K-25

OAK RIDGE K-25 SITE

MARTIN MARIETTA

Potential Detection Systems for Monitoring UF₆ Releases

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September 1994

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MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

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ACROYNMS

ACGIH	American Conference of Governmental Industrial Hygienists
ATI	Analytical Technology, Inc.
cw	continuous wave
DIAL	differential absorption lidar
DOAS	differential optical absorption spectrometry
DOE	U.S. Department of Energy
EIT	Exidyne Instrumentations Technologies, Inc.
Energy Systems	Martin Marietta Energy Systems, Inc.
ETG	Environmental Technologies Group, Inc.
FP-IMS	fixed-point ion mobility spectrometry
FTIR	Fourier transform infrared
GC	gas chromatography
GDP	gaseous diffusion plant
HeNe	helium-neon
HF	hydrogen fluoride
IH	Industrial Hygiene
IMS	ion-mobility spectrometry
IR	infrared
IST	International Sensor Technology
Utility Services	Martin Marietta Utility Services, Inc.
MS	mass spectrometry
NRC	Nuclear Regulatory Commission
OPO	optical parametric oscillator
PGDP	Paducah Gaseous Diffusion Plant
PORTS	Portsmouth Gaseous Diffusion Plant
SERS	Stimulated Enhanced Raman Scattering Tunable Infrared
TDL	tunable diode laser
TLV	threshold limit value
TWA	time-weighted average
UF ₆	uranium hexafluoride
UO ₂ F ₂	uranyl fluoride
UV	ultraviolet

Potential Detection Systems for Monitoring UF₆ Release

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ABSTRACT

In the near future, the Nuclear Regulatory Commission (NRC) will begin to regulate the gaseous diffusion plants. There is a concern that the smoke detectors currently used for uranium hexafluoride (UF₆) release detection will not meet NRC safety system requirements such as high reliability and rapid response. The NRC's position is that licensees should utilize state-of-the-art equipment such as hydrogen fluoride (HF) detectors that would provide more dependable detection of a UF₆ release. A survey of the literature and current vendor information was undertaken to define the state-of-the-art and commercial availability of HF (or other appropriate) detection systems. For the purpose of this report, classification of the available HF detection systems is made on the basis of detection principle (e.g., colorimetric, electrochemical, separational, or optical). Emphasis is also placed on whether the device is primarily sensitive to response from a point source (e.g., outleakage in the immediate vicinity of a specific set of components), or whether the device is potentially applicable to remote sensing over a larger area. Traditional HF point source monitoring typically uses gas sampling tubes or coated paper tapes with color developing indicator; portable and small area HF monitors are often based upon electrochemical or extractive/separational systems; and remote sensing by optical systems holds promise for indoor and outdoor large area monitoring (including plant boundary/ambient air monitoring).

1. INTRODUCTION

This survey is intended to aid in determining a selective, reliable, and cost effective method for detecting UF_6 outleakages from gaseous diffusion plant (GDP) equipment, using state-of-the-art instrumentation. GDPs enrich natural uranium in ^{235}U content. Uranium is processed in the form of uranium hexafluoride (UF_6). A UF_6 release is characterized by reaction of UF_6 with water to form uranium oxyfluorides and hydrogen fluoride (HF). The currently used "smoke detectors" are similar to commonly used household detectors and respond to the presence of uranyl fluoride (UO_2F_2) particulates. Unfortunately, they have often performed poorly (e.g., visible UF_6 releases go undetected by the smoke detectors). A potential monitoring alternative to these smoke detectors is HF detection; accordingly, HF monitoring, classified into broad categories by mechanism of reaction and discussed in terms of general suitability to the application, is the primary topic of this survey. The information presented is the product of a literature search, an examination of vendor information, and a review of the present status of HF monitoring investigations within Martin Marietta Energy Systems, Inc. (Energy Systems).

Monitoring systems besides HF detection to be considered might include extractive collection of uranium particulate, as demonstrated by Bostick et al., in isokinetic sampling of UO_2F_2 aerosols,^{1,2} or improved smoke/particulate detection systems. Overall, though, it appears that HF detection will be the most selective and sensitive safety system for the GDPs. This was indicated in one study, in which four different monitors were tested for UF_6 release detection: an alpha dust monitor, an ionized smoke detector, and two HF monitors (electrochemical and thin-film electrolyte).³ In this testing, both of the HF sensors showed better sensitivity and faster response time than either the uranium alpha or the smoke detector.

Essential considerations in choosing new monitoring systems for the GDPs will include how well the method works as a safety system for protection of personnel and the surrounding environment [i.e., will the system comply with the Nuclear Regulatory Commission (NRC) requirements], whether it provides data of sufficient quality to meet this particular application, and whether the system is rugged enough for practical application and deployment within the operating GDPs. The choice of the most suitable monitoring instrument will depend on the most acceptable trade-offs between sensitivity and reliability, response time, and economics.

2. BACKGROUND

Operating GDPs handle massive quantities of UF_6 under conditions that may be above, near, or below atmospheric pressure. The UF_6 release potential in cascade equipment, cylinder storage yards, and other areas associated with the GDPs has mandated, from early times, some method of outleakage detection. In the past, GDPs have relied on visual observation and smoke detectors to detect UF_6 releases. These smoke detectors have proved unreliable and overly sensitive to ambient conditions unrelated to UF_6 releases. Recently, the smoke detectors have come under increased scrutiny due to their high false alarm rate. Hundreds of smoke detector false alarms per month have been reported at one of the GDPs. Many of these false alarms appear to be associated with the detector threshold alarm voltage that is set too close to the normal firing or discharge voltage to adequately discriminate a release. In general, the smoke detectors have inadequate sensitivity and are nonselective to the reaction products produced during a UF_6 release. Other limiting factors in smoke/particulate detection are that only a fraction of the material actually becomes airborne, and dispersion may be limited and non-homogeneous; thus, the reaction products of a release may not reach an active smoke detector.

In the near future, the NRC will begin to regulate GDPs. There is a concern that the UF_6 smoke detectors currently in use at GDPs will not meet NRC requirements for a safety system, such as high reliability, rapid response, and redundancy. Under U.S. Department of Energy (DOE) oversight, the smoke detectors are considered safety systems in those parts of the GDPs where the UF_6 process gas is above atmospheric pressure. The exact NRC requirements for the smoke detectors are unknown at present because NRC has not yet promulgated its final regulations for GDPs. However, NRC has stated a position with regard to the use of smoke detectors at the Allied and Sequoyah uranium fuel-cycle facilities to the effect that the smoke detectors are inefficient and do not provide an immediate alarm. Those facilities and Fernald have all been host to incidents in which UF_6 releases went undetected by facility smoke alarms.^{4,5} NRC's position is that licensees should utilize state-of-the-art equipment, such as HF detectors, that would provide more reliable and rapid detection of a UF_6 release, for personnel and environmental protection.⁴

The smoke detectors in the GDPs monitor cell housings, seal cavities, and other selected points throughout the process buildings. The Paducah Gaseous Diffusion Plant (PGDP) cascades are monitored by 4500 smoke detectors and Portsmouth Gaseous Diffusion Plant (PORTS) by about 1100 smoke detectors.* The ambient conditions within operating GDP facilities place some constraints and significant durability requirements for the selection of potential replacements for the inexpensive, but questionably reliable, passive smoke detection systems. Physical conditions within operating plants include operating floor temperatures of 90–100°F in summer and 70–80°F in winter. On the cell floor, temperatures are 90–100°F on the concrete, and about 140°F over the top of the cell. Inside cell temperatures are higher, at about 150°F. Currently, smoke detectors are mounted over the top of the cell, with the probe down inside and around the building outside the cell housing. There is vibration, caused by compressor and other motors in the operating facility. Typically, vibrational magnitude is <0.1 in./s, but when the plant is operating at full power, it can be as large as 0.2–0.3 in./s. Although not of as much immediate concern, storage facilities at GDPs are also at risk for UF_6 leaks. For example, the cylinder storage yards at the K-25 Site and a storage building for explosive gases at PGDP may be the source of UF_6 or HF releases into the ambient air. Monitoring problems and ambient conditions in the storage facilities are very different from those in the process buildings and may require different solutions.

*The plants are now operated by Martin Marietta Utility Services, Inc., for the United States Enrichment Corporation.

A characteristic of a UF₆ release from cascade equipment is the rapid hydrolysis of UF₆ by ambient moisture to form a cloud of very fine particulate UO₂F₂ and gaseous HF, according to the following equation:¹

Coagulation and sedimentation will cause settling of the UO₂F₂ particulates. Hydrogen fluoride gas tends to hydrate and eventually settles out of suspension (Fig. 1). The settling characteristic may prevent effective monitoring if passive diffusion alone is relied on.

Fig. 1. Concentrations in air as a function of time, following a UF_6 release.

3. URANIUM- AND PARTICULATE-BASED DETECTION SYSTEMS

One monitoring scenario is to continue using smoke or particulate detection since, from the equation, a particulate cloud is always a result of a UF_6 release into ambient air. Another possibility is to use uranium detection techniques, which might include laser-light scatter sensors, laser-light absorption sensors, and extractive particulate collection systems and air sampling for uranium.

3.1 LASER-LIGHT SCATTER SENSORS

Conventional passive photoelectric smoke detection systems sample only a small volume of ambient gas suspension within the light path, which limits their sensitivity; use of longer path lengths increases the effective sensitivity. The dimensions of the uranyl fluoride particulate are comparable to the wavelength of visible light (0.4–0.7 μm); under these circumstances, the scattered light is strongly concentrated in the forward direction (Mie-type scatter).^{1,2} Detection of light scatter over an extended beam path is relatively sensitive but inherently nonselective (e.g., vapor condensate, such as steam or hydrated HF, can also cause light scatter). However, the technique may be a good choice in an enclosed volume; Bostick and Bostick demonstrated the sensitivity of both light transmission (optical attenuation) and light scatter for the detection of UF_6 release products using a helium-neon (HeNe) laser or inexpensive near-infrared (IR) diode laser sources.⁶ Measurement of light scatter (orthogonal to the excitation beam) in ambient lighting conditions did not provide adequate sensitivity; laser-light attenuation was judged more reliable under these conditions.

Commercial instrumentation based on laser-light scatter includes the AnaLASER Advanced Technology Smoke Detection system (Kidde/Fenwell, Inc.) Unlike conventional smoke detectors that passively wait for smoke to reach them, this system actively draws in air to the detection system, which is shielded from ambient illumination. The device also includes a particle-size discriminator selected for the size range for smoke. The system can measure the rate of change in particulate count and can provide an alarm at a selected threshold level. Sensidyne's LD-Portable Laser Dust Monitor is a similar laser-light scatter system.

3.2 LASER-LIGHT ABSORPTION SENSORS

Figures 2 and 3 show portions of a high-resolution Fourier-transform infrared (FTIR) spectrum taken before and during an experimental release of UF_6 into an enclosed chamber.⁷ The uranyl ion absorption near 955 cm^{-1} (about 10.5- μm wavelength) overlaps a major lasing transition of the carbon dioxide laser, which can be used for relatively sensitive, selective detection of uranyl fluoride aerosol, with minimal interference from major atmospheric gases. However, for use in exposed beam paths, low-power lasers would have to be considered to avoid possible eye damage from accidental personnel exposure to the light beam. Low-power waveguide CO_2 lasers are available; simultaneous monitoring at two laser transitions (one at peak uranyl absorption and a reference beam at a wavelength of minimal absorption) would allow discrimination against nonspecific beam attenuation by an opaque object.

Fig. 2. Absorbance spectrum of UF_6 release into ambient air.

Fig. 3. Absorbance spectrum of pre-release humidity.

3.3 EXTRACTIVE SYSTEMS

Bostick et al. describe an apparatus that actively samples air by drawing it through a housing containing two membranes; the first one is for the collection of particulates (including uranyl fluoride), and mounted behind it is a chemically treated membrane for sorption of HF vapor (see Sect. 4.1.2 for a similar HF-only system).¹ After exposing the membranes for a given collection interval, they may be separated for off-line measurement of the uranium and fluoride ion. This configuration is well suited for ambient air sampling to give time-integrated exposure information but by nature does not give real-time measurements required for potential safety system devices. An array of similar stationary gas sampling devices has been utilized to provide concentration gradients for uranium and fluoride in ambient air during a series of controlled UF_6 release tests at a French government site; these data were collected in support of atmospheric dispersion modeling for postulated UF_6 release accident scenarios.⁸

Active sampling can be achieved by bubbling the drawn air into a scrubber liquid and measuring the concentration of constituents of interest dissolved into the solution. Powell et al. describe an on-line analyzer for monitoring uranium in vent stacks to GDPs.⁹ The system scrubs drawn air through an electrolyte solution, and uses square wave polarography to quantitatively measure hexavalent uranium concentrations; reported sensitivity for uranium using the prototype instrumentation (1985) was about 0.12 mg/mL in solution. Corresponding sensitivity to ambient air concentrations will be dependent on the flow rate of sampled air, the total sample collection time before measurement, and the volume of scrubber liquid; for the prototype system (assuming an air flow of 4 L/min and a 30-min sampling interval before measurement), the computed sensitivity for uranium in air was about 0.09 mg/m³. The time-weighted average (TWA) concentration of natural uranium in air is limited to 0.2 mg/m³. For HF, the American Conference of Governmental Industrial Hygienists (ACGIH) has set the threshold limit value (TLV)—TWA, 8h/40h, with no adverse effect—at 3 ppm when workers are present¹⁰ (Tables 1 and 2).

Scrubber-based monitoring systems can be made highly selective (depending upon the mode of detection), and can provide the means for near real-time monitoring. When scrubbing efficiency and detection sensitivity are both high, measurement can be made in a continuous-flow stream of scrubber solution to minimize the lag-time between sampling and detection; alternately, the ambient air can be scrubbed into a solution for a prolonged time, with monitoring for the rate of change in integrated concentration, indicative of a rapid concentration excursion.

In addition to electrochemical detection of uranium, other possible detection systems for use in an extractive solution phase include fluorimetric detection of uranyl ion, ion-selective electrode detection of fluoride ion, and determination of solution pH excursions with use of a potentiometric electrode or a colorimetric pH indicator system. Danchik et al. describe several systems for sampling and analysis of fluoride in potroom air and stack gases;¹¹ the most promising technique evaluated in this study was one in which soluble fluoride compounds are removed from the gas sample with a continuous gas impinger/scrubber, and fluoride ion concentration is continuously monitored with use of an ion-selective electrode.

Table 1. Health effects of UF₆ hydrolysis products

Species	Health Effect	Exposure Level*		Exposure Time
		<i>ppm × min</i>	<i>mg/m³ × min</i>	
UO ₂ F ₂ (as soluble U)	50% Lethality	2800	35,000	Indefinite
	Renal injury	99	1,250	< 30 min
		60	750	> 60 min
	No effect	52	650	< 30 min
		31	390	> 60 min
		<i>ppm</i>	<i>mg/m³</i>	
HF	Detection by smell	1	1	Indefinite
	Irritation	32	26	< 10 min
		16	—	> 10 min
	Lethal	65,000	53,000	0 to 60 min

*American Conference of Governmental Hygienists, *Threshold Limit Values for Chemical Substances and Physical Agents*, 1992–1993.

Table 2. Guidelines for indefinite exposure to airborne soluble uranium and hydrofluoric acid

Species	% of ²³⁵ U	Concentration	Reference
UO ₂ F ₂ (as soluble U)	< 18%	0.05 mg/m ³ (.004 ppm)	OSHA ^a (20 CFR 1910.1000)
	< 5%	0.2 mg/m ³ (.016 ppm)	ACGIH ^b (1976) NRC ^c (10 CRF 20)
HF (as fluoride)	—	3 ppm (2.5 mg/L)	OSHA
		3 ppm (2.5 mg/L)	ACGIH (1986)

^aOSHA = Occupational Safety and Health Administration

^bACGIH = American Conference of Governmental Industrial Hygienists

^cNRC = Nuclear Regulatory Commission

4. HYDROGEN FLUORIDE-BASED DETECTION SYSTEMS

A number of sensors are commercially available from several manufacturers of HF monitoring devices. The sensors may be made essentially equivalent in capabilities and output because they can be configured to do about anything desired (remotely alarm, digital or analog readout, portable or not, diffusion or sample draw). Available money and creativity are the only limitations.

Although there is some overlap, we have loosely classified each of the HF monitoring devices described in this survey by its major mechanism of reaction. These mechanisms are defined as colorimetric, electrochemical, separational, and optical. The first three measure a secondary event that occurs after the HF comes in contact with the sensor and are point-source samplers. The last category directly measures light absorption by HF and includes the remote (area or path) sampling technologies. Table 3 lists applicable HF detection technologies with their perceived strengths and weaknesses.

Among the earliest HF detection devices were the colorimetric methods; in these, the chemical reaction causes a color change on a paper tape impregnated with, for example, a pH indicator or in tubes coated with a reactive powder. These detection methods are still valid and useful for certain applications and are in use at DOE facilities managed by Energy Systems.

Electrochemical monitoring devices are designed so that a specific chemical reaction will cause an electrical signal. This category includes sensors such as probes/electrodes, galvanic cells, solid-state devices, thermal conductivity technologies, and polarographic cells. Some of these technologies have been investigated at the K-25 Site by Bostick et al. Others are now being studied by Branam for replacing the smoke detectors, by Ernstberger at PGDP for monitoring toxic gas storage, and by Bicha at the Y-12 Plant for the 9212 fluid beds and other locations.

The separative methods employ extraction by absorption, gas chromatography (GC), mass spectrometry (MS), or ion-mobility spectrometry (IMS) to physically separate HF from other gases in order to provide a means for selective measurement of this component.

Optical sensors detect changes in light transmission caused by interaction of the HF molecule with optical radiation. Interaction with the incident radiation is unique to the molecule and is proportional to the analyte concentration. Some optical sensors are commercially available, but in general remote optical monitoring is still under development. It is perhaps the most promising monitoring technique for large areas.

Wherever possible or applicable, fitness to the following parameters was considered in reviewing the different kinds of HF sensors: selectivity for HF, with preferably no major interferences; sensitivity to 3-ppm levels of HF (i.e., to the 8-hour TLV concentration); rapid response time at low levels of HF; good reliability and maintainability; simple calibration; ruggedness in extreme environments of high temperature, steam releases, and vibration. In addition, the probable usefulness of a device for monitoring point sources or large areas, enclosed or open areas, and areas in which people work are considered. Overall cost will be a consideration, but unit cost as quoted by vendors may not be particularly relevant here. Many of the small, point-source monitors are quite inexpensive individually but can be very costly when monitoring several thousand point sources. By the same token, costly remote monitoring units that can simultaneously or sequentially scan hundreds of potential leakpoints may be far more inexpensive per point.

Table 3. Quick checklist of HF detectors

Technique	Advantages	Disadvantages
<i>Colorimetric (point)</i>		
Tube-type samplers	Inexpensive, throw-away tubes. Somewhat specific for HF.	Very labor intensive. Sensitivity may vary with humidity.
Paper tape	Reliable, easy to maintain. Leaves real-time record.	Tape is perishable, expensive.
<i>Electrochemical (point)</i>		
Refillable electrode replacement	Sensitive, fast response time.	Requires frequent maintenance and electrolyte. Intolerant of extremes of heat and humidity.
Pop-in cartridge	More rugged than the above. No electrolyte refill.	Reduced sensitivity. Intolerant of temperature extremes.
Solid state	No electrolyte or expendables. Communicates via electronic signal. Withstands low temperatures.	Subject to poisoning. Will not work in oxygen-poor environment. Intolerant of high heat.
<i>Separational (point)</i>		
Mass spectrometry	Can be extremely specific and sensitive.	Complexity fosters unreliability. Not real time. Expensive.
Gas chromatography	Good quantification, specificity.	Can be expensive. Heated hoses are required if multiplexing a number of points through a central instrument.
Ion Mobility Spectrometry	Very sensitive, fast response time. Low maintenance. Not affected by humidity.	Expensive. Requires instrument air.
<i>Optical (remote)</i>		
FTIR	Performs well in heat and other adverse conditions. Simple to set up. Can monitor boundaries, large areas.	Interferences possible from H ₂ O, CO ₂ (dependent on resolution). Can be affected by humidity.
UV/DOAS	Short response time. Sensitive. Less interference than with IR.	Expensive (but multipoint, requiring less instrumentation than point-source monitoring).
Tunable Diode Laser	Modern devices are said to be rugged, reliable, and economical.	Requires development. Water vapor may interfere. May require shielding in work areas.
DIAL-Pulsed Laser	Can provide complete range-resolved map of pollution distribution over large areas.	Interferences from other molecular or aerosol species are difficult to eliminate. Must be shielded in work areas.
Tunable Infrared (SERS)	Multipoint monitoring.	Equipment probably relatively cumbersome; requires skill to set up and operate. Laser and SERS beams must be shielded in work areas. Requires development.
Fixed Infrared Laser	Wavelength specific for HF. Commercially available.	Promising for remote sensing over large areas. Requires development.

Source: Modified from A. T. Bacon, R. Getz, J. Reategui, "Ion Mobility Spectrometry Tackles Tough Process Monitoring," *Chemical Engineering Progress*, pp. 61-64, June 1991.

4.1 COLORIMETRIC SENSORS

Colorimetric sensors are typically tubes or tapes coated or impregnated with chemicals that develop a characteristic color when exposed to HF vapor. They are point-source monitors, rather than remote; they may be extractive (using a pump to draw in ambient air) or passive/diffusive. Colorimetric methods are traditionally used for point source monitoring for HF in ambient air. Energy Systems industrial hygiene personnel use Draeger tubes with a pump, in addition to their more recent use of electrochemical sensors.

4.1.1 Tube Samplers

Tube-type samplers include Sensidyne's Gastec HF Detector Tubes and Draeger tubes. The colorimetric tube-type monitors make use of the chemical reaction that occurs when acidic HF vapor is contacted with a trapping solution containing an indicator dye or a pH indicator, which is then measured colorimetrically. The Gastec tubes, for example, depend on a color reaction with a pH indicator.⁶ Gastec tubes "contain a selective reagent adsorbed onto a silica gel matrix. A known volume of air, containing the constituents to be measured, is drawn through the tube with use of a manual syringe pump."¹ The indicator dye in the tube changes color when exposed to acidic vapors. The tube is calibrated to show HF concentration by color migration within the tube after a specified number of pump strokes (Fig. 4).

The technology may be automated; the Kyoto HF 08 analyzer, in use since the late 1970s, may operate unattended for up to 5 days.¹² Ambient air is sampled over a 3-hour period so that the fluoride is absorbed into a solution containing the dye zirconium eriochrome cyanine R. The absorbed HF discolors the dye, which is monitored by a photocell. A rotameter measures the volume of air sampled, and the cumulative fluoride (registered on a chart recorder) divided by the volume of air gives the HF gas concentration.

It has been shown that extremes of temperature (outside 40–120°F) or humidity (below 50% and above 90%) can cause Draeger and Gastec tubes to read too high or too low.¹³ The variance in the referenced tests was especially high in tests for CO₂ and CH₂O (HF was not tested).

An advantage to the tube sampler colorimetric method is that the material cost per sample is low; however, the overall cost may be relatively high if many samples are required. A disadvantage is that the tubes are very labor intensive when manual pumping is employed. Although it can be adapted, the method is not well suited to continuous area monitoring when, as now, other more easily employed methods might be used. Colorimetric tube sampling is not applicable to automated safety systems with rapid response.

4.1.2 Paper-Tape Samplers

Paper-tape samplers are an accepted monitoring method for ambient air fluoride detection and are commercially available. A chemically reactive film coated on the paper-tape base support will change color when exposed to HF.¹⁴ The sampler may be single- or multi-point, alarmable, and portable or wired to a remote location. They are very easy to maintain, but the tapes are perishable, lasting two weeks opened or fewer than six months sealed. Results in the field have varied, with sometimes "considerably more" operator attention required than was originally planned.¹² The tapes are sensitive (to around 1 ppm or lower) and selective for HF. The monitors are useable in ambient temperatures: 14–104°F, according to one manufacturer. They are expensive, however. Single-point monitors cost about \$4000 per point. The tapes, at \$35 each, are a continuing operating cost; the manufacturer claims each tape lasts one week in use, but in fact, an entire cassette may be consumed in less than 24 hours if any significant HF is present in the sampled gas.¹⁵ Manufacturers include MDA Scientific, Inc., and Bacharach/GMD Systems, Inc.

Fig. 4. Colorimetric tubes after HF sampling.

The MDA paper-tape system is used by Energy Systems in several locations. The Y-12 Plant Industrial Hygiene (IH) Department uses a model TLD-CK, a single-point, continuous monitoring, portable, direct readout instrument. It weighs about ten pounds. The same box can be used for any of about forty different chemicals by changing the tape and the "key". The IH paper-tape sampler is used to monitor their laboratories and to investigate any spill or leakage of HF. It can be left in place and programmed to give a TWA concentration, if desired.¹⁶ MDA model SPM-CK paper-tape HF monitors are also in place at the Y-12 Plant but not yet in use for facility safety/ambient air monitoring. These are single-point monitors much like the TLD model but for more rugged applications. These monitors will be evaluating very low levels of HF and will be set to alarm at less than 1.5 ppm. The users will depend on manufacturer calibrations.¹⁷ At the K-25 Site cylinder storage yard, a section of colorimetric tape is affixed to a card that is enclosed at the valve location of each cylinder in a Teflon bag, with a twist tie around the valve stem¹⁸ (Figs. 5 and 6). A control piece of tape is sealed in a clear plastic envelope and attached to the card for comparison. The entire apparatus is covered with an opaque plastic bag, to protect the tape strips from sunlight and deterioration. The tapes are checked weekly and replaced if a positive response is seen. Three sequential positive responses are taken as evidence that a leak exists at that point.

This system, in this application, is not so much quantitative as it is qualitative. A portable paper-tape monitor is used to test the cylinder yard ambient air and for quantitative verification at the valves. Two portable toxic gas detectors were tested and compared for the purpose. Of those, the MDA Scientific model TLD-1 was judged to be more responsive and require less operator involvement than the Sensidyne SS2000 model. Reliability in the field is still under investigation.

Fig. 5. Sampling tape affixed to cylinder valve.

Fig. 6. Comparison of an exposed tape and a control.

In a non-colorimetric application, paper-tape separative samplers were used near an aluminum smelter to monitor ambient air.¹⁹ The samplers had two separate impregnated tapes automatically drawn from reels between the sampling blocks at a preset timing interval. The upper tape, impregnated with citric acid, collected particulate matter, while the gaseous fluoride passed through to the second tape where it was absorbed by the impregnated caustic soda. The tapes were collected at infrequent intervals and analyzed in the laboratory by specific ion electrode after elution. The fluoride concentration was determined by dividing by the volume of air samples (2.5 m³ maximum).

4.2 ELECTROCHEMICAL SENSORS

Electrochemical HF sensors operate by allowing extractive or passive diffusion of the gas of interest through a semi-permeable membrane barrier into an electrolytic cell or, if the instrument is solid state, through a semiconductor type of material where the electrochemical reaction causes a measurable electromotive force. A portable electrochemical sampler with a pump (PortaSens) is used at PGDP for industrial hygiene monitoring prior to personnel entry into an area. This particular configuration is not appropriate for remote monitoring; however, continuous monitoring with an average concentration readout is possible. PortaSens is similar to other electrochemical monitors in its sensitivity (0–20 ppm HF), response time (5–10 min), and response to other gases as interferences.

Electrochemical sensors have in common a probe, positive and negative electrodes, a microporous permeable membrane and electrolyte or a crystalline solid, and electronics for transmitting data. They are readily available commercially as “off-the-shelf” merchandise. Depending on the manufacturer and customer preference, the equipment can be single point or multi-point, portable or not. It may extract air samples, or it may detect by passive diffusion. Some require periodic replenishment of the electrolyte solution, some have self-contained electrodes with replaceable cartridges, and some are of solid-state materials that require no direct maintenance. Manufacturers include Sensidyne, Inc., Exidyne Instrumentations Technologies, Inc. (EIT), International Sensor Technology (IST), Analytical Technology, Inc. (ATI), and ENMET Corporation. Some of their products are discussed in this report.

The electrochemical instruments are very sensitive to high heat. They operate within ambient temperatures, [23–104°F (Sensidyne) and –13–122°F (EIT), according to their vendors]. Selectivity seems moderately good; however, the sensors can respond to other gases such as HCl, Cl, SO₂, Br, NO₂, and O₃. In the presence of steam, condensation may plug the permeable membrane (or coat the material, in the case of a solid-state probe) and hinder passage of HF to the electrolyte.²⁰ Electrochemical sensors are appropriate for point monitoring in ambient air, where temperature and relative humidity are kept within bounds (the electrolyte solution is susceptible to freezing or drying) but may not be most appropriate for use in detecting UF₆ hydrolysis products in the cascade buildings due to the high temperatures and the occasional presence of steam. The passive diffusion type of monitoring instrument could have distinct disadvantages because of the settling characteristic of hydrated HF (Fig. 7).

4.2.1 Refillable Electrode

The electrochemical device with refillable electrode is exemplified by Sensidyne’s HF Alert unit, in which acidic HF vapor diffusing through a microporous, hydrophobic Teflon-like membrane into the electrolyte solution causes a galvanic response. An intensive evaluation of the Sensidyne system was performed at the K-25 Site by Bostick et al. in the mid-1980s.²¹ The study evaluated response time, interferences, and calibration method. Response time is rapid (seconds to minutes). In Bostick’s Sensidyne studies, the time required to reach 50% of the equilibrium response ($t_{1/2}$) for a change from clean air to 3-ppm HF ranged from 7–42 s, depending on the membrane assembly. The vendor claims 10 s for 5 × TLV. Calibration is required often and is user intensive. The stated temperature range

Fig. 7. Effect of forced convection of HF within chamber.

within which the instrument operates is 23–104°F, and the relative humidity range is 20–90%, non-condensing.²² W. J. Bicha tested the monitor at Fernald and concluded that it consumed more than its share of maintenance resources. The Sensidyne sensor has a very delicate membrane producing its fast response; it is fragile, difficult to maintain, and the electrode must be refilled often.¹⁵ H. G. Ernstberger, at PGDP, likewise rejected use of this type of monitor in view of its “anticipated recurring maintenance”.²³

4.2.2 Cartridge

EIT’s “SensorStik” is an electrochemical monitoring device incorporating a fully sealed and weatherproof sensor containing the electrolyte (with snap-in cartridge replacement sensors) and encapsulated microprocessor electronics. Ernstberger has been testing the EIT and ATI cartridge-type instruments for HF detection in the PGDP C-350 toxic gas cylinder storage area. Laboratory testing of the EIT’s SensorStik and ATI’s similar unit at PGDP, in the 0–25-ppm HF range, showed a sluggish EIT response time of 15–60 min. ATI’s unit was somewhat more responsive than EIT’s. Both units did respond to all levels of HF between 3 and 25 ppm. Both also responded to chlorine in laboratory calibration tests,²³ but calibration will be a concern regardless of which monitoring technique is chosen, if the monitoring is for HF; and though some vendors say their instruments can be calibrated using HCl, it is not recommended by either Armstrong or Bicha.^{24,15}

The laboratory data showed no zero shift on either model, indicating reduced likelihood of false alarms.²⁵ Both are now being field tested at PGDP, and have been in the field for about two months with essentially no problems. An EIT sensor similar to the current SensorStik model (slightly more cumbersome) was tested for HF by Bicha at the Y-12 Plant dry chemistry area in 1988. The response time was “extremely slow”, about 1/2 hour.¹⁵ Bicha is now in the process of testing the more recent EIT model for use in “areas scattered throughout” the Y-12 Plant, including the 9212 Fluid Bed—a hot, dusty area, expected to be contaminated with nitric acid mist. To date the response times recorded have not borne out vendor claims: response time is less than 60 seconds at 3-ppm HF, according to the vendor;²⁶ but Bicha feels the EIT sensor is sensitive enough without being too delicate.²⁷ The EIT instrument has a very slow response time in comparison with Sensidyne; however, it is much more reliable and easily maintained. Although only laboratory testing has been done to date, field testing of the EIT instrument will begin soon and should be completed in several months.

Bicha is in the process of installing these in both no-flow (ceiling mounted) and flow (in ductwork) situations. The sensor/transmitter is said to operate in ambient conditions of 16°F (–13°F, according to the vendor) to 122°F and 10 to 95% relative humidity. The sensitivity of those instruments undergoing tests is 0–10-ppm HF; however, lower sensitivity/higher range instruments are available. These instruments may require more testing with regard to selectivity. A similar membrane and electrolyte detector for HF is manufactured by the ENMET Corporation. It is apparently not currently being tested by anyone at Energy Systems but according to the vendor it incorporates a two-wire design to provide stability, has a 60 to 90 second response time at 1 ppm HF, and is subject to interference from HCl, Cl, SO₂, and other acid gases.^{28,29}

4.2.3 Solid-State Electrode

The IST-type “solid-state electrode” (crystalline solids, no electrolyte, communicates via an electronic signal) is being investigated to replace the existing Utility Services smoke detectors at Paducah and Portsmouth.³⁰ It has been field tested at PDGP.²⁰ The IST sensor probe contains two metal wires embedded in solid-state material. The probe is encased in a sintered stainless steel housing for physical protection. Sampling is by diffusion (heat convection), but pumps are available. The unit operates at low heat, thus does not “burn out”. The solid-state sensor is not damaged by 100% gas concentrations.³¹ Its life expectancy is up to 10 years, according to the vendor. A disadvantage to the

solid-state sensor is that it clogs from steam and water vapor. Capital cost for IST solid-state single-point HF monitoring is quoted at \$1180/point for up to 250 sampling points.³⁰ To equip all of a GDP's points, the cost per point would probably be somewhat less.

Unfortunately, the solid-state device is, as are the other electrochemical sensors, intolerant of sustained high heat. Solid-state monitors may be able to withstand short heat ventings such as the quick bursts of steam (up to 250°F) that occur in the autoclave areas, if they are not plugged by the steam. Also, the solid-state instrument is better suited to cold weather work than a liquid electrolyte type. Some of the autoclaves at GDPs are on a porch where winter weather might freeze liquid electrolyte solutions.

The IST solid-state system can be wired to remote monitoring controls via existing electrical wiring. It can act as an alarm. The typical full-scale sensitivity range is 0–20-ppm HF, although other ranges are available. Branam's tests will be with the 10–200-ppm HF sensitivity range monitors. He will examine sensitivity, response time, reliability, heat tolerance, and ease and frequency of calibration. (According to the vendor, calibration is easy. The instrument has good "zero stability" and is not affected by ambient temperature ranges or by sensor position.³¹)

Other tests, lab and field, have been performed on the IST semiconductor type sensor by Ernstberger at PGDP. He found that it drifted, with initial satisfactory sensitivity to HF but eventual sensitivity to water vapor with concurrent false alarms. Therefore, this sensor was not recommended for the C-350 replacement corrosive gas leak system.²³

4.2.4 Photoelectric

A variation of electrochemical detection is provided by ETG's "Shur-Shot" photoelectric detector with fiber optics. Detection is based on the reaction of HF with a coating on the sensor chips. As the coating is eaten away, light intensity to the monitor increases, causing an alarm at the specified level (the \$50 sensor chip must be replaced after an alarm). The vendor says that the HF Shur-Shot is "ideally suited for the leak monitoring of flanges and pump seals... or in any application where massive leaks of HF are at risk."³² Although this method might virtually eliminate false alarms, it is optimized for the detection of large concentrations of HF. The sensor end must be placed at the leak location, for a leak to be detected. The instrument can operate in temperatures as low as -40°F and as high as 185°F.

4.3 SEPARATIONAL SENSORS

The separative methods physically separate HF from other gases in order to provide a means for selective measurement of the HF. These methods include GC, MS, and IMS. MS and GC are well known and accepted laboratory analytical methods that are not easily portable and are not readily adaptable for use as a safety system. An economic and safety consideration of these or other analytical laboratory methods is that HF is a corrosive gas, requiring special chemically resistant components in the sampling and analytical system, which increases the cost and complexity of the equipment.

4.3.1 Fixed-Point Ion Mobility Spectrometry

Fixed-point ion mobility spectrometry (FP-IMS), "small, rugged, and dependable cells",³³ is commercially available from Environmental Technologies Group, Inc. (ETG), Sensidyne, Inc., and possibly other companies as well. Ion mobility spectrometry can provide continuous point monitoring in an industrial environment.

IMS works on the principle that ions of different sizes move at different rates through an electric field so that when each substance is ionized, it will have a unique mobility. In IMS a sampling pump

pulls ambient air past a semi-permeable membrane that passes the material of interest. The sample is ionized by reactions with a weak plasma and allowed to drift through the cell under an applied electric field. The ions separate in the drift tube, arriving at the detector according to their charge and mass. Figure 8 illustrates the process. One instrument can, with the appropriate adjustments, monitor hundreds of compounds and produce their spectra (Fig. 9 from Ref. 33 with permission). The analyzer is temperature controlled, with very little variability due to ambient temperatures. As used at an oil refinery, specifications were for a detection level of 0.5–10-ppm HF, with an accuracy of ± 0.5 ppm. Also specified were the ability to operate in 0–100% relative humidity and a total weight of less than fifty pounds.³⁴ After a one-year trial of FP-IMS, the refiner ordered 27 more IMS units to replace their “typical” electrochemical detectors.

According to vendor information, the operable temperature range extends from -40 to 122°F (the instrument could be set to operate at 140°F , if necessary³⁵), sensitivity is to 0.1 ppm, the response time to 4-ppm HF is 30 s, and response time to 10-ppm HF is 5 s.³⁶ The vendor states that the instrument is very easy to maintain, with no expendables and factory-set calibration. It has no zero drift and requires a 10-min recalibration every six months using a clean air sample and a calibrated source of the target gas. Interferences occur when NO_2 , HCl , or Cl_2 are present, but there is no interference from water, NO , or H_2S . Disadvantages are its cost ($\$15\text{K}$ – $\$20\text{K}$ per unit³⁵) and that it requires instrument air for cell operation.

4.4 OPTICAL REMOTE SENSORS

Optical sensors/absorptiometric methods [ultraviolet (UV), Vis, X-ray, IR, lasers] work because the chemical species of interest interacts with electromagnetic radiation, diminishing the intensity of the radiant beam at characteristic wavelengths. When this decrease in power is measured, concentration of the analyte may be determined. Optical spectroscopy may be the most promising of all the HF detection techniques, for the GDP monitoring needs. It is particularly appropriate for large areas of large process buildings. Remote sensing of atmospheric trace gases has several advantages over point measurement or extractive measurements on an air sample.^{37,38} Optical remote sensing does not require active air sampling, and it can probe inaccessible regions or regions otherwise difficult to sample. The optical methods can provide long path-averaged concentrations, rather than only individual point measurements. Response time can be short (seconds or minutes) for the remote technologies. The various laser techniques allow determination of the mean value of pollution concentration not only over a certain path length but also over a certain area or volume.³⁹ Disadvantages may include cost of the instruments and operator training required; spectral interference, which can be severe, from ambient gases [e.g., water vapor, CO_2 , and O_3 (see Fig. 10)]; incompleteness of the spectral database, to date; inavailability of an appropriate laser source; and minimum detectable concentrations may not be adequate for the application. It should be remembered that programs using point samplers with an associated analytical procedure can be very costly if an attempt is made to match the spatial and temporal coverage, which is easily achieved by the optical sensors. If HF is probed in the 2.4 – $2.5\text{-}\mu\text{m}$ frequency range (one that is difficult to access), spectral interference from ambient water vapor may be avoided. There are two commercially available lasers that operate in this selective region. One is the optical parametric oscillator (OPO) and the other is a solid-state laser that utilizes a Co:MgF_2 lasing medium, which is optically pumped. Two other lasers identified by the literature search, a continuous wave (cw) chemical-HF laser⁴⁰ and a modified HeNe laser operating on a lasing transition coincident with an HF rotational level,⁴¹ are probably impractical due to several unique aspects of the UE problem (see Appendix A).

The optical remote sensors may be placed in two different classes: (1) spectrally broad-banded FTIR and UV, which are both open-path spectrometers and (2) monochromatic [laser long-path absorption and differential absorption lidar/(DIAL)].³⁷ Optical techniques discussed here are the FTIR

ION MOBILITY SPECTROMETRY

Theory of Operation of IMS Cell

Fig. 8. IMS schematic.

Fig. 9. Three-ppm HF negative ion mobility spectra. Source: A. T. Bacon, Environmental Technologies Group, 1400 Taylor Ave., Baltimore, Md., 21284-9840, Paper #258: *Ion Mobility Spectrometry: A New Method of Monitoring for Hydrogen Fluoride, Ammonia, and Other Industrial Gases.*

Fig. 10. Atmospheric transmission as a function of wavelength.

spectrometer; differential optical absorption spectrometry (DOAS) in the UV, IR, and visible ranges; laser long-path absorption technique, including tunable diode lasers; and DIAL.

Fiber optics are sometimes combined with optical techniques, to give an increase or change in sampling locations (the fibers may be attacked by HF; one option is to protect the sensor end with sapphire or with a resistant fluoride coating, such as CaF_2).²⁹

4.4.1 Stimulated Enhanced Raman Scattering Tunable Infrared

The Stimulated Enhanced Raman Scattering (SERS) emission from optically pumped heat pipes holds promise for HF detection. It has the ability, with other pumped laser sources, to operate at high-output energy levels. Research was begun at the K-25 Site on this technology but was interrupted in 1987.

The basis of the SERS tunable IR process is described by Stockdale in detail in Appendix B. Briefly, it is as follows:

- A beam of monochromatic light input through a gas or vapor may produce Raman scattering.
- When the input is a laser of sufficient intensity, the Raman emissions can take on laser-like properties.
- Output Raman pulses of duration similar to the input laser are produced.
- With appropriate tuning near an allowed ground-state transition of the Raman medium, the Raman radiation becomes much stronger and is said to be "enhanced".

In the proposed process, using tunable IR produced by SERS, laser light is passed through potassium metal vapor in a pressurized, gas-filled, heated tube called an optical heat pipe. The ends of the tube are cooled, and a wick moves the cooled and condensed metal vapor back to the heated center for re-evaporation. Thus, metal vapor is always suspended in the laser-light path, and the end windows are kept clear. In order to use the SERS emission from the tube to detect HF through absorption, the SERS frequency must match a strong HF absorption line. The best match is with the HF P(6) absorption line at 3694 cm^{-1} ($2.7\text{ }\mu\text{m}$). This requires laser input to the heat pipe at $\sim 405\text{ nm}$, which appears difficult to reach with available laser dyes, but may be most easily accessed with a dye laser pumped by a XeCl excimer laser.

Equipment to monitor HF using the SERS method would require a pulsed pump laser (YAG with third harmonic capability, XeCl excimer, or nitrogen laser), a tunable dye laser, an optical heat pipe, optical path elements, a detector (probably a simple germanium diode), and all necessary electronics and power supplies. The system would be relatively cumbersome and would require considerable skill to set up and operate. If the output SERS beam were split and conveyed by fiber or reflectors to a number of remote monitoring sites, such a system might become attractive. In a plant environment it would be necessary to take precautions to shield laser and SERS beams in work areas.

4.4.2 Fourier Transform Infrared Spectroscopy

FTIR spectroscopy is an efficient, commercially available technology. The vast majority of molecules (those with dipole moments) absorb in the IR spectral region; an FTIR is capable of simultaneous detection of multiple gases because it measures all the applicable wavelengths of the spectrum simultaneously (cf. Fig. 10). Monitoring by remote sensing or open path-length technology employs the same principles in the field as are used in the laboratory:

- As an IR beam is projected through a sample, the energy of the light excites the molecules and a portion of the energy is absorbed.

- A reflecting mirror returns the beam to a photoelectric detector that determines how much energy is absorbed in the IR spectral region.
- Each molecule has a unique fingerprint, detectable by the instrumentation.

The information acquired is qualitative, quantitative, and in real time. Generally, information is obtained through IR absorption spectra, but, if the atmospheric area in question is significantly higher in temperature (i.e., aircraft exhaust, stack gas emissions), IR emissions may be studied against the cold sky background.

One manufacturer, ETG, who purchased the FTIR business of MDA Scientific, Inc., claims an FTIR sensitivity for HF of as low as 0.2-ppm path-integrated concentration (the sensitivity is path-length dependent). Open-path length is up to 650 meters one way; thus, FTIR can monitor a large area. Interferences occur from steam/H₂O and CO₂, but they may be minimized by using higher resolution scans. Some units do not require passing the beam through a cell; several units are available at the Y-12 Plant. Set-up or take-down of the equipment is uncomplicated and can be completed in less than 30 minutes. FTIR technology is commonly used in monitoring organic (VOC) emissions,^{42,43,44} but it has also been used as an HF monitor. It performed well at an aluminum smelter, despite heat, particulates, and strong magnetic fields.⁴⁵ The cost of an FTIR remote sensor system, including the FTIR interferometer, telescope, retroreflector, and computer cabling, starts at \$98,500, according to one vendor.⁴⁶ It is possible to multiplex the instrument to sequentially monitor several areas by directing an external beam to a series of retroreflectors (retroreflection doubles the effective path length and returns the beam to the fixed detector). Unlike many laser optic systems, expanded beam IR does not represent a significant eye hazard.

4.4.3 Differential Optical Absorption Spectrometry

UV (absorbance) DOAS is used in the UV and visible spectral region. It is useful for molecules having weak or no IR absorption spectra, or those which are subject to severe background interference in the IR region.³⁷ The technology is commercially available through companies such as ABB Power Plant Controls, which sells a system it calls OPSISSM.

In the OPSISSM UV DOAS Monitor, a high-pressure xenon lamp emits a focused beam of light down a path. Any HF or other selected molecules (computer software for the desired spectra is factory installed) in the beam will absorb light at the appropriate wavelength, causing the outer shell electrons to become excited. At the end of the measuring path, a spectrometer evaluates the amount of light absorbed along the path and calculates the molecule's concentration in the beam.⁴⁷ An OPSIS ambient air continuous monitoring system for measuring HF was installed inside an aluminum smelter in Norway in October of 1993 and has been operating "very well" since then.⁴⁸ Measuring equipment was mounted in the ceiling in such a way that the light path covered an area where gas concentrations would be representative (OPSIS uses fiber optics to define a path). The data terminal equipment, including a monitor for continuous observation of measured values, was set up in a laboratory. A path-averaged HF concentration as a function of time is provided (Fig. 11). The detection level for HF was as low as 0.1 mg/m³ or 0.1 ppm.⁴⁹ Response time was short, providing real-time information. Interferences from other gases that absorb light in this wavelength range are seen and adjusted for by the computer software (a reference spectrum is stored in the computer's memory).

The estimated cost for a DOAS system to monitor for HF and one other spectrum (Hg, for example) is \$140 thousand.⁵⁰ That figure includes the analyzer with two spectra installed and calibrated, transmitter/receiver, power supply, fiber-optic cable, and a remote computer workstation and software.

Fig. 11. OPSIS chart, showing HF average path concentration as a function of time.

Source: H. Nes, Elkem Aluminum Mosjoen, Sweden, *OPSIS Multi Gas Analyzer; Testing and Assessment of Measuring Equipment*, letter report, Aug. 24, 1992.

4.4.4 Laser Long-Path Absorption

Laser long-path absorption may use cw or pulsed lasers. This and laser power determine the path length obtainable. Laser spectroscopy for HF detection is under development and available at the research level but is not yet available commercially. The applicable spectral region for selected laser systems is illustrated in Fig. 10.

Different types of laser long-path absorption techniques exist. Among these are the CO₂ laser system (see Sect. 3.2), the tunable diode laser (TDL), and the "neutral gas lasers" HeNe and HeXe. The laser lines exist to extend the technique to HF using neutral gas lasers. The most sensitive laser for HF detection is the HF laser itself.⁵¹ Transition lines from the excited to the ground state coincide with the HF absorption lines in an optimum way.⁵² However, Armstrong states that this laser may be impractical for UE safety systems (see Appendix A).

Laser spectroscopy can monitor longer distances than IR, and open-path spectroscopy may be ideal for off-site monitoring in ambient air. Eye safety is of concern in most laser optical technologies when used in enclosed spaces where people work, but atmospheric monitoring at altitudes above the heads of workers or through pipes which contain holes to allow the gas to enter would pose few difficulties. Laser technology for HF monitoring is not yet commercial; the technique might require operator attendance and be labor intensive.

4.4.5 Tunable Diode Laser

A variety of near-IR diode lasers are available in the vicinity of 1.3-microns wavelength, at which it should be possible to detect the first overtone band of HF with fine tuning (the chemical composition of the TDL determines the coarse tuning range; temperature and current determine the fine tuning range). Stockdale describes the process in Appendix B. Without experimentation, the sensitivity obtainable is presently a matter of speculation.

Recently, S. Allendorf of Sandia National Laboratory at Livermore reported first results of a diode-laser-based absorption system that is aimed at providing a rugged, reliable, and economical means for continuous monitoring of certain stack emissions.⁵³ This method may hold promise for HF detection. Several important factors need to be considered. The band of HF detectable in this wavelength vicinity is much less strong than the fundamental, and parts of the water vapor spectrum may interfere with the HF absorption. Very good temperature and current control is necessary; the laser diode must be kept at a stable temperature. Nevertheless, the potential advantages of a diode-laser-based detection system in terms of simplicity, specificity, reliability, and relatively modest cost indicate that this option should be considered further.

4.4.6 Differential Absorption Lidar

DIAL "uses the atmospheric backscatter for a pair of transmitted laser frequencies to make range-resolved measurements of molecular species concentrations when the lasers are pulsed."³⁷ Unlike other laser methods, this one gives the range-resolved profile (i.e., background atmosphere) directly. The differential absorption technique can be used to obtain a complete range-resolved map of the pollution distribution over large urban or industrial areas. In production facilities, it could detect leakages in the process.

The DIAL laser system may be an Nd:YAG pumped dye laser, an excimer laser-pumped dye laser, or, less often, a CO₂ laser system; each of these systems pose potential eye hazards. Operation of the CO₂ laser system is complex because it requires the existence of sufficient aerosol in the atmosphere so that useful backscatter is obtained (other DIAL systems need only molecular backscatter). Interferences from other molecular or aerosol species are more difficult to eliminate in DIAL systems than with the FTIR.

A DIAL laser system using a pulsed CO₂ laser was utilized to detect and map water vapor from a cooling tower and the ethylene distribution over a refinery.³⁹ DIAL is appropriately used for 3-dimensional remote mapping of atmospheric constituents.

5. SUMMARY AND CONCLUSIONS

A variety of detection technologies exist for monitoring UF_6 releases in the gaseous diffusion plants. The possibilities include (1) uranium- and particulate-based detection systems (light-scatter, laser-light absorption, and extraction systems using separation on a membrane or in a scrubber solution, as well as the current smoke detectors), and (2) HF detection systems, which encompass both point-source sampling (colorimetric, electrochemical, or separational) and path sampling (optical) technologies.

Each of the types of detectors discussed may be useful and practical for certain situations. In the cascades, it is conceivable that the best solution will be to monitor all seal cavities per cell with one of the sturdier point-source detectors in combination with fiber optics and to simultaneously monitor the building ambient air using a remote optical technology. In resolving the issue, installation costs, maintainability, and required operator attention will be significant considerations. Stringent health physics and industrial hygiene restrictions on personnel working on the cell floor may influence the choice of instrument used. Because of limitations on time spent in the cell and frisking requirements, instruments requiring frequent or prolonged operator attention will significantly increase monitoring costs.

We recommend a survey of specific applications, special requirements for each, number of instruments required, rough costs, etc., to help in narrowing the scope for further studies and in matching instrument characteristics to specific requirements.

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Appendix A

LASER TECHNIQUES FOR HF MONITORING

by D. P. Armstrong

May 29, '94

Dianne Beck
Bill Bostick
Lee Trowbridge

re: Laser Techniques for HF Monitoring

As per your request, I have examined your draft literature search on the broad topic of HF detection/monitoring. My comments are addressed primarily to the area of laser techniques. The two basic ways to detect HF would involve measuring optical absorption by the HF species or measuring some other chemical property of either the HF or a species which reacts with the HF. The search shows quite clearly that the majority of HF monitoring techniques involve measuring some secondary event that occurs after the sensor comes into contact with HF (e.g., electrochemical changes, colorimetric changes, etc.). The laser techniques that were identified involved the use of a "modified" HeNe laser operating on a newly reported lasing transition which was coincident with a HF rotational level (in the vibrational ground state) and of an actual CW chemical HF laser. There are several important and unique aspects of our problem with HF monitoring which make these two methods impractical, if not impossible; consequently, they are removed from serious consideration. I have spoken with Dr. Stockdale and he has reported to you on the prospects of using the SERS emission from optically-pumped heat pipes for absorption spectroscopy. This technique holds promise; however, our research program on this was interrupted in 1987 and to revitalize it would essentially mean starting over again, from the table up. John has also communicated to me that he will provide you a memo covering the topic of the possible use of diode lasers for this application; hence, I will not address this issue either.

To avoid spectral interference from ambient air HF must be probed in the 2.4 to 2.5 mm frequency range, which is one that is difficult to access. To my knowledge, there are presently only two commercially available lasers which can operate in this spectral region. One is the optical parametric oscillator (OPO) and the other is a solid-state laser which utilizes a Co:MgF₂ lasing medium which is optically pumped. Regrettably, neither of these lasers is available in my laboratory. The actual detection of HF is not particularly difficult on

the lab scale; however, the unique problems associated with the UE business make the detection of HF a very complicated problem. To replace the ailing smoke detectors in the cascades involves monitoring at each seal cavity (a "point source"), and at selected points throughout the process buildings. In addition, there seems to be a desire to monitor at autoclaves and at cylinder yards. Monitoring cylinder yards for trace levels of HF is a virtually hopeless situation. The cost and complexity of a suitable monitoring scheme would make it unattractive, as the situation in the yards presently exists. Rather than attempting to monitor airborne HF optically, a more plausible approach is to monitor the "point source" (the cylinder valve) by encasing or enclosing it. This is described elsewhere in this report. A breached cylinder would eventually deposit HO_2F_2 on the ground. A device to measure the fluorescence of HO_2F_2 specifically could be used to monitor the ground around the cylinders. Monitoring in this fashion would be a much more effective method. An effective optical scheme, if one could be devised, could be completely negated if wind direction moves the HF out of the sample path. Dr. Bostick had described in his earlier works the use of light scattering techniques for detecting the "smoke" which accompanies a UF_6 release, and this would have to be considered as one of the front-running candidates for the autoclave areas. For the process buildings, detectors for point sources could involve optical, secondary, or a combination of both techniques, but this is an unanswered question since there has never been a dedicated development effort to address the problem. Compared with other methods, I would consider that a clever laser technique has a better chance than most of the other techniques (particularly if it involves monitoring large areas of large process buildings), and this certainly is worth looking into if a suitable light source were to become available. Of course, without hard data we are all just speculating anyway. It seems highly likely that eventually the interested parties will want a quick answer to a very complicated problem, and, predictably, that probably cannot happen.

D. P. Armstrong

Appendix B

**HF DETECTION USING TUNABLE INFRARED/SERS TECHNOLOGY
OR TUNABLE DIODE RADIATION**

by J. A. D. Stockdale

I N T E R O F F I C E M E M O R A N D U M

Date: 08-Jun-1994 01:35pm EDT
From: John A Stockdale
STOCKDALEJA
Dept: 1320
Tel No:

TO: BECKDE1

CC: ARMSTRONGDP BOSTICKWD LDT VANCEJM

Subject: HF Detection

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Detection of HF using Tunable Infrared Produced by Stimulated Enhanced Raman Scattering (SERS) of Laser Light in Potassium Vapor.

When a beam of monochromatic light is transmitted through a gas or vapor additional frequencies may be observed in the transmitted beam and in scattered light. Some of these frequencies correspond to the input frequency plus or minus multiples of known excitation frequencies of the atoms or molecules of the scattering medium. This phenomenon is called Raman scattering, after its discoverer. The "minus" frequencies (red shifted) are called the Stokes frequencies, while the "plus" frequencies (blue shifted) are called anti-Stokes. When the input beam is a laser of sufficient intensity the Raman emissions can take on laser-like properties and become narrowly collimated in the forward and backward directions. Particularly with intense pulsed laser input the Raman emission can occur in a stimulated manner analogous to the lasing process. Output Raman pulses of duration similar to the input laser are produced. When the input laser is tuned in the vicinity of an allowed quantum transition of the medium from its ground state the Raman radiation becomes much stronger and is said to be "enhanced".

High pressure gas-filled stainless steel tubes equipped with transmitting windows at each end have often been used as Raman "shifters" in conjunction with pulsed laser input. The vibrational frequencies of hydrogen or deuterium gas molecules contained in such a tube provide a range of Stokes and anti-Stokes outputs. Metal vapors have also been found useful in generating Raman output. It is possible to provide a length of metal vapor in such a tube by inserting the metal in a central heated section of the tube in the presence of a non-reactive buffer gas such as argon. The end regions of the tube (containing the windows) are cooled and a metal mesh "wick" is provided to line the inner heated section where the metal is located. Under the proper conditions the argon buffer is forced out to the cooled ends, protecting the windows from the metal vapor. The metal vapor itself is confined to the central heated region since on meeting the cold argon it condenses and wicks back towards the center to re-evaporate. Such a device is called an optical heat pipe.

An optical heat pipe containing potassium metal vapor at a pressure of the order of 10 torr can be used to generate a collimated beam of infrared light at a wavelength of approximately 2.7 microns when pumped by a suitable pulsed laser^{1,2}. This radiation is produced by a stimulated enhanced Raman scattering (SERS) process which occurs when the input pump laser is tuned⁻¹ in the vicinity of the atomic potassium 5P level near 24720 cm^{-1} (approx 404.5 nm). The Raman Stokes radiation occurs from the vicinity of the 5P level (actual origin at the laser frequency)

and terminates on the 5S level. As the laser is tuned around the two 5P fine structure levels the Stokes beam will correspondingly shift in wavelength.

Similar processes occur in the other alkali atoms and also when tuning the input laser to higher P or D states (in two photons in the latter case). In order to use the SERS emission to detect HF through absorption the SERS frequency must match a strong HF absorption line. The fundamental HF absorption band corresponding to the $v=0$ to $v=1$ vibrational transition stretches from approximately 3590 to 4260 cm^{-1} . The best match for alkali SERS₃ appears to occur between the P branch P(6) HF absorption line at approx 3694 cm^{-1} and the K SERS frequency corresponding approximately to the K $5P_{3/2} - 5S_{1/2}$ transition which is also at 3694 cm^{-1} . A good match should be obtainable by tuning the input laser close to the $5P_{3/2}$ level at 24720 cm^{-1} . Unfortunately this appears to be a region which is difficult to reach with suitable dyes pumped by either the third harmonic of a YAG laser at 355 nm or by a XeCl excimer laser at 308 nm . The chances appear better in the latter case. Strong water-vapor absorption bands occur in the region of the HF absorption and might preclude HF detection depending on the relative concentrations of water and HF present in the absorption path.

Equipment to monitor HF using the SERS method would be relatively cumbersome since it would require a pulsed pump laser (YAG with third harmonic capability, excimer or nitrogen laser), a tunable dye laser, an optical heat pipe, optical path elements, a detector (probably a simple germanium diode), and all necessary electronics, power supplies, etc. The system would require considerable skill to set up and to operate. If the output SERS beam were split and conveyed by fiber or reflectors to a number of remote monitoring sites such a system might become attractive. In a plant environment it would be necessary to take precautions to shield laser and SERS beams present in work areas.

Detection of HF by Absorption of Tunable Diode Laser Radiation.

A variety of diode lasers are available for operation in the vicinity of 1.3 microns wavelength. Turn-key systems tunable through approximately 100 nm are available. Output powers are approximately 1 milliwatt and the laser linewidths vary from very narrow (a few hundred KHz) to broad (50 nm). Some systems permit adjustment of the bandwidth.

The first overtone band of HF lies between approximately 1.28 and 1.36 microns. The HF₋₁ P branch P(1) absorption within this band occurs at 7710.27 cm^{-1} or 1.296 microns. It should be possible to detect HF by tuning a diode laser to this absorption.

Without experimentation the sensitivity obtainable is a matter of speculation. Recently S. Allendorf of Sandia National Laboratory at Livermore reported first results of a diode laser based absorption system which is aimed at providing a rugged, reliable and economical means for continuous monitoring of certain stack emissions⁶. By radiofrequency (RF) modulating the diode driver current the laser emission frequency was scanned across an ammonia absorption near 1.5 microns. The laser was scanned through approximately 4 nm at a 100 MHz rate. The demodulated absorption signal displayed a thousand-fold increase in the signal-to-noise ratio compared to the unmodulated case. This method may hold promise for HF detection. Two important factors would need to be considered. These are firstly the fact that the first overtone band of HF provides much lower absorption, by a factor of 100 to 1000, than the fundamental⁵, and secondly that water vapor may again interfere. Hertzberg⁵ lists water vapor absorption bands centered at 7251.6 and 8807 cm^{-1} which straddle the P(1) overtone absorption at 7710 cm^{-1} . The wings of these bands may interfere with the HF absorption. Nevertheless the potential advantages of a diode laser based detection system in terms of simplicity, specificity, reliability, and relatively modest cost indicate that this option should be considered further.

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John Stockdale
6.8.94

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