

Gas Measurement Using FTIR, GC/MS and Ion Selective Electrode Methods in Fire Suppression Tests

Joseph Z. Su, Zhigang Liu, Andrew K. Kim, Malgosia Kanabus-Kaminska and Ewa Luszyk
National Fire Laboratory, Institute for Research in Construction
National Research Council of Canada, Ottawa, Canada K1A 0R6

ABSTRACT

In full-scale fire suppression tests using HCFC Blend A, halogen acid gases were produced. The agent and the halogen acid gases were monitored using the Fourier transform infrared (FTIR) spectroscopic technique during the tests, to determine their time-dependent concentrations in a 121 m³ compartment. Gas samples were also analyzed using gas chromatography and mass spectroscopy (GC/MS) and ion selective electrodes (ISEs) after the tests. The GC/MS results for agent concentrations and the ISE results for the halogen acid concentrations were usually lower than those determined using the FTIR technique. Proper gas sampling and instrument calibration are most important to obtain reliable results for the gas measurement and analysis.

INTRODUCTION

In the first series of HCFC Blend A fire suppression tests conducted by the National Research Council of Canada's National Fire Laboratory [1], a Fourier transform infrared (FTIR) spectrometer was used to provide time-dependent monitoring of multiple chemical species, including the agent and halogen acid gas products, in a 121 m³ compartment. In addition, gas samples were taken for analysis using gas chromatography and mass spectroscopy (GC/MS) for agent concentration and using the ion selective electrode (ISE) method for halogen acid gases. This paper describes the gas measurements and also compares the gas analysis results from the three methods. Potential errors, in the sampling of the fire gases, the calibration of the instruments and the quantitative analysis of the agent and halogen acid products, are discussed.

GAS SAMPLING AND MEASUREMENT

Figure 1 shows a schematic of the gas sampling and measurement system. Gas samples were drawn by pumps from three locations in the test compartment through three gas sampling lines to the measurement system during the fire suppression tests. Each gas sampling line consisted of a quartz sampling port and a stainless steel pipe with a micro-fiber filter. A solenoid valve switching system was used to connect one gas sampling line to the measurement system, and the other two lines to an exhaust pipe concurrently. The gas samples from the three locations were alternately forwarded to the measurement system.

The FTIR gas cell was a Pyrex cylindrical glass cell (10 cm pathlength, 32 mm aperture, 110 mL volume) with KBr optical windows. The gas cell and the sampling lines were heated to prevent condensation of the sample gases. Both temperature and pressure in the FTIR gas cell were closely monitored. The FTIR spectrometer scanned the gas sample in the frequency range of 400 to 4500 cm⁻¹ at 1 cm⁻¹ resolution every 2 s. Thus, time-resolved infrared spectra were

obtained during each test. These spectra captured the "fingerprints" of several chemical species, including the agent, heptane vapour, hydrogen fluoride (HF), hydrogen chloride (HCl), carbon dioxide (CO₂), carbon monoxide (CO) and carbonyl fluoride (COF₂), as shown in Figure 2. Further analysis of the spectra gave quantitative results for the species.

Gas samples were collected during the tests for further GC/MS analysis. The collecting point (a tee with a teflonized septum under a Swage-Lok fitting) was on the gas sampling line downstream from the FTIR gas cell (see Figure 1). The gas samples were taken manually using airtight precision syringes and then injected into pre-prepared sorption tubes. The sorption tubes contained three-layer binding materials that adsorbed the organic gas compounds in the gas samples. **After** the fire tests, the gas samples that had been adsorbed in the tubes were thermally desorbed and fed to the GUMS instrument for analysis. Figure 3 shows a GC/MS gas chromatogram for one gas sample collected during a test. Appearing in the chromatogram are the components of HCFC Blend A and heptane vapour.

Gas samples were **also** collected during the tests for further electrochemical analysis using **ISEs**. A glass bubbler was located near the exhaust of the sampling line, as shown in Figure 1. (After the GC/MS sample collecting point, the sampling line was not heated.) The glass bubbler had a replaceable collection vial (22 mL) pre-filled with 10 mL of 0.1 N sodium hydroxide (NaOH) solution. For each collection, the gas sample was allowed to flow through the vial at a rate of 140 to 210 mL/min for 30 to 120 seconds. The acid gas products (such as HF, HCl and COF₂) generated during fire suppression were trapped from the gas sample in the NaOH solution by neutralization reactions. After the fire tests, the solutions in the collection vials were analyzed using ion selective electrodes for fluoride and chloride.

QUANTITATIVE ANALYSIS

FTIR Spectroscopic Analysis

The FTIR spectrometer was calibrated with commercial samples of HCFC-22, HCFC-124, HCFC-123, HF and HCl. Quantitative analysis of the agent and acid-gas products in the fire tests was obtained by comparing infrared absorption peaks from the fire gases with the reference peaks obtained using the calibration gases.

The calibration of the FTIR spectrometer for the agent, HCFC Blend A, was carried out using nitrogen mixtures with 7.5% HCFC-22, 0.4% HCFC-124 and 0.49% HCFC-123, respectively. For HCFC-22, three infrared absorption peaks that centered at frequencies of 3025, 2213 and 596 cm⁻¹, were selected as the reference. For components HCFC-124 and HCFC-123, the peaks that centered at the frequencies of 697 and 672 cm⁻¹ were used as the references, respectively.

Commercial HF samples, with concentrations of 970, 5339, 1400 and 75000 ppm, were used for calibration. Eight HF peaks at 3788.9, 3834.3, 3878.4, 3921.0, 4001.7, 4039.7, 4076.0 and 4110.7 cm⁻¹ were selected as the references for HF. The FTIR spectrometer was calibrated for HCl at 500 and 75000 ppm. The peaks in the low frequency branch at 2776, 2799, 2822 and 2844 cm⁻¹ were selected as the HCl references. This was done to reduce the interference from

the agent and heptane vapour (see Figure 2). The absorption peak heights were used to determine the HF and HCl concentrations. For each fire test, the HF and HCl concentrations in the test compartment at a given time were determined by averaging the values obtained using the selected reference peaks.

GC/MS Analysis

The GC/MS spectrometer was calibrated for HCFC-22 (7.5%), HCFC-124 (0.4%) and HCFC-123 (0.49%). The calibration gases were taken using a similar procedure as that used in the fire tests — drawn by airtight precision syringes, injected into sorption tubes, desorbed and fed to the GC/MS instrument. Each component had a characteristic retention time to pass through the separation columns and reach the detector of the instrument. The instrument response to each calibration gas was quantified as an MS count that was related to its concentration. A linear relationship between the concentration of each HCFC and the MS count was used to determine the concentration of HCFC Blend A in the fire tests.

Electrochemical Analysis

The ion selective electrode for fluoride was calibrated using NaF standard solutions in the concentration range of 0.0 to 8.0 mmol/L. The ion selective electrode for chloride was calibrated using NaCl standard solutions in the concentration range of 0.0 to 40.0 mmol/L. For each electrode, a semi-logarithmic plot of electrode potential versus halide ion concentration was obtained from a 30 point calibration.

The solutions collected during the fire tests were adjusted for pH and ionic strength and analyzed using the ISEs for fluoride and chloride. The concentrations of the F⁻ and Cl⁻ anions in the solutions were obtained from the measured electrode potentials with reference to the calibration plots. They were then converted to the concentrations of HF and HCl in the test compartment using the gas flow rate and duration.

RESULTS AND DISCUSSION

Measurement for Agent Concentrations

In most fire tests, the agent was discharged into the fire compartment after a 30 to 50 s pre-burn. Figure 4 shows the agent concentrations determined by the FTIR spectroscopic analysis versus the target concentrations intended for the tests. In four fire tests, the measured concentrations were lower than the targets. Since the micro-fiber filters were not changed in those tests, they were clogged with soot and other particles from the fire gas, resulting in a negative pressure in the sampling lines and the FTIR cell. This suggested that the filters must be changed prior to every test. Subsequently, new filters were used in each test. As a result, the concentrations measured by FTIR were very close to the target concentrations in the subsequent tests.

Figure 5 shows the concentration-time profile of HCFC Blend A, determined by the FTIR spectroscopic analysis, during a post-discharge ignition test. At 2 min after the discharge,

three heptane pans were remotely ignited and burned to depletion of the fuel. After the discharge and before the ignition, the same agent concentration was measured by the FTIR method for the gas samples from the three different locations, indicating uniform distribution of the agent throughout the compartment. During the burning period of the three heptane pan fires, the agent concentration decreased due to its decomposition under flame and heat conditions. This decrease in the agent concentration was more pronounced in the upper part of the compartment than in the lower part of the compartment due to the air movement under fire conditions. After the burning period, the concentration approached uniform distribution again.

The agent concentrations measured using the GC/MS method are also plotted in Figure 5. The number of data points was limited by the manual collection of the gas samples. The measured values obtained using the GC/MS method were lower than the target concentration as well as the values measured by FTIR. Figure 6 shows the agent concentrations measured by the FTIR and GC/MS methods after the completion of the agent discharge in the fire tests. The GC/MS results were lower than the FTIR values or the target concentrations.

The GUMS results were usually 0.5 to 0.7 of the target concentrations. The sizes of the syringes had an influence on the measurements. Some gas samples were analyzed a few days or weeks after they were collected. The sorption tubes needed to have the capability to retain the gas samples, since the samples could be affected by storage duration and storage conditions.

Measurement for Hydrogen Halide Concentrations

Figures 7 and 8 show the concentration-time profiles of HF and HCl determined by the FTIR analysis for a fire test. In that test, the agent, targeted for a 10% concentration, was discharged into the compartment where three heptane pan fires had been fully developed. One pan fire was extinguished in 30 s whilst two others burned till depletion of the fuel. The large spikes or jumps on the FTIR profiles reflect the rotation of the gas sampling locations. The concentrations determined by the ISE method are also plotted on the same figures for comparison. Considering that each ISE value shown on the figures reflects a 2-min 3-location average for the acid gas concentration, the HF concentrations determined by the ISE method were not significantly different from those determined by the FTIR measurement. However, the differences between the ISE values and the FTIR values for HCl were substantial.

The halogen acid gases are known to be very reactive with, and corrosive to, stainless steel [2]. Since stainless steel tubes were used as the gas sampling lines, the accuracy for acid gas sampling was affected. Some of the acid gases were already lost (by reacting with the metal) before reaching the measurement or collection points. This had a greater effect on the ISE method than on the FTIR measurements. The glass bubbler, collecting the gas samples for the ISE measurement, was located downstream from the FTIR gas cell and near the exhaust. Therefore, the gas samples had to run a few more meters in the stainless steel tube before reaching the bubbler. In addition, this part of the sampling line was not heated, which could result in condensation of moist gas samples. The flow rate of the gas samples could also affect the stripping of the acid components from the gas stream if the contact time of the gas samples with the solution was too short. For most tests, the ISE method gave lower concentrations for HF and HCl than the FTIR analysis.

In one test, the agent concentration was targeted for 15% and heptane fires (estimated at 200 kW) were extinguished before the completion of the 10 s agent discharge. The concentrations for HF and HCl determined by the FTIR analysis were 350 ppm and 700 ppm, respectively. However, the ISE method gave much higher concentrations for HF and HCl than the FTIR analysis, which was not reasonable for this case where the test fires were quickly extinguished. The cold part of the metal sampling line had probably been contaminated by the large quantities of halogen acid gases produced during the previous 8 tests when the test fires were not successfully suppressed because of low target concentrations for the agent ($\leq 10\%$). The contaminated sampling line affected the gas sampling for the ISE measurement in this subsequent test. This suggested that, after an unsuccessful fire suppression, the gas sampling lines needed a more thorough purge.

Uncertainties in Gas Analysis

Gas sampling error

As discussed in the previous paragraphs, errors in gas sampling could cause uncertainties in determining the concentrations of the agent and the acid products no matter which analytical method was used. Such errors could occur as the result of using filters and stainless steel tubes in the gas sampling lines. Additional sources of gas sampling errors include the manual collection of the samples using syringes and sorption tubes for the GC/MS measurements, and the gas flow rate through the bubbler for the ISE measurements.

Calibration error

Errors in the instrument calibration could also cause uncertainties in the quantitative analysis of the fire gas. The accuracy of the instrument calibration depends mainly on the concentration range of standard chemicals and the number of data points. Sufficient data points were taken for each calibrated concentration for the three instruments to ensure repeatability.

The FTIR and GC/MS calibration for the commercial HCFC-22, HCFC-124 and HCFC-123 was equivalent to a single-concentration calibration for HCFC Blend A at 8.5%. The GC/MS calibration was also conducted at lower agent concentrations by diluting the calibration standards. The target agent concentrations, used in the fire tests, usually exceeded the calibrated range. This could result in some uncertainties in determining the actual agent concentration.

The FTIR spectrometer was calibrated with HF at four concentrations and with HCl at two concentrations, which covered the concentration ranges of the acid gases produced in the fire tests. The FTIR calibration showed a nonlinear relationship between the HF concentration and its infrared absorbance. The limited concentrations for calibration could result in uncertainties in the determination of this non-linearity. The calibration for HCl was more problematic than for HF since only two HCl concentrations were used.

The calibration for each ion selective electrode was based on more than 30 calibration points. However, the F⁻ anion concentrations in some liquid samples, collected during the tests, exceeded the calibration range.

Direct measurement uncertainties

Some concentration uncertainties for the agent and the acid gas products were a direct result of the measurements. As shown in Figure 2, the agent, heptane vapour and HCl overlapped in the frequencies of 2800 to 3000 cm^{-1} on the FTIR spectrum. Such interference did affect the quantitative analysis of the agent and HCl. The FTIR signal noise made the baseline determination ambiguous in some cases.

For the ISE measurement, carbonyl halides (such as COF_2 and COFCl) produced during the fire tests were also dissolvable in the bubbler solutions, in addition to HF and HCl. The ISEs measured all the F and Cl anions from hydrogen halides and carbonyl halides in the samples, which were all counted as HF and HCl.

CONCLUSIONS

Each instrumental analysis method used in the fire tests had some advantages and disadvantages. The FTIR method provided an on-line measurement for multiple chemical species during the fire tests. When several chemicals overlapped in the same frequencies, their quantitative analysis became difficult. The GC/MS method had a powerful separation capability for organic compounds. The ISE method was simple for measuring the F and Cl concentrations. Both the GC/MS and ISE methods involved manual gas sampling during the tests and off-line measurements after the tests, providing limited data.

Stainless steel tubes were used as the gas sampling lines due to the severe fire conditions. The gas sampling lines, however, should be designed as short as possible to reduce the chances for reactions of the metal with HF and HCl and kept clean to reduce corrosion and contamination. The sampling procedures used for GC/MS and ISE analysis need to be improved. Proper gas sampling and instrument calibration are most important to obtain reliable results for gas measurements using all methods.

ACKNOWLEDGMENTS

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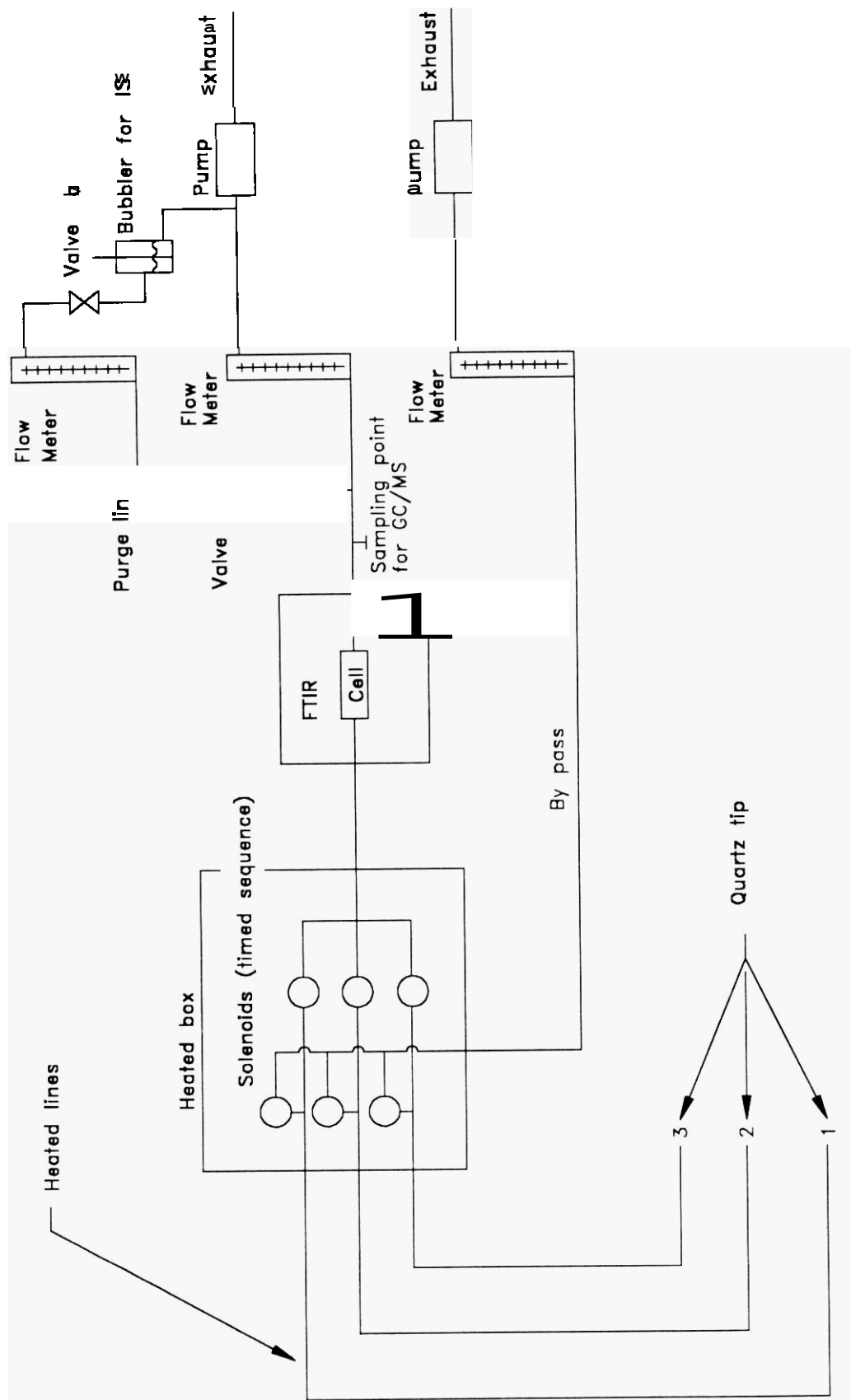


Figure 1. Schematic of gas sampling and measurement system

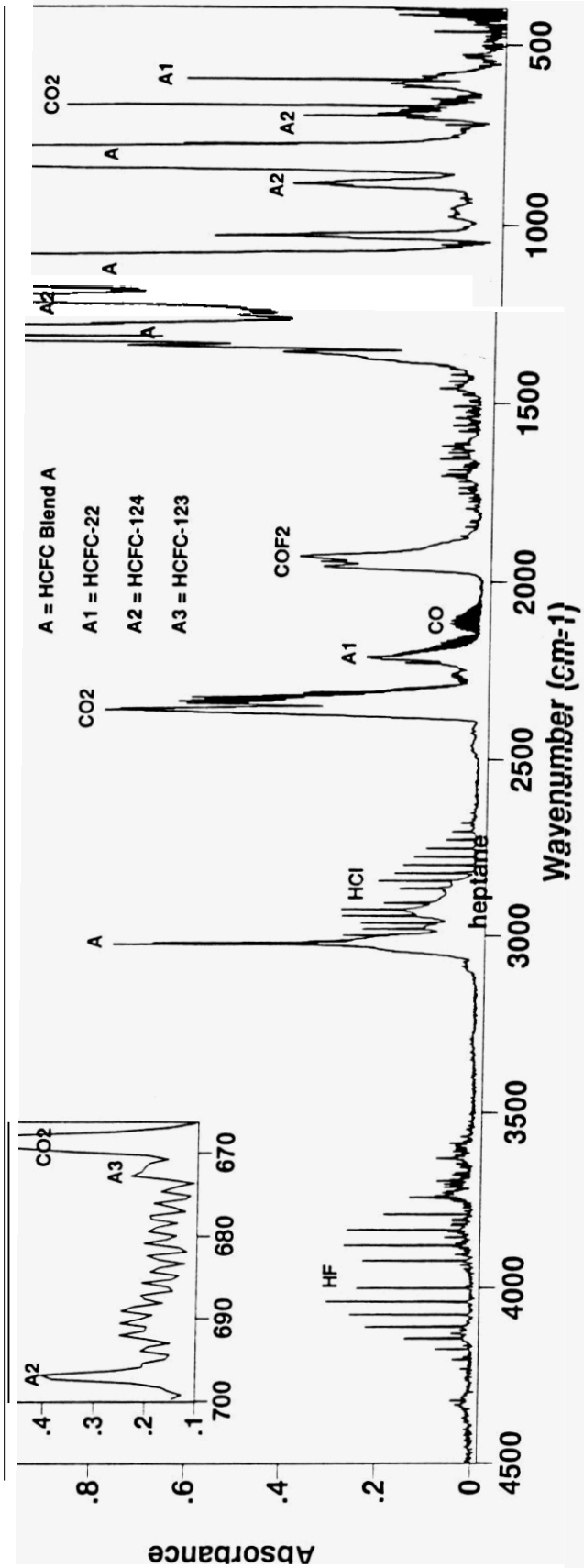


Figure 2. Infrared spectrum during an HCFC Blend A fire suppression test

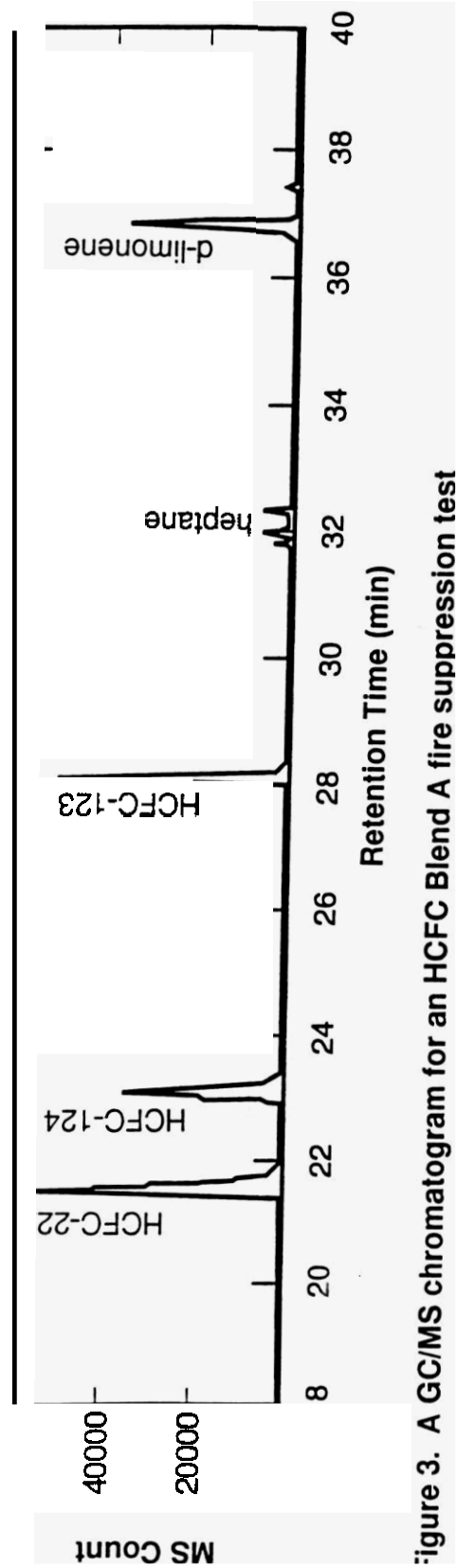


Figure 3. A GC/MS chromatogram for an HCFC Blend A fire suppression test

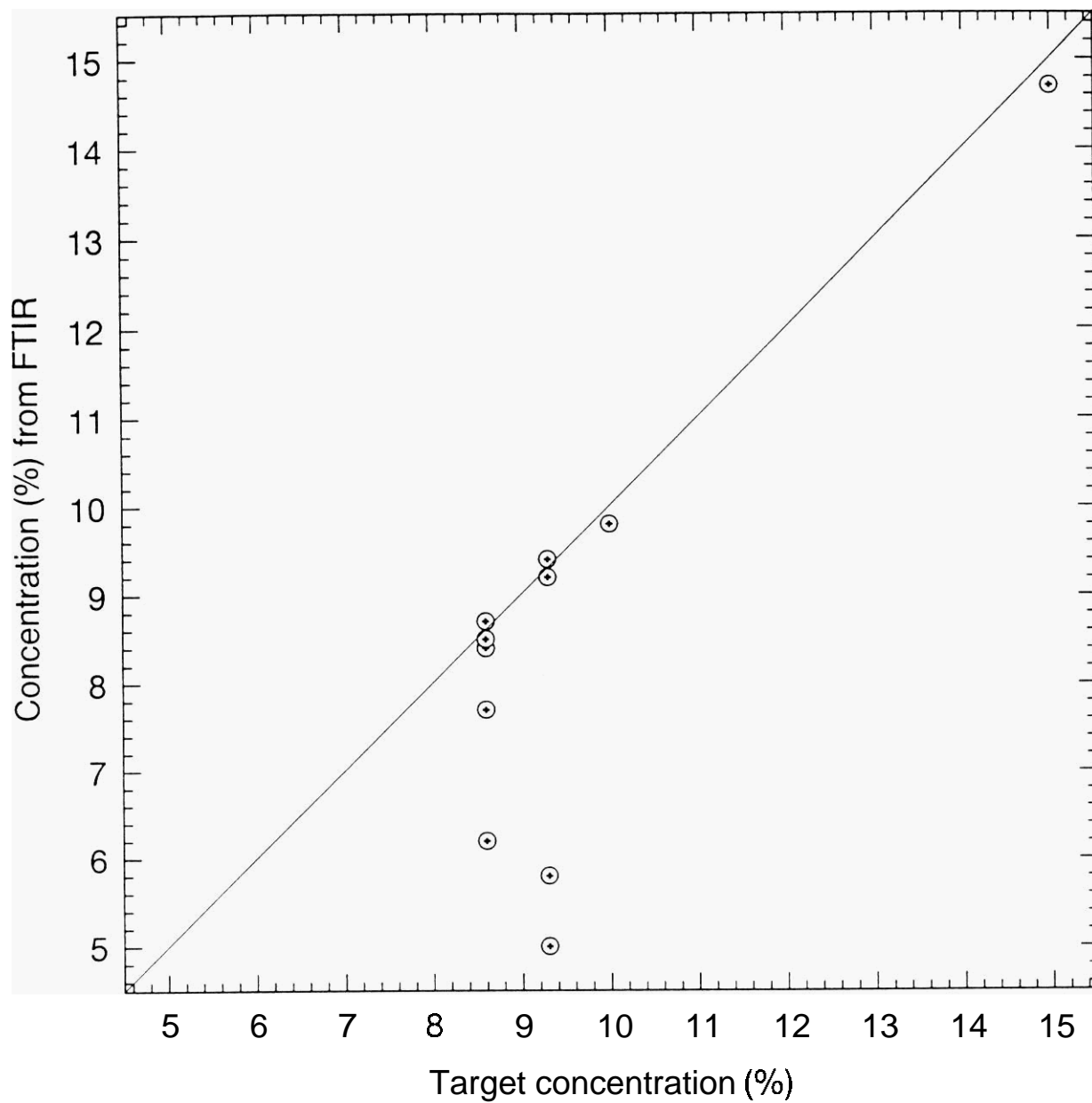


Figure 4. HCFC Blend A concentrations (first 30 s averages) determined using FTIR analysis versus target concentrations for fire tests

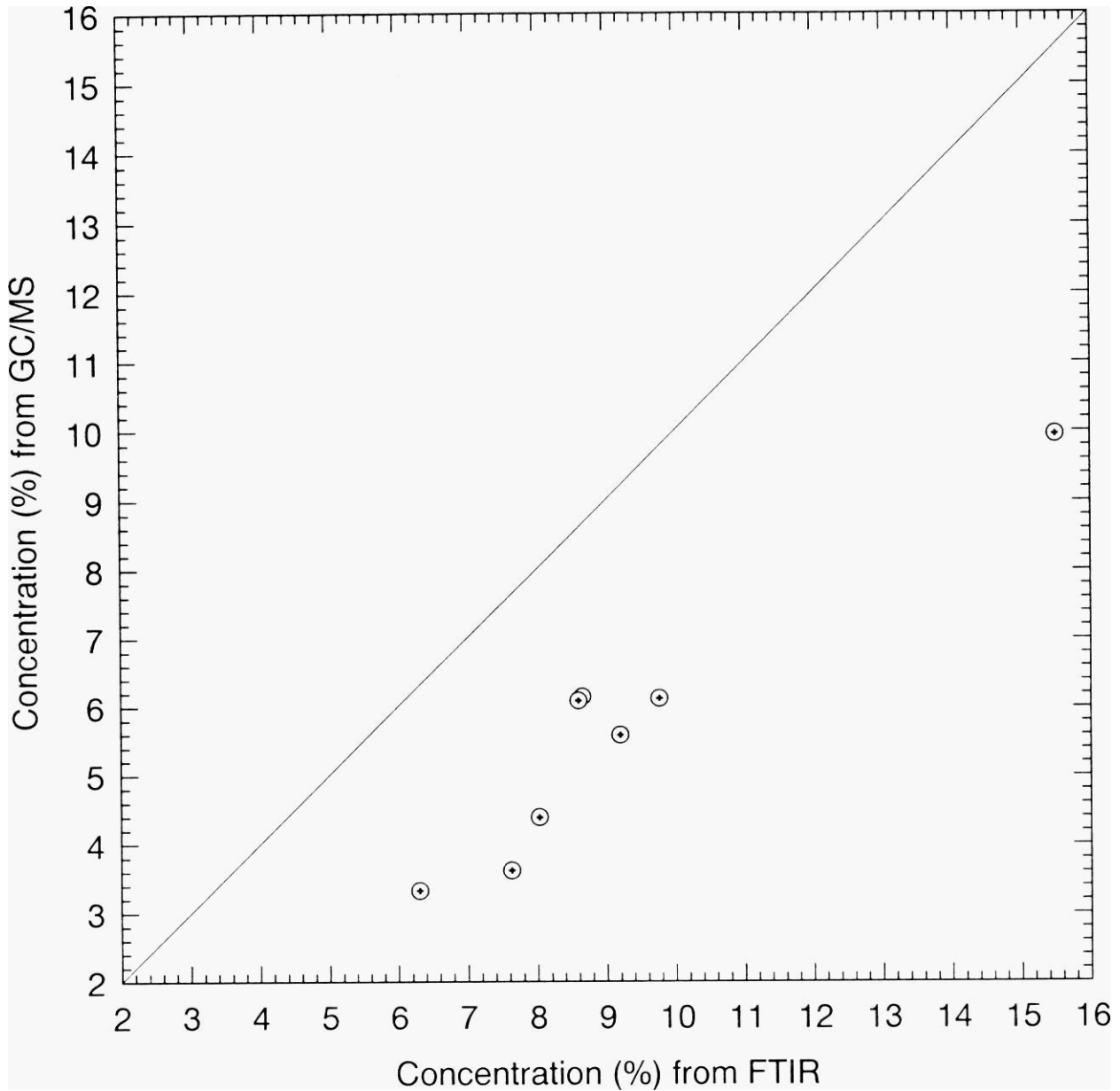


Figure 6. HCFC Blend A concentrations determined using FTIR and GC/MS measurements for fire tests

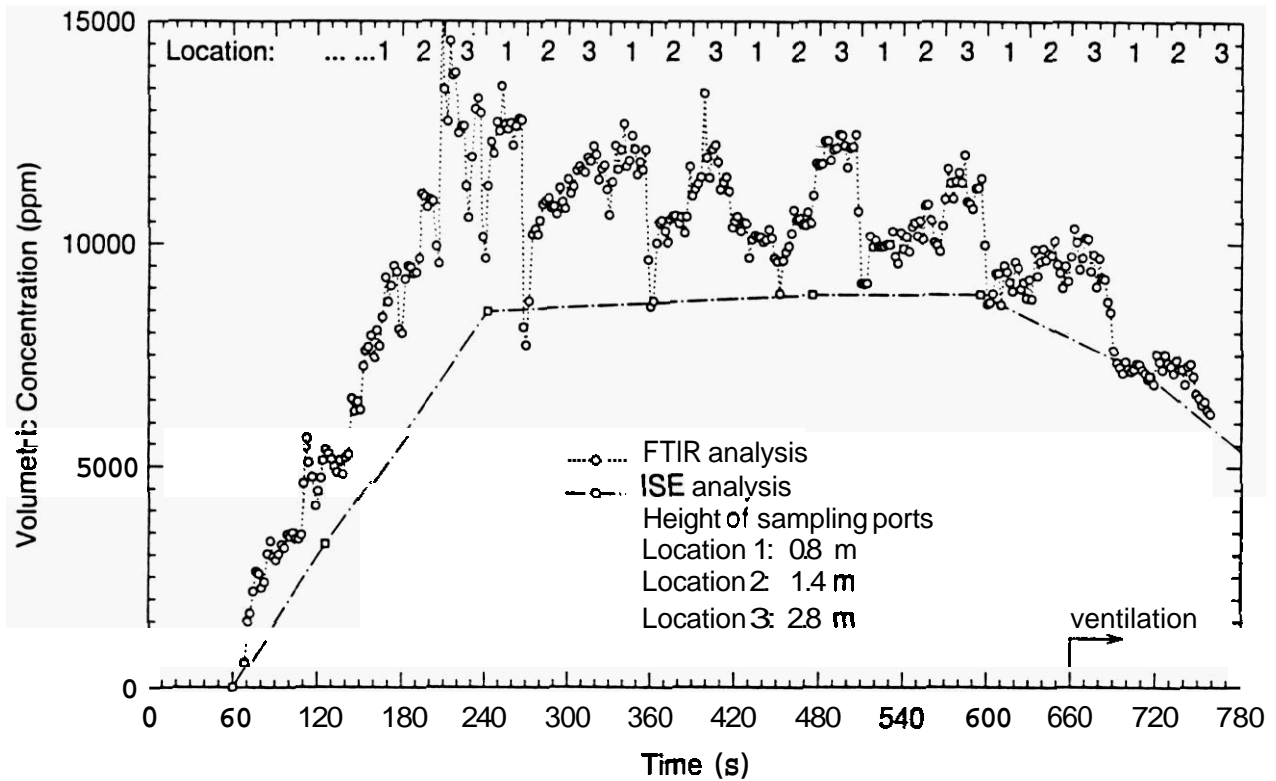


Figure 7. HF concentration-time profiles measured by FTIR and ISE for a 10% HCFC Blend A fire test (Test fires were not successfully suppressed.)

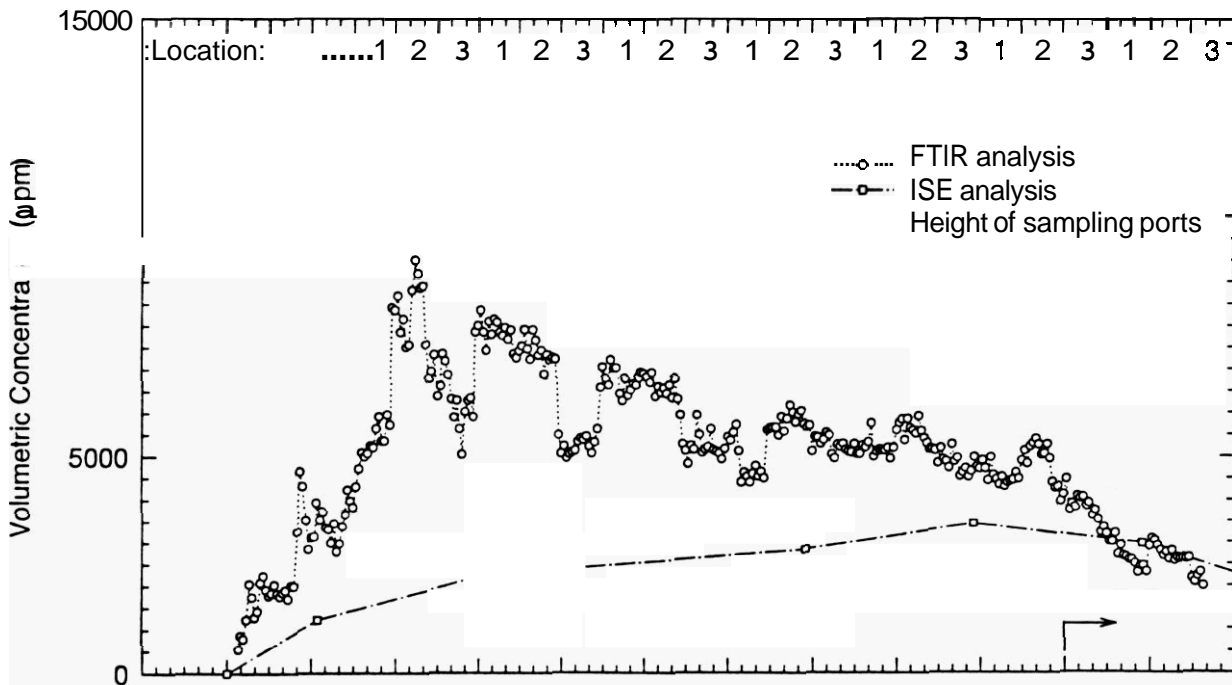


Figure 8. HCl concentration-time profiles measured by FTIR and ISE for a 10% HCFC Blend A fire test (Test fires were not successfully suppressed.)