to burn until heptane was exhausted or the WC fire was self-extinguished. The quantity of heptane fuel was varied to control the free burning time. Since Fire Scenario 2 had the largest heat release rate, the free burn test used a smaller quantity of heptane fuel so that the free burning time would not exceed 1 min in order to prevent thermal damage to the test compartment. The free burning times for the three scenarios are shown in Table 1.
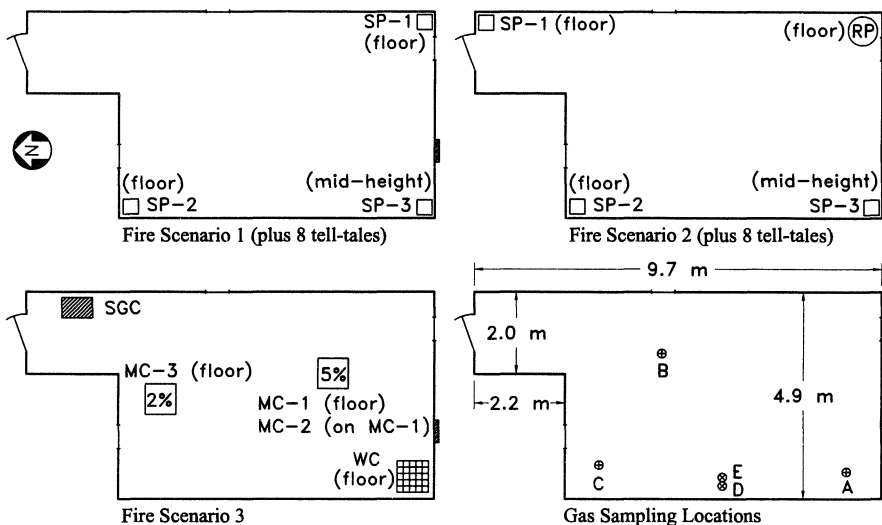
FIGURE 1. Plan view of test room, fire scenarios and locations, and gas sampling locations ($\oplus$: A, B, C for FTIR; $\otimes$: D, E for nondispersive infrared analyzers).

2.2 Fire Suppression Agents

The fire suppression tests were conducted in the total-flooding mode using two halon replacement agents (HFC-227ea and HCFC Blend A) and Halon 1301. The design concentrations were 7.6% for HFC-227ea, 12% for HCFC Blend A and 5% for Halon 1301. The discharge times were approximately 10 s. Fire extinguishment times using HFC-227ea, HCFC Blend A and Halon 1301 are summarized in Table 1.

TABLE 1. Time for Fire Extinguishment or Free Burn (by seconds)

Fire Scenario	Major Fires	HCFC Blend A	HFC-227ea	Halon 1301	Free Burn [a]
	SP-1	11	8	3	195 [b]
1 (heptane fuel)	SP-2	10	8	3	190 [b]
	SP-3	4	14	3	230 [b]
	SP-1	4	4	5	
2 (heptane fuel)	SP-2	5	4	5	40-50 [b]
	SP-3	2	6	4	(all four pans)
	RP	6	3	4	
3 (wood crib)	WC	30	15	11	180 [c]

[a] A pre-burn period is included in the free burn time.
[b] The fire burned until heptane was exhausted.
[c] The WC fire self-extinguished.

2.3   Gas Measurement

The Fourier transform infrared (FTIR) spectroscopic method and nondispersive infrared CO/CO_2 gas analyzers were used to measure the CO and CO_2 concentrations during the fire tests. The FTIR measurements of HFC-227ea, HCFC Blend A and halogenated compounds produced during the fire tests have been discussed in a separate paper [2].

FTIR Measurement and Analysis. Gas samples were drawn by pumps from Locations A, B and C in the compartment (as shown in Figure 1) through three gas sampling lines to an FTIR measurement system during the tests. Quartz sampling ports were mounted at 1.5 m (Location A), 0.6 m (Location B) and 2.8 m (Location C) above the floor, respectively. The sampling lines were made of stainless steel tubing of 7.75 mm inside diameter and 9 m length. A solenoid valve-switching device was used to connect one gas sampling line to the FTIR spectrometer and the other two sampling lines to exhaust concurrently. The gas samples from the three locations were alternately forwarded to the FTIR spectrometer for measurement. The gas samples flowed through a cylindrical gas cell (10 cm pathlength, 32 mm aperture, 110 mL volume) at a flow rate of 8 L/min. The spectrometer scanned the gas samples in the frequency range of 400 to 4500 cm^{-1} at 1 cm^{-1} resolution. Each spectrum from every single scan was recorded every 2 s. (The FTIR gas cell and the three gas sampling lines were heated to 160°C to prevent the condensation of sample gases.)

The FTIR spectrometer was calibrated using the Matheson certified standard mixtures (binary nitrogen mixtures). The gas standards had purity of better than 99.9% and certified concentrations with a 2% relative uncertainty. The calibration for each certified mixture was conducted at the same flow rate through the FTIR gas cell as that in the fire tests.

The FTIR spectrometer was calibrated for CO_2 at 2.23, 3.75, 3.91 and 5.08%. Figure 2 shows an infrared spectrum for the calibration of 2.23% CO_2. The characteristic absorption band in the frequency region of 2225 to 2400 cm^{-1} was integrated to give a reference peak area for each known CO_2 concentration. A linear relationship between the CO_2 concentration and the absorption area was derived. The infrared spectra from the fire tests were integrated in the same frequency range and the concentrations of CO_2 produced in the test compartment were determined using the linear relationship.

For the CO calibration, the concentrations used were 102 and 1091 ppm. Figure 3 shows the unique absorption band of CO in the frequency region of 2030 to 2250 cm^{-1} obtained during the CO calibration at a concentration of 1091 ppm. The absorption band has a high-frequency side (known as the R-branch) and a low-frequency side (known as the P-branch). The eight strongest peaks were selected from each branch as the references for determining the CO concentration. The CO concentration in each fire test was quantified by comparing the absorption peak heights from the fire tests with the reference peak heights obtained from the calibration.
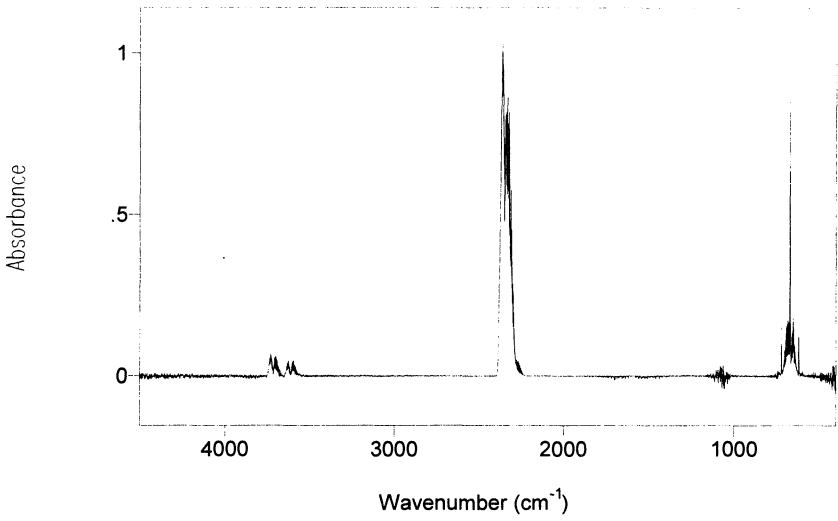
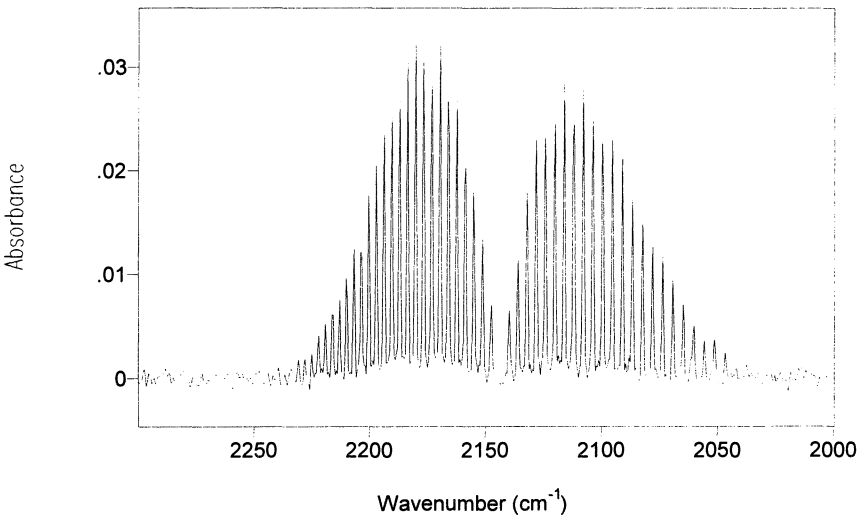FIGURE 2. FTIR spectrum for the calibration of 2.23% carbon dioxide.

FIGURE 3. Carbon monoxide absorption band in FTIR calibration with 1091 ppm CO.

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Measurement Using Nondispersive Infrared Analyzer. Nondispersive infrared analyzers were also used to measure the concentrations of CO and CO_2 during the fire tests. The analyzers were connected to two sampling ports located at Locations D and E (shown in Figure 1). The sampling ports were mounted at 1.5 m (Location D) and 2.8 m (Location E) above the floor, respectively. The concentration of oxygen was also measured at Location D or E using an O_2 analyzer. These gas analyzers gave direct readings of the concentrations of CO, CO_2 and O_2 in the test compartment.

3   RESULTS AND DISCUSSION

Figures 4 and 5 show a single frame of the time-resolved FTIR spectra in the HCFC Blend A and HFC-227ea fire tests, capturing the "finger-prints" of several chemical species produced during the fire suppression tests. The major fire gas products were halogenated compounds, CO and CO_2. The results from the measurements of halogenated compounds (hydrogen fluoride, carbonyl fluoride and hydrogen chloride) produced during the fire tests have been discussed in a separate paper [2].

Nondispersive infrared CO/CO_2 gas analyzers were designed to work in the frequencies of 2000 to 2400 cm^{-1} where CO and CO_2 have strong absorption to the infrared light. The two replacement agents, as shown in Figures 4 and 5, also absorb infrared light in these frequencies. The nondispersive infrared analyzers, therefore, count everything that absorbs infrared light in these frequencies as CO and CO_2 and give higher readings of the concentrations of CO and CO_2 in the HFC-227ea and HCFC Blend A tests. When such gas analyzers are used for the concentration measurement of CO and CO_2, the interference from the halon replacement agents should be corrected.
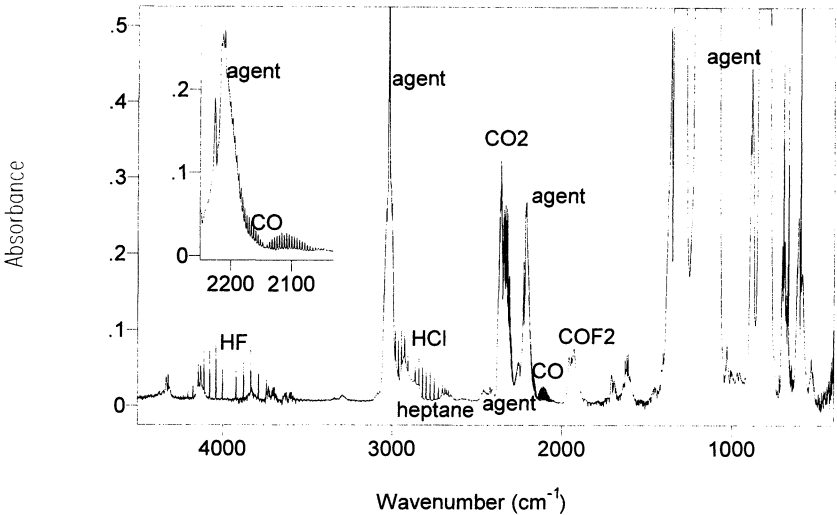

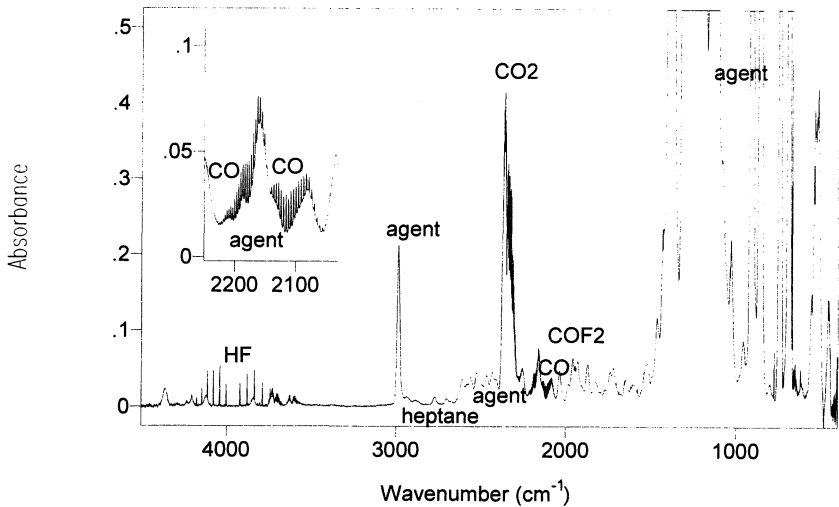FIGURE 4. FTIR spectrum in an HCFC Blend A test.

FIGURE 5. FTIR spectrum in an HFC-227ea test.

The gas analyzers are fast and reliable instruments for CO and CO_2 measurements when no other chemicals interfere in their working frequencies. In such cases, the gas analyzer readings for the CO and CO_2 concentrations are in good agreement with those determined using the FTIR spectrometer.

The FTIR method has advantages in monitoring CO and CO_2 production during fire tests and in determining their concentrations. When interference from other chemical compounds exist in the characteristic frequencies for CO and CO_2, proper spectroscopic analysis can eliminate or reduce the effect of the interference on the end results.

3.1   CO Production

In the FTIR analysis, a baseline correction is made to each spectrum to eliminate the interference from the agents in the CO and CO_2 frequencies. Figure 6 shows baseline-corrected FTIR spectra of CO in the HCFC Blend A and HFC-22ea tests. For a convenient presentation, these spectra have been averaged over the three sampling locations for 3 min starting 1 min after agent discharge. The average FTIR spectra for CO from the fire suppression tests using Halon 1301 and from the free burn tests are also plotted on the same figure for comparison. (The spectra for the free burn tests are the average over the three sampling locations for 3 min starting 1 min after closing the door. The free burning time after closing the door in the free burn tests was longer than the fire extinguishment time in the fire suppression tests.) The spectra indicate that the concentrations of CO produced during the HCFC Bend A and HFC-227ea tests are higher than those during the Halon 1301 and the free burn tests.
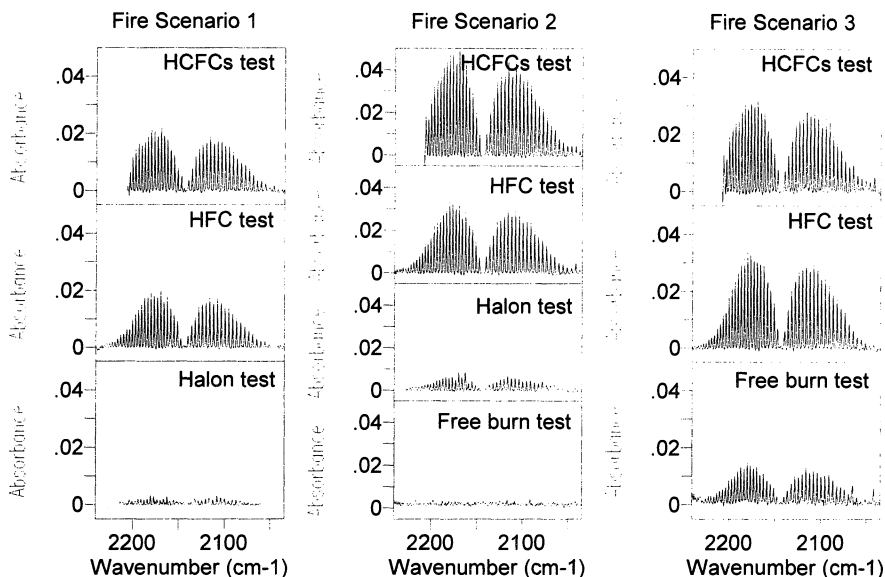
FIGURE 6. Average FTIR spectra of CO with baseline correction in fire tests.

CO concentration-time profiles are averaged over the three FTIR sampling locations for 3 min starting 1 min after agent discharge. The time-averaged concentrations of CO from the FTIR analysis are shown in Table 2. Combustion of the fuel can only account for part of the CO production in the HCFC Bend A and HFC-227ea tests. Extra CO production in the HCFC Bend A and HFC-227ea tests suggests that agent-flame interaction results in an increased CO production. The results indicate that variables such as fire size and extinguishment time have a large effect on the resulting concentration of CO in the test compartment. A large fire size and a slow fire extinguishment increase the CO concentration in the compartment, similar to the concentration of halogenated compounds. More work is needed to understand the chemical kinetics and explain the increased CO production in the HCFC Bend A and HFC-227ea tests.

TABLE 2. Time-Averaged CO Concentration from FTIR analysis
(Parts per million by volume)

Test → Fire Scenario ↓	HCFC Blend A	HFC-227ea	Halon 1301	Free Burn
1 (heptane fuel)	800	700	100	50
2 (heptane fuel)	1700	1200	200	30
3 (wood crib)	1300	1300		500

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3.2   CO/CO₂ Concentration Ratio

The ratio of the CO concentration to the CO_2 concentration in the fire tests provides a convenient way to assess the CO generation. The concentrations of CO_2 produced during the HCFC Bend A and HFC-227ea tests were less than 2% and consistent with those produced during the free burn tests. Table 3 shows the CO/CO_2 concentration ratios in the fire tests. For the heptane pool fires, the CO/CO_2 ratio in the HCFC Blend A and HFC-22ea tests is 20-30 times higher than those in the free burn tests and 3-5 times higher than those in the Halon 1301 tests. For the wood crib fire, the CO/CO_2 ratio in the HCFC Blend A and HFC-22ea tests is 2-3 times higher than those in the free burn test, even though the wood crib burned longer in the free burn test.

Recently, fire suppression tests were also conducted for water mist and argon, respectively, using the same fire scenarios in the same test compartment. The CO/CO_2 ratio is less than 0.02 in the argon tests and less than 0.03 in the water mist tests.

The high CO/CO_2 ratios in the HCFC Bend A and HFC-227ea tests also indicate that agent-flame interaction results in an increased CO production in these fire tests.

TABLE 3. CO/CO_2 Concentration Ratio

Test → Fire Scenario ↓	HCFC Blend A	HFC-227ea	Halon 1301	Free Burn
1 (heptane fuel)	0.15	0.11	0.03	0.006
2 (heptane fuel)	0.16	0.11	0.04	0.005
3 (wood crib)	0.12	0.17		0.052

3.3   Safety Implications

CO can combine with hemoglobin in human blood to form carboxyhemoglobin and reduce the carriage of oxygen in the blood [5-7]. It alone can cause incapacitation and even death if the product of its concentration and exposure time exceeds a safe dose. The upper permissible exposure limit for CO is 200 ppm, which has been established by the US Occupational Safety and Health Administration [7]. In the HCFC Blend A and HFC-227ea tests, the CO concentration already exceeds the allowed exposure limit. Although the primary safety concern is the toxic effect of HF, COF_2 and/or HCl produced in the HCFC Blend A and HFC-227ea tests, an increased CO production in these tests further compounds the issue of toxicity. The combined toxic effect of CO and the irritating halogenated compounds on humans is not well understood but safety measures should be taken to prevent human exposure to the fire gases.

4   CONCLUSIONS

Gas measurement showed that an increased quantity of carbon monoxide was produced during fire suppression tests with HCFC Blend A and HFC-227ea, in addition to the toxic and corrosive halogenated compounds, such as HF, COF_2 and HCl. As with the production of halogenated compounds, the quantity of CO generated during the tests

increased with increasing fire sizes and extinguishment times. Combustion only contributed to part of the CO production. Agent-flame interaction caused the increase in CO production in the fire tests, as indicated by higher CO concentrations and CO/CO_2 ratios in the HCFC Blend A and HFC-227ea fire tests. The combined toxic effect of CO with the halogenated compounds would be greater than that of any single gas product in the fire gases. Safety measures should be taken to prevent possible exposure to the toxic gases. Risk assessment of potential exposure to toxic gases generated during fire suppression using halon replacements should include not only the toxic effect of halogenated compounds but also the toxic effect of CO and their combination. Further investigation of the chemical kinetics involved in the CO production is needed.

ACKNOWLEDGEMENTS

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