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FORMATION AND DETECTION OF HYDROGEN FLUORIDE GAS DURING FIRE FIGHTING SCENARIOS

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Formation and Detection of Hydrogen Fluoride Gas during Fire Fighting Scenarios

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Abstract: Hydrofluorocarbon-based (HFC) fire extinguishing agents generate hydrogen fluoride (HF) gas [HF(g)] during thermal decomposition. Potential HF(g) exposure represents a health risk to any personnel not wearing proper Personal Protective Equipment (PPE) during scenarios where HFC extinguishers are deployed. HF(g) is harmful to humans at vapor concentrations greater than 3 parts per million (ppm), with an Immediately Dangerous to Life and Health (IDLH) level of 30 ppm. Controlled live-fire tests with HFC fire suppression confirm that HF(g) is produced at concentrations that greatly exceeded IDLH levels within seconds and demonstrate the need for real-time detection of HF at high concentrations and within very short time frames. Current commercial sensors are limited in capability for measuring high concentrations of HF in the vapor phase, and within the time frame required to prevent exposure to dangerous levels of this toxic gas. This review provides a comprehensive overview of HF detection methods, including colorimetric, electrochemical, mechanical, and optical sensors. The applicability of sensor types to HF detection within the complex environment of a fire event is evaluated regarding response time, selectivity, and sensor saturation.

Keywords: hydrogen fluoride, fire suppression, colorimetric, electrochemical, mechanical, optical, smart sensors

1. Introduction

Hydrogen fluoride (HF) is used in many industrial applications such as electronics manufacturing, metal cleaning, and glass etching, as well as residential use applications such as rust removal and car washing [1]. HF with a pKa of 3.15 is classified as a weak acid; the classification of “weak”, however, is purely from a chemical perspective and relates to the fact that the acid does not readily dissociate below a pH of ~5.5. Owing to its low dissociation constant, HF is a neutral lipid-soluble molecule that can rapidly penetrate tissue, and as a result, poisoning can occur through exposure to the skin, eyes, or if inhaled or swallowed [2, 3]. Dermal burns from accidental exposure to HF are severe but may not immediately be painful and, as a result, can go unnoticed, delaying treatment and increasing the extent of the injury [4–6]. HF also has a high affinity for calcium and magnesium in the body, resulting in hypocalcemia and hypomagnesemia that can lead to cardiac arrest [7, 8].

Due to the inherent toxicity of HF, detection and monitoring is critical. The concentration of HF that is Immediately Dangerous to Life or Health (IDLH) is 30 ppm, as defined by the Occupational Safety and Health Administration (OSHA). The current Permissible Exposure Limit (PEL) is 3 ppm, with a short-term exposure limit (STEL) of 6 ppm. These concentrations can be reached very quickly in leak or spill scenarios [9]. Risk of HF exposure has also been reported from the thermal decomposition of hydrofluorocarbon (HFC)-based fire suppression systems and during lithium-ion battery fires [10–24].

This review was prompted by results and interest from testing being conducted at the Air Force Civil Engineer Center (AFCEC) to address future protection of firefighters. Recent work at AFCEC Fire research facility confirmed that thermal decomposition of HFC in fire suppression systems can create high concentrations of HF gas and, depending on the HFC chemistry and the size of the fire, the IDLH of HF gas can be easily reached within less than 45 seconds. This hazard is especially dangerous if an HFC extinguisher is deployed indoors. The generation of toxic byproducts during fire scenarios poses additional risks to first responders (and any personnel in the vicinity) beyond that of the actual fire, which they could potentially be unaware of. In 2012, for example, an automatic fire suppression system in a military vehicle received a direct hit from a rocket-propelled grenade. HFC in the fire suppression system released HF that resulted in the death of three U.S. military personnel from acute respiratory failure [24]. Sensors are needed that can measure peak HF concentrations in a very short time frame to alert personnel to potential harm and signal evacuation protocols. This article reviews the state-of-the-art technologies in respect to HF detection and monitoring in the gas and vapor phase, with particular focus on application to fire event applications.

2. Hydrogen Fluoride during Fire Suppression

HFC fire suppression systems are used primarily to extinguish electrical fires in confined spaces, including aircraft, storage compartments, and crew compartments of armored vehicles (as previously described). To accurately assess exposure levels and potential health hazards, as well as developing tests for HFC and replacement agents, accurate measurements of HF must be made in real-time. During recent testing at AFCEC, discharge of an HFC-based fire suppression

system confirmed the rapid generation of HF from a small, contained Jet-A fire in a closed environment. Commercial off the shelf (COTS) HF gas sensors recorded an exponential increase in HF concentration within approximately 40 seconds and saturated the detectors at 50 ppm. The concentration near the fire remained above the maximum detection limit of the sensor for more than 4 minutes, making the maximum concentration unclear. Extrapolation of the lines provides an estimated total HF concentration of 750 ppm for the sensor in closest vicinity to the fire testing. The concentration gradually decreased to below 3 ppm (equivalent to the PEL) over the course of approximately 30 minutes from the initial detection of HF gas (Figure 1), however, that sensor may likely have been poisoned by the large concentration of HF and the actual time to a decrease below 3 ppm may have been significantly faster than 30 minutes. Determining the intersection point for the extrapolated rising and falling signals shows that HF concentrations may have been approximately 210 and 750 ppm at the two collection points.

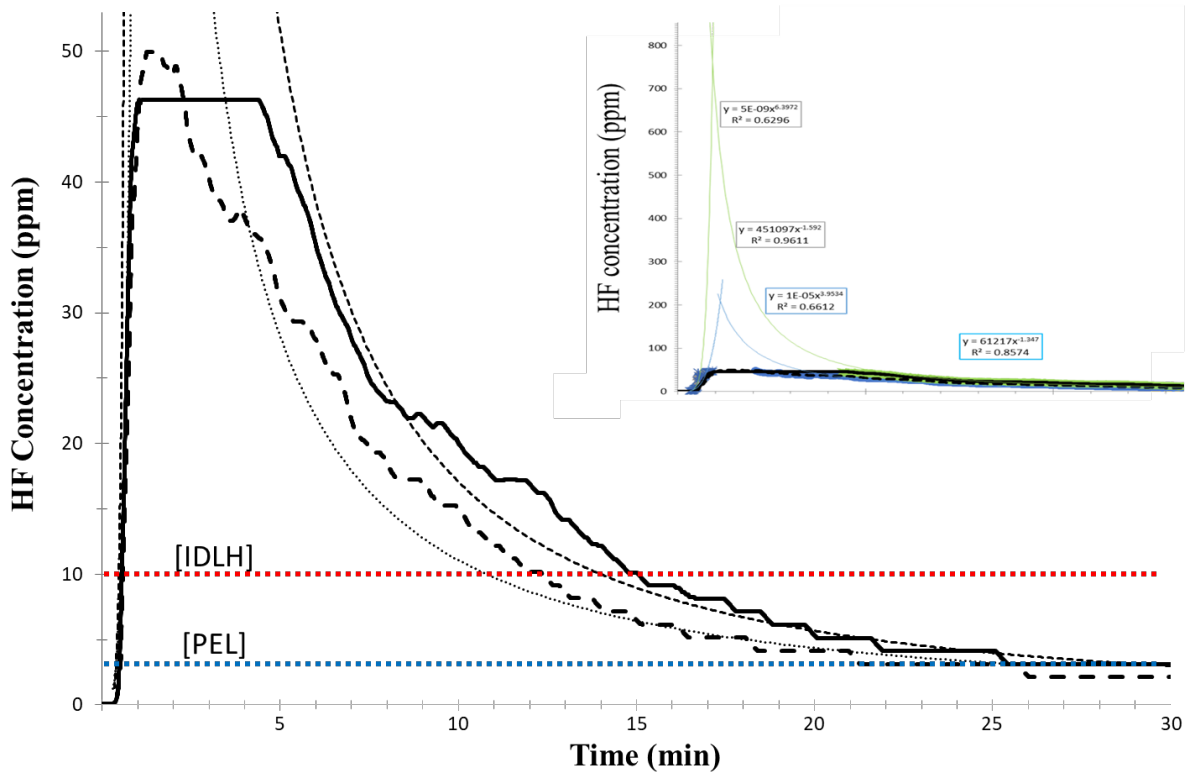


Figure 1. HF generation during HFC extinguishment of a Jet-A fuel fire (1ft² fire size); with extrapolation of the sensor readings (inset) to estimate maximum concentration. Work was conducted at AFCEC, Tyndall Air Force Base (2020). Data was collected from HFC fire suppression tests in an enclosed fire test room (3.7 x 4.9 x 2.4 m) with 1.5 L of Jet-A fuel in a 30.5 cm diameter steel pan. After a minimum 30 second preburn, the fire suppression system was activated at Time 0 in Figure 1. Electronic sensors to record HF were placed at the floor level. The black solid and dotted lines reflect time averaged data from two sensors and the inset plots are extrapolations of the same data.

2.1 HF Detection Standards

The current OSHA standard method (ID-110) for fluoride (F^- and HF) detection in workplace environments is active sampling of ambient air through a cassette containing a mixed-cellulose ester filter using a calibrated sampling pump [25]. The filter is fused with sodium hydroxide and analyzed by using an ion chromatography (IC) system or an ion-specific electrode. This method has limited sensitivity below 1 ppm and involves a lengthy stepwise extraction procedure.

National Institute for Occupational Safety and Health (NIOSH) Method 7906, which is consistent with ISO 21438-3, has a similar technique for detecting particulate and gaseous HF [26]. This method uses a personal sampling pump with a cellulose nitrate pre-filter and an alkali-treated cellulose nitrate filter impregnated with sodium carbonate, the latter of which detects gaseous HF with IC used for analysis after ultrasonic extraction. These analytical methods are not suitable for HF detection during fire events as the techniques are labor-intensive in respect to analysis and are predicated on knowledge of the presence of HF prior to sampling.

2.2 Colorimetric Sensors

Colorimetric technologies are typically inexpensive, simple to use, and can aid in rapid identification of a chemical release or exposure risk. Colorimetric chemical reactions indicate the presence of a targeted compound, with color intensity occasionally estimating concentration, but typically limited to qualitative assessment rather than quantitative. A report on emergency responder's experience with colorimetric detection methods, published in 2007, indicated that colorimetric technologies account for nearly 50% of chemical detection methods used by Hazardous Materials Management (HAZMAT) professionals, but a secondary quantitative technique is typically required for characterization [27]. Techniques for detecting HF range from simple fluoride ion detection papers to dye-based materials using organic and inorganic catalysts. A comprehensive review by Zhou *et al.*, reports on a variety of colorimetric sensors for fluoride

ion detection, but particular focus is on aqueous phase detection. In contrast, this review will focus primarily on reactions with HF in the gas and vapor phase (as derived from fire events) while briefly describing detection with aqueous HF when the applications may find dual-purpose use [28].

In a study by Kim *et al.*, a film sensor was developed using pH indicators in a coating of sodium alginate crosslinked with calcium chloride [29]. When this coating included benzoquinone, the response rate to the presence of toxic gases from 10–20 ppm was under 10 seconds. The coating chemistry is amenable to wearable devices, and a proof of concept showed a visible color change from blue to yellow for 20 ppm HF within as little as 5 seconds. Significant development would be needed, however, to confirm the reproducibility of the response. Similarly, in 2017, Devadhasan *et al.*, used a hydrogel approach to develop a smartphone-coupled handheld array reader for real-time toxic gas detection [30]. This sensor technology used a coupled colorimetric reaction based on titanium nanoparticles blended with poly vinyl alcohol hydrogel test strips patterned with chemically responsive dyes. These dyes were comprised of common, chemically responsive pH indicators (bromophenol blue, bromocresol green, bromocresol purple and chlorophenol red), to detect corrosive gasses, combined with tetrabutyl ammonium hydroxide as a phase transfer catalyst. The technology was able to detect various toxic gases at 1 ppm (HF, chlorine, ammonia, and formaldehyde). HF was investigated in the range of 1–8 ppm and responses were recorded within 10 seconds. The colorimetric response was partnered with a smartphone app to demonstrate a proof of concept that provided constant monitor for “safe, warning, or evacuation alert” based on the gas content. While these colorimetric approaches provide rapid responses, the working ranges are too limited for the high concentration events observed during HFC fires.

Many reported detection techniques utilize transition metals in solution or in combinations with dyes to create a colorimetric change. Lee *et al.*, for example, demonstrated a pyrocatechol violet-titanium (IV) bis(ammonium lactato)dihydroxide complex with selectivity for HF acid [31]. The pyrocatechol violet dissociates when exposed to HF, due to the high electronegativity of the fluoride ion. This dissociation and subsequent formation of fluoro-metal ion complexes results in a visible color change from dark blue to light yellow. When immobilized in a hydrogel, the colorimetric response was visible to the naked eye, with potential for application as a simple colorimetric sensor. Most of the initial testing of this material was conducted in aqueous conditions, but encapsulation in hydrogel extended the detection to HF in the vapor phase. When tested against vapor phase HF, the hydrogel material has a complete reaction time of approximately 3 minutes. The detection limits of this technology were not confirmed in relation to the ability to detect HF at IDLH concentrations.

Similar development in colorimetric sensors have considered other transition metals including nickel and copper in their detection of fluoride ions in solution. Sarkar *et al.*, used anthraimidazoledione derivatives to selectively detect fluoride ions when in the presence of copper (II) ions [32]. The anthraimidazoledione derivative initially showed cross-reactivity with another ion, in this case CN^- . Cross-reactivity of fluoride ions, and more specifically HF, is a common problem with the detection of these molecules and other toxic compounds, and may be a compounding limitation in fire events, when high levels of particulates and compounds such as carbon monoxide are usually present in high concentrations. A combination of an anthraimidazoledione derivative and the copper (II) ion showed selectivity for fluoride ions with a visible wavelength shift of 50 nm from a yellow-colored solution to a green solution. A nickel

(II) complex of a naphthoquinone-imidazole hybrid developed by Parthiban *et al.*, showed similar selectivity with fluoride ions and visible colorimetric changes [33].

A wide variety of other Lewis acids are used for fluoride ion sensing, due to its strong Lewis basicity. Ren *et al.*, employed the fluoride-promoted Si-O cleavage mechanism in their sensor based on 4-(tert-butyldimethylsilyloxy)-N-butyl-naphthalimide (TBS-NA) [34]. When fluoride is added to an acetonitrile solution including TBS-NA, the solution changes from colorless to yellow and is highly selective for fluoride over other anions. The review by Zhou *et al.*, details additional silyl moieties investigated for the Si-O based cleavage, such as tert-butyldiphenylsilane or triisopropylsilane, as well as detection based on Si-C cleavage using BODIPY dyes with silylacetylene, substituted 1,8-naphthalene diimide with trimethylsilylacetylene moieties, or pyrene derivatives containing trimethylsilylethynyl substituents [28]. Zhou *et al.*, also describes boronic acid groups that have been studied for the creation of fluoroborate anions with the associated color and electrical changes, allowing for either colorimetric or optical sensing. Similarly, Ueta *et al.*, makes use of the high phosphorous-fluoride bond energy with 2,4-bis(2,4,6-tri-t-butylphenyl)-1,3-diphosphacyclobutane-2,4-diyls to provide a change in visible photoabsorption [35]. Unfortunately, these studies focusing on the detection of the fluoride ion have limitations regarding HF vapor reactivity, due to experiments being conducted in solution.

Fluoride ion detection can also be carried out through hydrogen bonding, such as with thiourea, urea, amides, imidazole, and Schiff base groups [28]. In an example study, Maity *et al.*, tested a variety of anions with calix[4]arene based molecules and found that only the fluoride ion forms a complex with their ionophores, encountering a sharp color change of the acetonitrile-chloroform solution in the process [36]. Kang *et al.*, further investigated the use of amides, in the form of

rhodamine hydrazide derivatives, for detection of volatile acidic gases [37]. The hydrogen ion of the acids promoted ring opening of the spirocyclic rhodamine amide, which fluoresced after 15 seconds of exposure. While they showed that volatile bases and other volatile organic components would not cause fluorescence, additional research is needed to investigate counteracting chemicals and concentrations above IDLH. In 2020, Lu *et al.*, exposed a rhodamine-imidazole complex impregnated onto a porous silicon photonic crystal to HF concentrations at 14, 29, and 59 ppm [38]. Each concentration showed saturation with extended exposure, indicating full reaction of the dye with HF over time (6, 3, and <3 minutes for 14, 29, and 30 ppm [IDLH], respectively). The response of this sensor was compared with interfering chemicals at a variety of humidity values with no significant response from ammonia, hydrochloric acid, or volatile organic carbon (VOC) mixture TO-14A. Octane showed some interference; however, intensity changes were small compared to HF, suggesting high selectivity of HF even in the presence of contaminants.

Fluorescent reactions using the fluoride ion as a catalyst or a reactant with polymers have also been documented for fluoride ion detection. Aminophenyl pyridinium salt undergoes cyclization in the presence of fluoride ions, creating a fluorescent benzimidazole [28]. This reaction shows high selectivity toward the fluoride ion over other anions and a strong increase in fluorescence intensity. The fluoride ion also causes polymerization of N-methylmaleimide, which produces a dark red color and 10-fold increase in fluorescence [28]. These reactions using the fluoride ion as a catalyst may have limited applicability in the solid state.

Because of the diversity of colorimetric reactions, these materials can be used to create arrays of reactive compounds with varying responses to acids, bases, and selected elements. Feng *et al.*, demonstrated a concept for color reactive arrays to various toxic industrial chemicals by using a

range of dye-based colorimetric arrays [39]. As shown in Figure 2, the response demonstrated good differentiation between toxic gases, as well as facile determination of the presence/absence of chemicals at IDLH levels after two minutes of exposure. Some limitations were noted due to humidity with certain dyes, but modification of the concept to take advantage of detection through fluorescence or in the visible spectrum was also presented. It is unknown whether the presence of multiple toxic industrial chemicals would yield a proportional response that would allow for an accurate determination of the most concentrated chemical present. Furthermore, the array could potentially experience false negatives, and/or less definitive results with the presence of counteracting chemicals such as HF and ammonia. Whether the sensor discrimination would be affected by concentrations above the IDLH or cross-reactivity with other atmospheric contaminants remains to be determined.

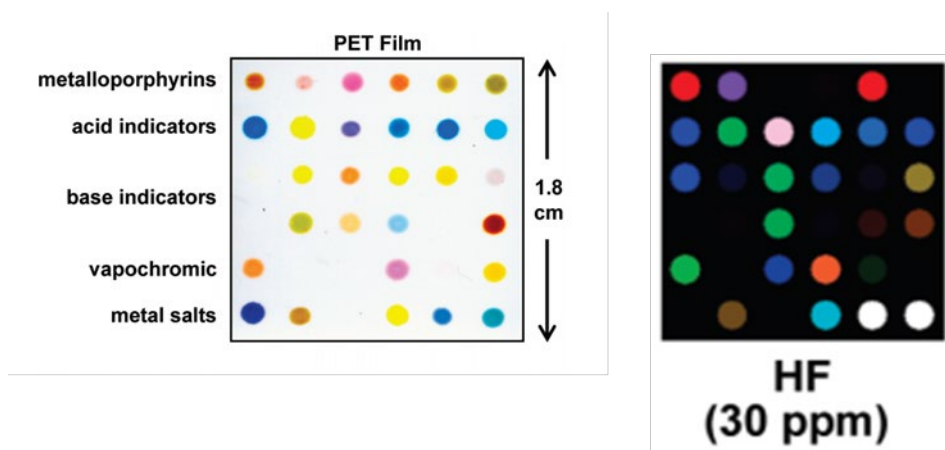


Figure 2: Reaction of colorimetric array after 2 minutes of exposure to toxic chemicals at their IDLH concentration. Each array has a unique colorimetric and patterned response to the gas the array is exposed to. Reprinted with permission from Analytical Chemistry, Vol 82, Issue 22, Feng et al., Colorimetric Sensor Array for Determination and Identification of

[39]

Reactions of fluoride with polymers may have greater potential than dye-based arrays, due to multiple recognition sites. For example, the fluoride ion can produce a dramatic color change from yellow to purple when added to dipyrrolylquinoxaline (DPQ) monomers, whereas a DPQ-containing polymer shows much higher sensitivity [28, 40]. In 2018, Zhao *et al.*, explored a fluorescent array using 36 sets of conjugated polymeric nanoparticles for volatile component sensing [41]. The polymers contain diverse backbones (phenyl, spirobifluorene, triphenylamine, 1,1,2,2-tetraphenylethene, pyrene, and 3,4-disubstituted thiophene) and end groups (phenylboronic acid, anthracene, naphthalene, methyl benzoate, and benzophenone) to tune fluorescence of the array. In exposure testing, the array was excited with a UV lamp before and after exposure. Distinct color changes allowed for identification of the individual analytes tested, including HF vapors, up to 4300 ppm, with an exposure time of 3 minutes. They developed a 108-dimensional vector based on the resulting color array using multivariable analysis methods to create a library of chemicals with prediction capability of 99.5% accuracy. This approach provides HF detection relevant to the IDLH, but more research would be needed to address the concern of counteracting chemical impact on detection of targeted chemicals using the array.

pH indicating dyes, transition metals and other Lewis acids, hydrogen bonds, catalysts, polymers and arrays have all been utilized for HF or fluoride ion detection with visual indication by color. A common limitation, especially for studies focused on fluoride ion detection, is the lack of HF vapor sensing at higher concentrations. Saturation of the sensor and long exposure times required for indication will result in the same issues currently experienced for HF detection during and after fire suppression. Additional research into these limitations of colorimetric methods along

with interfering chemicals could allow for clear determination of HF concentrations without extensive analysis.

2.3 Electrochemical Sensors

Electrochemical detection occurs via reaction between a gas and catalyst interface, creating an electrical response proportional to the gas concentration. Tin dioxide (SnO_2) is one of the most widely studied metal oxides for solid-state gas sensing and is commonly used in industrial applications. In an example sensor, a thin film of SnO_2 is surrounded by multiple SiO_2 insulating layers and a Pd-doped polysilicon heater [42] (Figure 3). The SnO_2 layer reacts with HF gas, forming SnF_4 on the surface and an increase in conductance. However, increasing concentrations of HF led to a plateau in conductance, indicating saturation of the SnO_2 layer around 10 ppm HF [43].

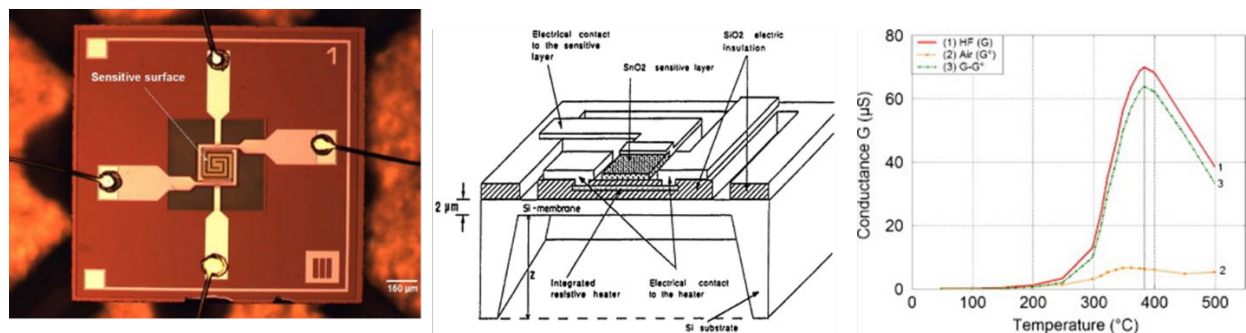


Figure 3. Gas sensor (left) fabricated with a SnO_2 sensitive layer (center) results in a change in conductance (right) in the presence of HF gas. Reprinted from Sensors and Actuators B: Chemical, Volume 143 Issue 1, Berger and Sanchez, 2009, Detection of hydrogen fluoride using SnO_2 -based gas sensors: Understanding of the reactional mechanism. p. 152–157, with permission from Elsevier [42], and reprinted from Thin Solid

Films, Volume 436, Issue 1, Sanchez, *et al.*, 2003 Tin dioxide-based gas sensors for detection of hydrogen fluoride in air, p. 132–136, with permission from Elsevier [43].

Resulting signals for HF were found to be dependent upon the temperature of the SnO₂ layer; Temperatures above 380 °C show desorption of HF on the SnO₂ layer which results in decreased detection, but reversibility of the SnO₂ layer itself. Because SnO₂ based sensors are not selective, Sanchez *et al.*, designed a gas chromatography column for this sensor using micro-machining and tested HF detection in the presence of VOCs [44, 45]. When a mixture of HF, toluene, o-xylene, and benzene are injected into the system, HF was shown to emerge first from the GC column with a retention time of 15 seconds. Because a similar response in the form of an electrical signal occurs for each of the compounds, knowledge of the presence of HF and other compounds may be necessary to accurately interpret the chemical detection and may cause false positive readings.

Further research in this area has focused on other semiconductor-based techniques that are more reactive to fluorine and HF gas. In a study by Moritz *et al.*, platinum and lanthanum trifluoride electrodes deposited on silicon wafers were able to detect concentrations of HF in the range of 6.5–185 ppm within 5 minutes [46]. Potentiometric monitoring of reactions at the Pt/LaF₃/gas three phase boundary provides concentration-dependent signal due to the exchange of fluoride ions on the Pt surface and in the LaF₃ lattice. The Pt/LaF₃ sensor on silicon was limited to temperatures below 200 °C. HF gas detection using this technique was most efficient and stable at low temperatures (between ambient and 100 °C). The same sensing layers could be deposited on silicon carbide to provide fluorine sensitivity across a wider range of temperatures (from ambient up to 400 °C) [47]. With only slight variation in reactivity across these temperatures, it

was confirmed that heating Pt/LaF₃ sensors is not necessary to achieve maximum reactivity, in contrast to the SnO₂ sensors discussed previously.

In 2002, Hoke *et al.*, investigated using a LaF₃ sensor within an electrochemical flow cell for HF sensing. They created an analyzer that extracts HF into an aqueous trapping solution, pulls the solution through an electrode flow cell, and measures electrical potential against a calibration standard [48]. The electrode flow cell contains a LaF₃ crystal sensor, an Ag/Cl wire, and a 0.01 N NaF solution; the resulting voltage output indicates HF concentrations from approximately 1 to 6,000 ppm with a response time of up to 15 seconds. Figure 4 shows the analyzer's response during an example fire suppression test. Interference by hydroxide ions is mitigated by maintaining a pH of 7–8 for the trapping solution. Other potential interfering chemicals have not been studied; however, this sensor has an overall benefit over other systems described because it was specifically designed for fire suppression systems.

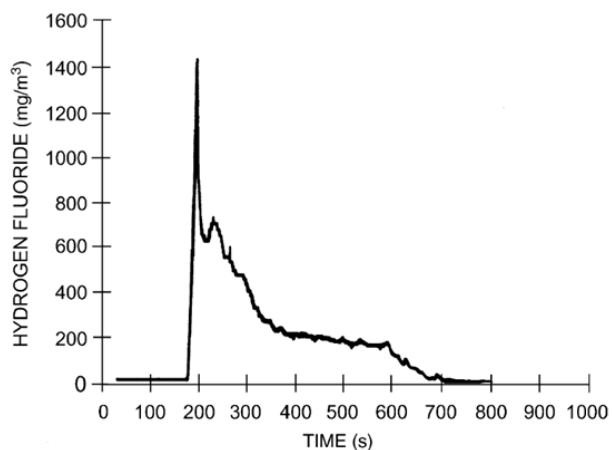
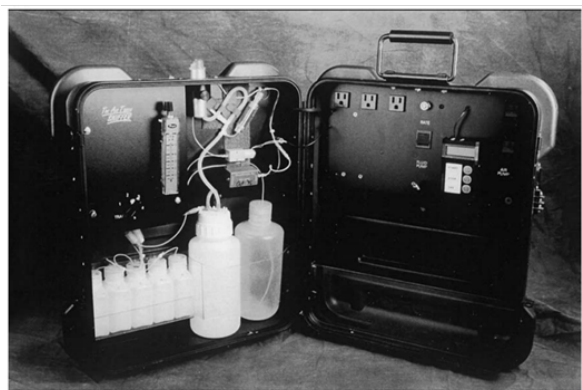


Figure 4: HF analyzer (left) and response (right) during fire suppression testing. Fire suppression agent was released at 190 seconds. Reprinted from *Analytica Chimica Acta*, Vol 255, Issue 3, Hoke. S., Hydrogen fluoride analyzer for gases and aerosols, Pages 219-225, 2002, with permission from Elsevier.

An alternative electrochemical cell for HF sensing utilized a combination of halide and halate ions in solution [49]. The sensor consisted of an Au working electrode, Ag wire counter and reference electrodes, and electrolyte solution. When 6 ppm HF was applied, a cathodic current increase was observed for sensors containing $\text{Br}^-/\text{IO}_3^-$ and I^-/IO_3^- with the response of I^-/IO_3^- being 1.4 times larger. $\text{Br}^-/\text{IO}_3^-$, however, showed higher selectivity against ozone interference. Although the sensor described was designed to detect a variety of acidic gases, the selectivity can be controlled with the type of halide-halate in the system.

The boronic acid groups that have been studied for colorimetric detection of HF have also been used in electrical sensing. Bresner *et al.*, investigated the sensing capability of 2-(N,N-dimethylaminomethyl)ferrocene boronic acid and found this compound to be selective for HF over other acids in solution [50]. Upon addition of HF, a cathodic shift of -80 mV is observed, whereas addition of HCl causes an anodic shift of 149.5 mV. These opposing electrochemical shifts of HF and HCl correspond to the selectivity of the boronic acid moiety for the fluoride ion and the protonation of the amine group of HCl. Carbon nanotubes (CNTs) have been used in conjunction with the boron-fluoride interaction to create a capacitance sensor for HF gas. In 2018, Hu *et al.*, extended this approach and spin coated a triarylborane compound onto CNT aligned via dielectrophoresis on gold electrodes [51]. The sensor was able to detect a capacitance change with the addition of HF at 250 ppm within 15–25 seconds. However, the chemosensor shows higher affinity to ammonia than to HF, indicating a need for further research into selectivity against competing chemicals.

Computational studies have investigated the sensing capability of boron nanotubes. Peyghan *et al.*, analyzed the electronic sensitivity of Al-doped and Si-doped BC_2N nanotubes to HF using density functional calculations [52]. They found that pristine BC_2N nanotubes create negligible

electronic changes after HF adsorption, while Al and Si doping improve sensitivity by 12.3% and 65.5% change in energy gap, respectively. This indicates that Si-doped BC₂N nanotubes may provide sufficient change in electrical properties for HF sensing. In a study by Yoosefian *et al.*, boron nitride nanotubes were studied for their interaction with hydrogen halides [53]. Geometry optimization showed HF to have the highest binding energy with chemical adsorption, whereas HCl and HBr exhibited weaker, physical adsorption. Density functional calculations indicated that all three molecules provide an electrical response, suggesting that this approach could be used for gas sensing of hydrogen halides. Further research efforts are necessary to test proof-of-concept devices for detectable concentrations and selectivity.

Sensors that utilize electrochemical detection of HF gas provide the most sensitivity currently available, but the often-irreversible saturation of electrochemical reactions can limit sensors to single-use exposure events. For a fire scenario, an alarm set to sound at a desired setpoint of HF would be sufficient to prompt evacuation of an area, but may not pinpoint the HF gas, show spread, or convey potential danger based on concentration. One additional limitation of many current sensors is an inability to detect very high concentrations of HF within a very short timeframe. The detection limit for electrochemical sensors is high, but the detection time can be relatively slow – on the order of minutes. The limited selectivity of electrochemical sensors has seen improvements in recent years, particularly in the ability to differentiate between HF and HCl.

2.4 Mechanical Sensors

Mechanical bending or acoustic waves caused by chemical reactions can be converted to electrical signals for alternative forms of HF sensing. Wallace *et al.*, demonstrated that a silicon

microcantilever with a porous silicon layer showed good sensitivity to gaseous HF, particularly in humid air [54], however, nonreversible changes in microcantilever bending upon HF exposure meant that a new or regenerated system would be required for each measurement, and limits application. HF levels from 30–3000 ppm exposed to a porous silicon oxide layer were detected in stress changes of microcantilever static bending, which were recorded as voltage changes by a position sensitive detector. The sensitivity did not change when a contaminant gas, HCl, or increased humidity was mixed with the HF gas stream. Similarly, Porter *et al.*, used a piezoresistive microcantilever embedded with a keratin matrix for HF gas sensing [55]. Upon exposure, HF protonates the keratin, causing a rapid downward movement of the cantilever and increase in voltage. This response is followed by an upward deflection and reversal of the voltage for high concentrations (up to 2,300 ppm), which is likely a result of bulk diffusion and the associated chemical reaction. The overall response to HF occurred within seconds of exposure and negligible responses occur when water vapor or sulfuric acid vapor was present. One limitation of this technology is that high concentrations of HF can overwhelm the sensing layer and even small concentrations can lead to irreversible changes in microcantilever bending. Quartz-based surface acoustic wave (SAW) resonators have greater long-term stability because they do not rely on sensitive films that may degrade upon exposure to HF. Meulendyk *et al.*, evaluated a quartz-based SAW sensor for detection of HF concentrations from 1 to 18 ppm [56]. HF reacts with the quartz substrate to form SiF₄ and water, which increases the reaction rate by ionizing HF. Excess water, along with the fluorosilicic acid that is produced as a result, builds up to form a liquid layer on the quartz surface. Because etch depths caused by HF are less than 10 nm, this built-up condensed liquid layer acts as the primary sensing mechanism. Analysis of the propagating acoustic waves caused by the perturbing liquid layer allowed for determination of

HF concentration, while potential interferents, R-134a, isopropanol, acetone, and carbon monoxide, were below the limit of detection. This technology is constrained due to environmental sensitivity and maximized reactivity at low temperatures, resulting in long reaction times.

Approaches such as ion mobility spectrometry (IMS) can provide continuous monitoring for contaminants by ionizing a sample with weak plasma and allowing the ions to separate in a cell with an applied electric field. Because ions have different sizes and move at different rates, IMS can monitor a variety of compounds and indicate the presence of HF by producing its spectra. Beck *et al.*, describe an IMS sensor that detects HF from 0.5–10 ppm within a minute [57]. The system has little variability with temperature but is vulnerable to interference from other chemicals such as NO₂, HCl, or Cl₂.

Mechanical sensors have the potential for fast response times and high selectivity, but their experimental nature causes them to be a better fit for controlled environments. The rapid increase in temperature, humidity, and other contaminants that accompany a fire event may overwhelm these systems. Overall, they appear to be constrained to low concentrations of HF with irreversible changes often occurring with increased concentration.

2.5 Optical Sensors

HF determination using laser systems have become more popular in recent years due to advancements in laser diodes. Many systems use tunable diodes and near-IR (NIR) or IR wavelength lasers for HF detection where the peaks in the spectrum are highly specific based on molecular structure [58–60]. Craig *et al.*, utilized tunable diode laser absorption spectroscopy (TDLAS) to provide detection of transient variations in HF concentration at parts-per-trillion

(ppt) by volume concentrations [58]. In this method, a single-mode laser is tuned to measure one or more rotational-vibrational states of HF and the resulting spectrum is used to determine concentration via non-linear least-squares fitting to a model spectrum. The TDLAS provides determination of HF concentration within seconds at the ppt to parts-per-billion (ppb) range. Interference by other chemicals was minimal due to small absorption magnitudes at low concentration in the spectral region measured. Increased concentration of the interferents may result in inaccurate measurements of HF, due to overlap of absorption peaks. Another study by Civis *et al.*, utilized vertical cavity surface emitting lasers for TDLAS [61]. The 7568 cm^{-1} absorption line of HF at a concentration of ~ 39 ppm was detected with lock-in amplifier technique in 300 ms. Ammonia absorption spectra were shown to overlap with the HF absorptions lines; however, adjustments of operating temperature and current could improve coverage.

Tunable diode-based HF sensors have found application in measuring short-term personal peak HF exposure in aluminum smelters because of the unique ability to selectively measure HF concentrations in the presence of SO_2 ; a capability that is not provided by commercial sensor systems [62]. Due to the potential for high concentrations of HF within a short period of time, a sampling gas cell with high optical path length was used, providing detection of HF from 0.1 ppm to 1300 ppm within 2–5 seconds and had improved accuracy over the NIOSH sampling method. The disadvantage of the resulting increased gas cell length is an increased response time for low levels of HF, which could be mitigated with increased sampling flow rate. For continuous monitoring, Linnerud *et al.*, designed a gas monitor with TDLAS for detecting HF in industrial applications with fast response times and no known interference [63]. Improvements in TDLAS HF monitor portability were further explored by Skaugset *et al.*, [64]. The battery-

powered gas monitor had a detection range from HF concentrations of 50 ppb to several hundred ppm with a response time of 10 seconds. This instrument had high specificity for HF and could be combined with video exposure monitoring systems to provide visualization of exposure in real-time.

When environmentally friendly replacements for Halon were being investigated in the 1990s, experiments were conducted to determine if NIR lasers would be able to detect and measure the presence of HF in a fire scenario. NIR tunable diode laser systems were used to monitor HF gas during chemical decomposition of Halon fire suppression replacements during fire testing. Laser systems give extremely rapid detection times with low noise, which is beneficial in scenarios where HF gas is rapidly generated [65]. NIR-TDLAS can be used to measure HF at concentrations up to 5,000 ppm, using a lock-in amplifier to measure change in intensity within a wavelength range of interest. Derivative spectroscopy minimizes light attenuation caused by particulate matter, which results in stable signal intensity unless an absorbing gas is present. In the initial testing, these laser systems registered concentrations of HF gas over 2,000 ppm during fire suppression [15, 18]. Because this method does not rely on the detection of the fluoride ion, it can differentiate HF and CF_2O , which are both produced during fire suppression [15].

However, McNesby *et al.*, acknowledged the degradation of materials during the testing of these decomposition reactions due to the harsh environment being tested [15]. Furthermore, it was also noted that this technique of NIR-TDLAS had a higher detection threshold (40 ppm) than a Fourier Transform Infrared Spectroscopy (FTIR) (10 ppm) system used as a comparison.

Diode lasers have also been used to detect HF in combination with photoacoustic spectroscopy, which measures the sound produced by absorption of light [66]. Wolff *et al.*, developed a photoacoustic detection method using a single frequency diode laser for selective excitation of

HF [67]. High precision measurements of 80 ppb to 1,000 ppm HF in N₂ were achieved with the tunable laser. Tombert *et al.*, also investigated the use of photoacoustic spectroscopy with the addition of a cantilever for enhanced sensitivity of trace gases [68]. In these experiments, measurements of 5 ppt HF were achieved within 1 second, however, concentration of HF varied based on water concentration. This correlation was expected to result from decreased HF reaching the measurement cell due to adsorption onto surfaces when interacting with water. Therefore, monitoring of humidity was necessary to obtain accurate data, especially at low concentrations.

FTIR is an alternative analytical technique to measure toxic gases and has been used to assess liberation of HF during fire suppression tests with halon replacements and Li-ion battery fires. Both Andersson *et al.*, and Larsson *et al.*, used a FTIR spectrometer calibrated to measure the full spectral range of HF during Li-ion battery fires for concentrations of 18–1,245 ppm [10, 12, 13]. To detect gases produced from Li-ion battery fires, a pump drew the sample through particulate filters and into a gas cell where the spectrometer measured a spectral range from 650–4800 cm⁻¹ with a 12 second response time per spectrum [10]. Spectral bands from 4202–4203 and 4172–4175 cm⁻¹ indicated the presence of HF with Fourier Transformation processing providing concentration measurements [12, 13]. FTIR was able to detect multiple chemicals simultaneously by the signature bond stretches caused by using IR wavelengths without interference.

Similarly, Su *et al.*, investigated the use of FTIR for HF production during fire suppression tests [69]. Gas was sampled at three locations with a FTIR spectrum, covering a frequency range of 400–4500 cm⁻¹, recorded every 2 seconds. A calibration curve for HF concentration versus the intensity was determined with a least square fit for eight HF reference peaks within the range of

3600–4300 cm^{-1} . HF concentration was averaged for the three sampling locations starting 1 minute after agent discharge with concentrations reaching 1,000–10,000 ppm within a 3 minute time period for various fire suppressants [70].

FTIR gas analysis has been used successfully in determining combustion by-products and is capable of detection at low limits and high concentrations. However, FTIR has limitations in not being inherently portable (although advancement in FTIR detection have been made in this regard). Furthermore, because these FTIR methods measure IR transmission through gas samples removed from the environment, they are limited to gaseous HF and may not detect HF aerosols [48]. In humid conditions, actual concentrations of HF will be higher than that measured, due to the high solubility in H_2O , which leads to condensation of HF on the walls of the probe or particulate filters [70].

Instead of using spectroscopy to identify HF directly, detection of optical changes due to a chemical reaction has also been explored. A chemically sensitive tag was investigated by Appelhans *et al.*, for changes in polarization properties upon exposure to HF [71, 72]. HF concentrations from 1–30 ppm was detected by monitoring the reflected polarization signature from the tag, which consists of a silicon-based multilayer substrate produced by photolithographic processes and coated with amorphous titanium dioxide. The titanium dioxide reacts with HF to form a hydronium oxofluorotitanate structure. Although the presence of water vapor was shown to be essential to the reaction, the tag was selective for HF with no responses to HCl , H_2SO_4 , or HNO_3 . Additional research is required for real-time measurements and interference from ammonia on either the amorphous titania precursor or reacted film, caused by the structural similarity of ammonium oxofluorotitanate to the hydronium oxofluorotitanate phase.

Corbellini *et al.*, reported a sensor designed to detect low concentrations of HF in gas mixtures [73]. The sensor uses a plastic optical fiber (POF) made of polymethyl methacrylate (PMMA) etched with an organic solvent. The fiber is then treated with plasma-enhanced chemical vapor deposition or plasma sputtering to deposit a thin layer of glass-like material (SiO_x). The coated POF is fabricated using low-pressure plasma-enhanced chemical vapor deposition fed with tetraethoxysilane, oxygen, and argon to form a glass-like film at low temperature without damaging the fiber core. Due to the higher refractive index of SiO_x versus PMMA, the thin layer causes the fiber to have a poor transmission ratio. When HF attacks the glass, the fiber's transmission capability is altered, which is relayed for detection using a simple light-emitting diode and photodiode. This sensor has high selectivity but is nonreversible with effects cumulating on the sensor, leading to sensor saturation. As a result, applications for this sensor are best fit for total exposure measurements rather than fast responses.

Optical sensing using diode lasers or FTIR allows for detection of high HF concentrations within seconds. These methods are capable of fingerprinting specific gases and quantifying the concentration. However, overlap of absorption peaks when high concentrations of multiple chemicals are present can result in interference. In the case of diode lasers, tuning the operating parameters can reduce the impact of other chemicals on HF concentration measurements.

Another disadvantage of optical systems comes from the effect of harsh environments, such as a fire event, which may cause damage to expensive equipment, thus limiting operating life.

Furthermore, many of these methods show sensitivity to humidity, which may require additional monitoring of water content to accurately determine HF concentration.

2.6. Smart Sensors

As sensors become more commercially available and more cost effective, suites of sensors can be integrated to provide real-time actionable information. Sensors are now widely installed in buildings to track environmental conditions and hazard status, and first responders are likewise equipped with an array of sensors to track location, monitor health, and sense the surrounding environment. When combined, the data from all of these inputs provide a powerful capability to detect and characterize exposure hazards and to monitor the firefighters' physiological status and location during emergency response.

Many organizations in the fire protection community are working towards standardized sensor networks, and the need to collect, analyze, and act upon vast quantities of available data in real time [74]. To detect HF gas in an open hangar, for example, a meshed network of detectors could provide coverage for the large area. Hayes *et al.*, developed a wireless chemical sensor network that utilizes multiple colorimetric sensing nodes [75]. Within each sensing node, a chemically responsive film coated onto a PMMA window indicates the presence of a toxic gas. Upon reaction, a light sensor detects the change in light intensity and this measurement is sent to the base-station using radio frequency communication. This simple design could be implemented to cover a large space without adjusting current protective gear.

In fire events, a personal monitor worn by the firefighter coupled with an alarm system may be recommended to detect HF within an immediate area. Griessler *et al.*, describe a SnO₂ nanosensor for toxic gas detection with the potential for a smart application [76]. By incorporating a nanometer-scale metal oxide sensing layer with a microheater onto a chip, the nanosensor can communicate with a complementary metal oxide semiconductor integrated circuit. This system can then be applied to mobile phones or other smart devices. Although this sensor is designed to monitor SO₂ and H₂S, a similar method could be employed for HF

detection, such as the method by Devadhassan *et al.*, where a handheld colorimetric array reader replaces the metal oxide sensing layer [30].

One consideration of HF detection during a fire is that the sensors will also be exposed to smoke, ash particulates, and heat, which could all negatively impact the sensitivity and reactivity of the gas sensors and yield potentially inaccurate results or false positives. In order to mitigate these effects, reviews by Feng *et al.*, and Chen *et al.*, identify signal processing and machine learning techniques that have been applied to sensing mechanisms [77, 78]. They described sensor drift, which are small variations in sensor response caused by aging, temperature, or humidity, as a regression issue that can be addressed using algorithms, such as semi-supervised learning. Other signal processing techniques such as normalization, principal component analysis, or linear discriminant analysis allow for better feature extraction to improve pattern recognition from chemical fingerprints within the sensor data. After processing the signal, pattern recognition technology using Support Vector Machine (SVM), or Artificial Neural Networks can help improve accuracy by distinguishing similar chemicals and calibrating the sensor. In an example study, Zhao *et al.*, used SVM to predict a volatile analyte compound from a colorimetric array with 99.5% accuracy, although interference within gas mixtures was still challenging [41].

3.0. Summary and outlook

In the last two decades, significant advances were made in awareness of HF generation during fire scenarios, but there has not been a parallel advancement in sensor technology for specific applications. The various technologies for the detection of HF as discussed in this review are summarized in Table 1.

Table 1: Summary of HF vapor detection methods

Detection Method	Operating Principle	Advantages	Limitations	Ref.
Colorimetric	pH Indication	Capable of 10-15 second response time	Additional study for concentrations above IDLH needed (1–20 ppm measured); issues with interfering chemicals	[29, 30, 39]
	Metal Complex	High selectivity for HF	Mostly studied in solution; additional study for concentrations above IDLH, response time, and interfering chemicals needed	[31–33]
	Hydrogen Bonding	14–59 ppm HF measured; capable of being highly selective for HF; low interference	Saturation with extended exposure; additional study for response time needed	[37, 38]
	Reaction with Polymers	1–4300 ppm HF measured; 99.5% prediction accuracy	Issues with interfering chemicals; 3-minute exposure for pattern change	[41]
Electrochemical	Solid State Metal Semi-conduction	Reversible; 6.5–185 ppm HF measured; selective for HF with modifications	Response time on the order of minutes; some temperature dependency	[42–47]
	Electrochemical Cell	1–6,000 ppm HF measured; capable of 15 second response time	Additional study for interfering chemicals needed	[48, 49]
	Boron Derivatives	250 ppm HF measured; capable of 15–25 second response time	Additional study for selectivity and interfering chemicals	[50–53]

Mechanical	Piezoresistive Microcantilever	30–3,000 ppm HF measured; low interference; capable of 10–15 second response time	Irreversible; may have issues with high concentrations	[54, 55]
	Surface Acoustic Wave	High selectivity for HF	Response time on the order of minutes; maximum reactivity at room temperature; additional study for concentrations above IDLH	[56]
	Ion Mobility	Capable of response time under a minute	Additional study for concentrations above IDLH needed (1–10 ppm measured); issues with interfering chemicals	[57]
Optical	TDLAS	ppt–3,000 ppm HF measured; real-time monitoring	Damage to optics during exposure; additional study for interfering chemicals needed	[15, 58, 61-65]
	Photoacoustic Spectroscopy	ppt-1,000 ppm measured; real-time monitoring; selective for HF	Requires humidity monitoring	[67, 68]
	FTIR	Low interference: 2- 10,000 ppm measured; capable of 2 second response time	May not detect HF aerosols	[10, 12, 13, 48, 69, 70]
	TiO ₂ Tag	High selectivity; low interference from other acids	Additional study for response time and concentrations above IDLH needed (1–	[71, 72]

			30 ppm measured); may have issues with saturation or NH ₃ interference	
	Optical Fiber	High selectivity	Irreversible; additional study for response time and concentrations above IDLH needed	[73]

Electronic sensors utilizing electrochemical reactions provide high sensitivity; however, the detection time for some electrochemical sensors and potential interference may not be acceptable for fire events. Mechanical sensors allow for fast responses with high selectivity, but these sensors are best fit for laboratory environments where temperature, humidity, and contaminants can be controlled. Optical systems offer the most developed detection technique for a fire suppression scenario, providing the fastest detection time at high concentrations and are not as susceptible to failures due to overexposures. However, they have inherent cost risks in case a system becomes accidentally damaged within the harsh environment of a fire event. Unlike optical techniques that require more expensive equipment, colorimetric detection methods are typically used as a disposable warning technique, with the potential for one-time use smart sensing. Colorimetric sensors could be worn by personnel that are close to the point of fire generation for a portable detection method. Additional research into detection at higher concentrations within a short timeframe along with interfering chemicals is necessary to ensure that colorimetric methods can withstand the changing environment within a fire event. Carbon monoxide, for example, is a primary component of combustion and was noted as a cross-reactant of many of the sensor systems reviewed. Most hydrocarbon fuel fires produce carbon monoxide, but plastics and fabrics can also generate high levels of hydrochloric acid, hydrogen cyanide, and other toxic components.

A brief review of market sensors revealed numerous commercial manufacturers covering all categories of detection. This list is not intended to be exhaustive, or suggest any recommendation or endorsement, but merely representative of the market and type of COTS sensors available (Table 2). A 2014 report evaluated commercially available portable HAZMAT sensors for hazardous gases, and provided an extensive review of gas detection technologies, but found no commercial products that met first responder requirements in full [66]. Similarly, Fox *et al.*, found that colorimetric detection accounts for nearly 50% of total detection methods used by HAZMAT professionals, but these technologies are primarily qualitative [79].

Table 2: Summary of commercial detection systems for HF

Detection Method	Sensor	Manufacturer	Detectable range for HF (ppm)
Colorimetric	Gas HF detector tubes	Sensidyne®	0.17 – 30
	Dräger X-am® 5100	Draeger Inc.	0 – 30
	MDA Scientific SPM Chemcassette®	Honeywell	0.6 – 9
	Matheson-Kitagawa Gas Detector Tubes	Matheson Gas	0.17 – 30
	Chameleon® Cassette	Morphix® Technologies	3 – 15
Electrochemical	PortaSens III	Analytical Technology, Inc	10 – 200
	MGS-150	Bacharach®	0 – 10
	TARGET Multi Gas Detector	Enmet Corporation	0 – 10
	Shur-Shot™	ATB Analytics LLC	Go/No-Go
	ToxiRAE Pro	RAE® Systems	0 – 10
Mechanical	SABRE™ 5000	Smiths Detection	Low ppm range
	ChemPro100	EnviroNics USA	30

Mechanical/ Electrochemical	GDA-FR Detector Array First Response	Airsense Analytics®	5
Optical	L500 Laser Diode Gas Analyzer	OPSIS	100
	EM27/SUN spectrometer	Bruker	0–500+
	Antaris™ IGS analyzer	Thermo Scientific™	0–10 ppb
	GASFINDER3-OP	©Boreal Laser Inc.	0–250 or 4–1000
	Senscient Enhanced Laser Diode Spectroscopy (ELDS)™	MSA	Various
	O & M GasSens	Analytical Technology, Inc	0–200
	Ultima® XE	MSA	0–10
	DX4000	Gasmet™	ppb, ppm

The ideal system for fire suppression scenarios would be portable, allow personnel to confirm the presence of HF immediately upon arrival, provide situational awareness of actual concentration in real-time, receive visual warning of concentrations above the IDLH (or PEL) so that a safe concentration can be established, and ultimately be ruggedized (good storage stability, and preferably contain no batteries). Real-time concentration determination and visual warnings are key to providing first responders with sufficient and immediate situational awareness to don appropriate PPE. By continuously monitoring the air quality in real-time, the sensor may also be able to indicate an “all clear” situation when concentrations have dropped to a specific level.

While the sensors used in testing provide data in controlled test environments, it was clear that there are no current COTS HF sensors that can meet the criteria to detect high concentrations of HF vapors, monitor across very short time periods, and be portable enough for first responder

use. Gas grab sampling using either liquid impingers or sorbent tubes is the simplest technique, but only provides a snapshot of a time-weighted-average concentration. FTIR is highly accurate for real-time monitoring, but it is not readily portable and requires trained operators. Ion-selective electrodes measure HF gas, but response times are on the order of minutes, and too slow for first responder purposes. Similarly, electrochemical sensors tend to be slow in response (≥ 30 s) and have low detection range, particularly in the vapor phase. All of these techniques meet some of the requirements for HF detection from fires, but none of them meet all. The development of a rapid, sensitive, accurate, and field-portable HF sensor would have significant impact across military and civilian sectors, but currently no one technology provides a complete solution.

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