An In-Situ Monitor for HCl and HF

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A modified nondispersive infrared technique, Gas Filter Correlation (GFC), was demonstrated in the laboratory to provide a sensitive and specific means of measuring pollutant concentrations in the presence of interfering gases. The basic idea of GFC is that a pollutant gas matching the spectral characteristics of the pollutant to be detected can be used in a reference cell and thus provide high specificity. A theoretical analysis of the GFC technique is presented. Experimental results given demonstrate that the technique can be used to measure HCl and HF concentrations of less than 0.1 ppm.

Nomenclature

A_d = detector area (cm^2)
C = gas concentration
$C(\lambda)$ = spectral attenuation due to optics
D^* = detector detectivity (cm-Hz$^{1/2}$-w^{-1})
$E(\lambda)$ = spectral radiance at the detector
ΔE = change in radiance due to attenuation by the gas to be detected (w-cm^{-2}-μ^{-1}-sterad^{-1})
Δf = instrument electronic band pass (Hz)
f/no = instrument f-number
$k(\lambda)$ = absorption coefficient (cm^{-1}-atm^{-1})
K = instrument constant
L = sample cell length (cm)
M = instrument a-c modulation function
n = number of usable spectral lines
N = instrument noise
$N^0(\lambda,T)$ = blackbody radiance (w-cm^{-2}-μ^{-1}-sterad^{-1})
P = pressure (atm)
S = instrument signal
T = temperature
u = optical thickness (cm-atm)
λ = wavelength
ν = wavenumber
τ = transmissivity
η = over-all instrument efficiency

Subscripts

1,2 = refers to two optical paths through the instrument
a = refers to adjustable aperture
f = refers to optical filter
i = refers to interfering gases
l = refers to a spectral line
0 = refers to gas in specifying cell

Introduction

HYDROCHLORIC and hydrofluoric acid are released during testing of high-energy rocket propellants. Since these gases are toxic, their release to the atmosphere requires compliance with air quality criteria established by various state and federal agencies. The present techniques for measuring these gases in the ppm range suffer particularly in the areas of sensitivity, response time, and selectivity in the presence of interfering gases.

Dispersive optical correlation techniques[1-9] which are based on the spectral fine-line structure of radiating or absorbing gases have recently shown promise for measuring concentrations of pollutants in the atmosphere. These techniques allow the characteristic line structure to pass to a detector; interfering lines are rejected by means of matched filters or optical correlation tapes. Thus, a high degree of specificity is obtained. Dispersive instruments require very high resolution and extensive time to analyze the fine-line data; hence, they become very complex. The nondispersive GFC technique achieves a considerable reduction in complexity.

This paper presents an analysis of the GFC technique, describes an experimental program that applies the technique to detecting HCl and HF, and shows how the technique can be employed to monitor HCl and HF under field conditions.

Theoretical

Analysis of Gas Filter Correlation

Nondispersive infrared techniques[10] are based on the concept that a sample of gas will provide a selective filter for radiation absorbed by a polluted mixture of atmospheric constituents. In a sense, they may be considered the reverse of matched-filter techniques in that they selectively absorb radiation from a source, while matched filters selectively transmit radiation from a source.

If a reference cell containing a particular pollutant is used, radiation is modulated only at wavelengths at which the pollutant absorbs. That is, the spectral characteristics of the pollutant in the reference cell will closely match the pollutant to be detected. Depending upon the optical depth, temperature, and collision broadening species selected for the reference pollutant, exceptionally high spectral resolution may be attained. In instrument terms, resolutions of better than 0.1 cm^{-1}, i.e., an effective spectral resolution on the order of the width of the spectral lines themselves, may be achieved. Thus, a high specificity is attained for the detection of a particular pollutant. This technique is called Gas Filter Correlation (GFC).

A schematic diagram that illustrates the GFC technique is presented in Fig. 1. The basic components are a high-temperature infrared source; a sample cell in which the gas mixture to be analyzed is placed; a rotating chopper; a

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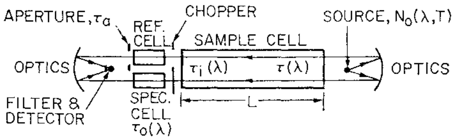

Fig. 1 Schematic diagram illustrating GFC technique.

reference cell containing a vacuum, or a transparent gas such as nitrogen; a specifying cell that contains a sample of the gas to be detected; an adjustable aperture that limits the radiation passing through the reference cell; an optical filter that confines the radiation to the spectral region where the gas to be detected possesses absorption bands; a sensitive infrared detector; and optics to collimate the radiance from the source and to focus it on the detector.

The radiation from the source passes through the sample cell, where it is spectrally absorbed by the specific gas and possible interfering gases. The radiation, having traversed the sample cell, is alternately passed through the reference and specifying cells. When the radiation passes through the reference cell it is unattenuated; but when the radiation passes through the specifying cell, it is further attenuated by the spectral absorption character of the gas in the cell. Thus, an alternating signal is generated at the detector. The magnitude of this signal is related to the concentration of the gas to be detected in the sample cell.

Referring to Fig. 1, when the chopper is in the position indicated, the energy from the source which reaches the detector is given by

$$E_1(\lambda) = \int_{\Delta\lambda} C_1(\lambda) N^0(\lambda,T)\,\tau_i(\lambda)\tau(\lambda)\tau_a d\lambda \tag{1}$$

$E_1(\lambda)$ is obtained by integrating over the spectral wavelength interval $\Delta\lambda$ defined by the optical filter. Radiation, due to self emission by the gases, windows, etc., is neglected since, for source temperatures greater than 1000°K and wavelengths less than 3.5μ, the radiance from the source is at least four orders of magnitude greater than the radiance from 300°K materials.

Similarly, when the chopper passes radiation through the specifying cell, the energy reaching the detector is given by

$$E_2(\lambda) = \int_{\Delta\lambda} C_2(\lambda) N^0(\lambda,T)\tau_i(\lambda)\tau(\lambda)\tau_0(\lambda) d\lambda \tag{2}$$

The peak-to-peak signal produced at the detector by chopping, is proportional to the difference between $E_2(\lambda)$ and $E_1(\lambda)$; that is

$$S \propto \int_{\Delta\lambda} N^0(\lambda,T)\tau_i(\lambda)\tau(\lambda)[C_2(\lambda)\tau_0(\lambda) - C_1(\lambda)\tau_a] d\lambda \tag{3}$$

Now, for slowly varying functions in λ, $N^0(\lambda,T)$ and $C_2(\lambda)$ can be averaged over the interval $\Delta\lambda$. Thus,

$$S \propto \langle N^0\rangle\langle C_2\rangle \int_{\Delta\lambda} \tau_i(\lambda)\tau(\lambda)\{\tau_0(\lambda) - [C_1(\lambda)/C_2(\lambda)]\tau_a\} d\lambda \tag{4}$$

where the sharp brackets denote average values. Now, $\tau_0(\lambda)$ and $\tau(\lambda)$ are strongly correlated, since they represent the spectral transmission due to the same gas. On the other hand, $\tau_i(\lambda)$ is assumed to be uncorrelated; i.e., the spectral lines due to interfering gases are randomly positioned with respect to the spectral lines due to the gas of interest. Also, since the two parameters $C_1(\lambda)$ and $C_2(\lambda)$ differ from each other due to only very minor differences between the nominally identical paths their ratio will not be correlated with $\tau(\lambda)$. Thus, the average values of the terms remaining under the integral are extracted by applying the mean value theorem; viz.,

$$S \propto \langle N^0\rangle\langle C_2\rangle\langle\tau_i\rangle[\langle\tau\tau_0\rangle - \langle C_1/C_2\rangle\langle\tau\rangle\tau_a] \tag{5}$$

Finally, the product $\langle C_1/C_2\rangle\tau_a$ may be considered an effective adjustable instrument aperture τ_a'. Thus

$$S \approx K[\langle\tau\tau_0\rangle - \langle\tau\rangle\tau_a'] \tag{6}$$

To zero the instrument, the sample cell is evacuated ($\tau = \tau_i = 1$) and the aperture adjusted such that $\tau_a' = \langle\tau_0\rangle$, yielding

$$S \approx K[\langle\tau\tau_0\rangle - \langle\tau\rangle\langle\tau_0\rangle] = KM \tag{7}$$

That is, the signal is only a function of the a-c modulation and fixed instrument parameters.

In general, the mean transmission for small gas concentration in the sample cell can be written

$$\langle\tau\rangle = \frac{1}{\Delta\lambda}\int_{\Delta\lambda} \exp[-k(\lambda)u] d\lambda \tag{8}$$

Expanding the exponential, it may be shown[9] that to the first order, M is proportional to $u = CLP$. It has also been shown[9,11] that for

$$\langle\tau_0\rangle \approx 1,\ M \approx \langle\tau_0\rangle(1 - \langle\tau\rangle) \approx 1 - \langle\tau\rangle$$

Examination of Eq. (7) shows $M = 0$ for $\langle\tau_0\rangle = 1$ and 0. Thus, for a particular value of τ, a point of maximum sensitivity is implied for a particular value of $\langle\tau_0\rangle$. This point of maximum sensitivity may be determined theoretically by assuming a particular line shape for the absorption lines (e.g., convoluted Doppler-Lorentz). But this would be a tedious procedure. More simply, the characteristics of the GFC technique for detecting specific gases may be determined experimentally.

As seen from Eq. (5), the instrument signal may be increased by increasing the radiance from the source. The signal may also be increased by judicious selection of the transmission through the specifying cell. It should also be noted that S will be attenuated by the mean transmission of interfering gases $\langle\tau_i\rangle$; however, by using narrow-band optical filters, $\langle\tau_i\rangle$ will be very nearly equal to one for most gas concentrations up to 100s of ppm.

Feasibility of Detecting HCl and HF Using GFC

The GFC technique is based on the rotational fine structure of molecules. In this respect HCl and HF are well suited. Both gases have line spacing to line half-width ratios that exceed 200. And, if absorption lines due to interfering gases are present, they will likely occur randomly and no correlation signal will occur.

This section discusses the amount of spectral overlap of HCl and HF with other gases that may be present in a normal atmosphere contaminated by rocket exhaust. The gases considered and their likely maximum concentrations were specified by AFRPL.[11] Also, this section presents a calculation that describes the conceptual performance of a GFC laboratory instrument. It is demonstrated that the GFC technique will satisfy all of the requirements of AFRPL.

The first logical step in investigating the spectral overlap of interfering gases with HCl and HF is to look at the band locations. If the bands do not overlap with HF and HCl, no problem of interference will be encountered, since narrow-band optical filters are used. If the bands do overlap, the line overlappings have to be investigated.

Thus, as a first step, the band contours of all gases of interest were calculated[11] and are plotted in Fig. 2. The ordinate indicates the absorption coefficients in cm^{-1}atm^{-1}. The area under the curves gives the strength of the bands, which is proportional to the absorption for low gas concentrations.

Examination of Fig. 2 indicates that HF may be determined specifically if the spectral band pass is confined between about 4000 and 4200 cm^{-1}. On the other hand, for HCl measurements, potential interferences may arise due to the presence of methane (CH_4), hydrazine (N_2H_4), ozone (O_3),

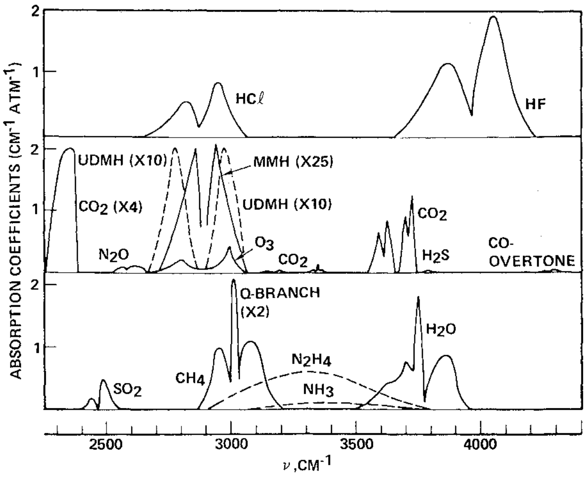

Fig. 2 Band spectra of HCl and HF and interfering gases.

unsymmetrical dimethylhydrazine (UDMH) and monomethylhydrazine (MMH). Experiments are required to ascertain the ability of GFC to determine HCl specifically in the presence of these potential interfering gases.

The conceptual performance of a GFC instrument may be determined on the basis of a previously developed signal-to-noise equation[12]; viz.,

$$S/N = \eta D^*(\Delta E)(n\Delta\lambda_i)(A_d/\Delta f)^{1/2}(f/\text{no})^{-2} \qquad (9)$$

This equation may be used to calculate the instrumental parameters required for a specified sensitivity.

HF will be easier to measure than HCl for two reasons: the integrated band intensity is about three times greater for HF than for HCl, and there is essentially no spectral interference from other gases. Therefore, S/N calculations applied to the problem of HCl detection are conservative. For HCl, the ΔE in Eq. (9) may be expressed by

$$\Delta E \approx \langle N^0 \rangle M \approx \langle N^0 \rangle (1 - \langle \tau \rangle) \approx \langle N^0 \rangle \langle k \rangle CLP \qquad (10)$$

From Eqs. (9) and (10), note that the sensitivity of the instrument may be increased by several means. Practical limitations do exist, however; i.e., detector detectivities and sizes, source temperatures, optical f-numbers, and data integration times. Considerable latitude is available in selecting sample cell length (or optical path length). If necessary, cell lengths of 10 m or greater may be obtained in a compact package by folding the optical path.

Experimental

Apparatus

A laboratory instrument, theoretically capable of detecting about 100 ppb HCl, was designed using Eqs. (9) and (10), and constructed. The major components are:

1) Source—A tungsten-filament sun-gun lamp with a relatively diffuse reflector which provides radiances of up to 2.0 w-cm^{-2}-μ^{-1}-sterad^{-1}.

2) Optics—A 5-in.-diam, $f/1$ spherical mirror is used to focus the energy from the source onto the detector.

3) Sample Cell—The sample cell is 30 in. long, 3 in. in diameter, and constructed using stainless steel and sapphire windows with Teflon seals.

4) Chopper—A six-bladed chopper, directly coupled to an a-c induction motor is used to minimize the noise level; the nominal chopping frequency is 177 Hz.

5) Instrument Specifying Gas Cell and Reference Cell—These are identical cells, one containing the gas to be detected (HCl or HF) and the other containing a vacuum or a transparent gas (N_2 or He); they are 4 in. long, 1 in. in diameter, and constructed using stainless steel and sapphire windows with Teflon seals.

6) Aperture—An adjustable iris aperture is used to balance the energy through the two instrument cells with no gases present in the sample cell; this "zeroes" the instrument.

7) Optical Filters—Two narrow spectral bandpass optical filters are used. For HCl detection, a filter centered at $\lambda_0 = 3.47$ with a half bandwidth, $\Delta\lambda = 0.15\mu$ and $\tau = 0.31$ is installed. For HF detection, a filter with $\lambda_0 = 2.42\mu$, $\Delta\lambda = 0.12\mu$, and $\tau = 0.67$ is installed.

8) Detector—An ambient temperature operation (ATO) PbSe detector (Santa Barbara Research Corp.) is used; its D^* at 3.0μ and 780 Hz chopping and 1 Hz bandwidth frequencies is greater than 10^9 cm-Hz$^{1/2}$-w^{-1}. It is mounted on a heat sink maintained at 20°C by a thermoelectric cooler. Its temperature is sensed by a thermistor imbedded in a heat sink and a feed-back electrical circuit is used to control temperature within 0.01°C.

9) Electronics and Readout—The detector output is fed into a specially designed preamplifier[11] and into a Princeton lock-in amplifier, Model 120. Using a reference signal generated by the chopper, the preamplifier signal is synchronously rectified and recorded on a standard 10-in., 0–10 mv strip chart recorder and observed on a digital voltmeter. The detector current is monitored continuously to prevent overloading. All cells and optical components are mounted on a 3-in. standard aluminum I-beam.

A major problem in evaluating instrument performance, particularly in the ppm range, is preparing test gas mixtures with known concentrations. A clean, stainless-steel, high-vacuum (10^{-6} mm Hg) system was previously developed[13] for the accurate preparation of test gas mixtures; this system was modified for the present program. Several techniques are provided to prepare known gas concentrations and to check the concentrations by physical and/or chemical methods. After a test gas mixture has been prepared with the desired concentration, it can be led into any of the cells of the GFC instrument. A chemical scrubber and reactor are used to react or neutralize toxic gases before they are released to the atmosphere.

The experiments were conducted using test gas mixtures prepared from gases of CP grade or better (this exceeds MIL-SPECS). The gases were available in lecture bottles supplied by Matheson Gas Products, except for UDMH and MMH, which were obtained from AFRPL. The test gas mixtures were diluted with dry nitrogen or helium.

Test Procedures

To evaluate the instrument, the first step is to charge the instrument specifying cell with a diluted mixture of HCl or HF. This is done by admitting pure HCl, for example, to the cell and then adding N_2 or He to bring the pressure to one atmosphere. In doing this, the reference cell is blocked off and the sample cell is evacuated. By observing the signal before and after charging the cell with diluted HCl at a pressure of one atmosphere, $\langle \tau_0 \rangle$ is measured.

The instrument is zeroed by closing the aperture on the reference cell, which is filled with pure N_2 or He, until the same radiance passes through each instrument cell. To check the degree of zero (or balance) obtained, the source temperature is raised and lowered. From Eqs. (5) and (7), it may be seen that if the instrument is properly zeroed, the source temperature will not affect the output signal when no gas is present in the sample cell.

Test gas mixtures containing known amounts of HCl, HF, and interfering gases are prepared, admitted to the instrument's sample cell, and the signal and the noise of the instrument are recorded. Through this procedure the efficiency, sensitivity and specificity of the instrument are determined.

Prescribed concentrations of the constituents of the test gas mixtures were determined by partial pressure measurements and successive dilution. However, in the case of test gas mixtures containing HF, this procedure was unsatisfactory due to wall absorption effects. For this reason, an independent analysis, based upon the colorimetric determination of the lake formed by excess thorium ion and sodium alizarin sulfonate dye, was used to determine HF concentrations.[11]

Results

Preliminary experiments were conducted to evaluate the sensitivity and specificity of the instrument for detecting HCl in the presence of CH_4. A sample result is shown in Fig. 3. Under the conditions noted in Fig. 3, 100 ppm HCl was added to the sample cell and a S/N ratio of 62 was observed; similarly 100 ppm CH_4 was added to the sample cell and no observable signal was recorded. Thus, we see that despite significant band overlapping between CH_4 and HCl (Fig. 2), the line overlapping is random, and CH_4 does not contribute to the signal.

Limitations of system were determined by measuring the signal and the noise as a function of source intensity for a fixed HCl concentration. These results indicate that for $\langle N^0 \rangle < 0.5$ w-cm^{-2}-μ^{-1}-sterad^{-1}, the instrument is detector-noise limited, but for larger $\langle N^0 \rangle$ the signal and the noise increase at the same rate, indicating a system-noise limit. This system noise limit is due to the highly critical $f/1$ mirror. Fluctuations in the ambient temperature (10°C in the particular laboratory environment) and vibrations due to the heating and ventilating system were the major extraneous source affecting the mechanical stability of the optical system. A more rugged, better designed optical system could overcome these limitations. However, in this study for demonstrating the basic capability of the GFC technique, the system was not further stabilized. Table 1 gives the instrument parameters [Eqs. (9) and (10)] used for the final results.

$\langle N^0 \rangle$ was determined from brightness temperature measurements and the tables in Ref. 14. The effective instrument f/number was determined from the actual geometrical optics of the laboratory GFC instrument. Over-all instrument efficiency, which consists of the optical and electronic efficiency, was measured using the HCl optical filter ($\tau = 0.31$).

Sensitivity

Systematic investigations were made of the sensitivity of the laboratory instrument for monitoring HCl and HF. First, the optimum value for $\langle \tau_0 \rangle$, the transmission through the instrument specifying cell was established. This measurement was made for fixed HCl and HF concentrations in the sample cell for various values of $\langle \tau_0 \rangle$ and source temperatures. $\langle \tau_0 \rangle$ was measured by blocking off the reference instrument cell and using the instrument as a radiometer. The results for HCl are shown in Fig. 4, where the signal in arbitrary units is plotted vs $\langle \tau_0 \rangle$.

Table 1 Instrument parameters used for HCl and HF experiments

Item		Specification
Spectral characteristics		HCl − $\lambda_0 = 3.47\mu$, $\Delta\lambda = 0.15\mu$
		HF − $\lambda_0 = 2.42\mu$, $\Delta\lambda = 0.12\mu$
Lead selenide detector	D*	$= 1.5 \times 10^9$ cm-Hz$^{1/2}$-w^{-1}
(ATO)	A_d	= 5 mm × 5 mm
	T_d	= 20 ± 0.01°C
Center chopping frequency	f_0	= 177 Hz
Integration time	Δt	= 10 sec
Source radiance	N_0	= 0.5 w-cm^{-2}-μ^{-1}-sterad^{-1}
Instrument f-number	$f/3$	
Instrument efficiency	η	$\sim 10^{-2}$
Sample cell length	L	= 76.2 cm
Instrument pressure	P	= 1 atm

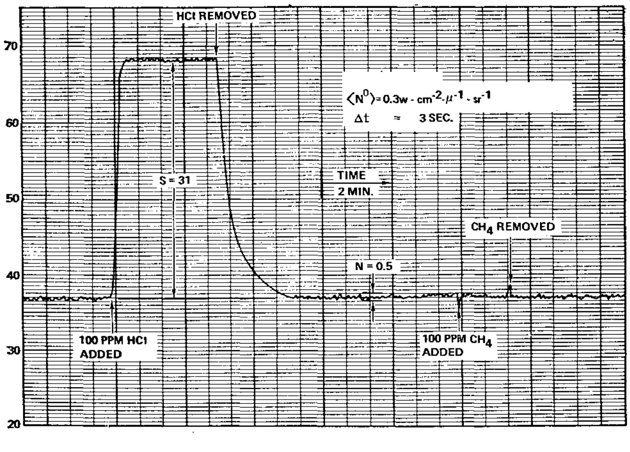

Fig. 3 Example of sensitivity for detecting HCl and CH_4, respectively.

The important thing to note from these results is that for even very high HCl concentrations, the optimum value for $\langle \tau_0 \rangle$ is about 0.9 and, as the HCl concentration is reduced, the optimum value for $\langle \tau_0 \rangle$ increases. These results are in agreement with the qualitative analysis presented previously. It has been shown previously[11] that the GFC has greatest discrimination for large $\langle \tau_0 \rangle$. Thus, $\langle \tau_0 \rangle$ (HCl) was set at 0.95 for the final experiments. Similar experiments were conducted using the instrument as an HF detector; $\langle \tau_0 \rangle$ (HF) = 0.97 was determined to be an optimum value.

The sensitivity of the instrument for monitoring HCl was measured over a concentration range of 0.6–2500 ppm HCl. Test gas mixtures of helium-diluted HCl at a pressure of one atmosphere were placed in the sample cell alternately with samples of pure He at a pressure of 1 atm and S/N was measured. (Helium was used as the dilutent to minimize certain sample-cell wall-adsorption effects, as will be discussed later. The results are shown in Fig. 5. The different symbols represent data taken on different days and cover a one-month time span. A threshold sensitivity of 0.25 ppm HCl (2×10^{-5} atm-cm) is indicated for the present system. Repeatability is within ±10%.

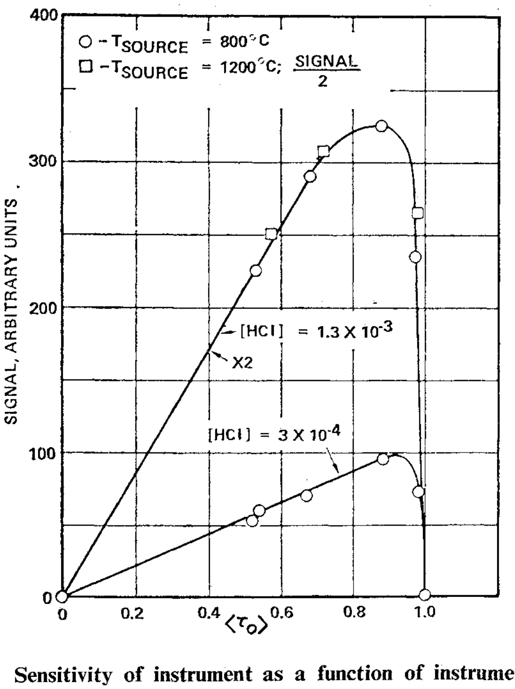

Fig. 4 Sensitivity of instrument as a function of instrument cell transmission.

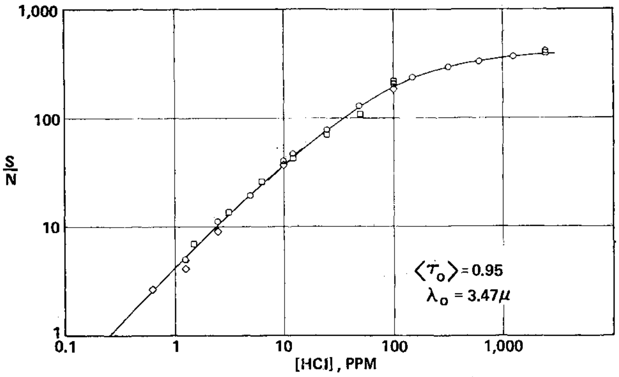

Fig. 5 Sensitivity of laboratory GFC instrument for detecting HCl.

Likewise, the sensitivity of the instrument for monitoring HF was measured. As with HCl, test gas mixtures of helium-diluted HF at a pressure of one atmosphere were placed in the sample cell alternately with samples of pure He at a pressure of one atmosphere, and S/N measured.

In these experiments, wall adsorption effects were very pronounced. To account for the desorbed HF, He blanks were run through the system before and after each test. The data was then interpreted by subtracting the average signal due to the He blanks from the signal due to the helium-diluted HF test gas mixture.

The results of these experiments are shown in Fig. 6. The HF concentration was determined by correcting the indicated partial pressure concentration on the basis of independent chemical analyses. This data indicates a threshold sensitivity to HF of less than 0.1 ppm.

Specificity

Potential interfering gases and their maximum anticipated concentrations have been specified[11]; these are shown in Table 2, column 2. A complete specificity evaluation was made for each gas. These experiments were conducted by placing each interfering gas in the sample cell and observing S/N. For example, $S/N = -2$ was observed for 100 ppm MMH, indicating that MMH has a slight negative correlation with HCl. Regardless, the results show that 200 times as much MMH as HCl is required to give equal magnitude signals and, within the requirements listed in Table 2, MMH would have a negligible effect on detecting 0.25 ppm or greater of HCl. The previous statement is true from a spectroscopy viewpoint; however, certain wall adsorption and chemical reaction effects occur that cause problems.

Additional experiments were conducted to ensure that negligible decomposition of the interfering gases, particularly the hydrazines, occurred. This was done by blocking off the instrument cell containing the HCl and using the instrument as a conventional adsorption device.

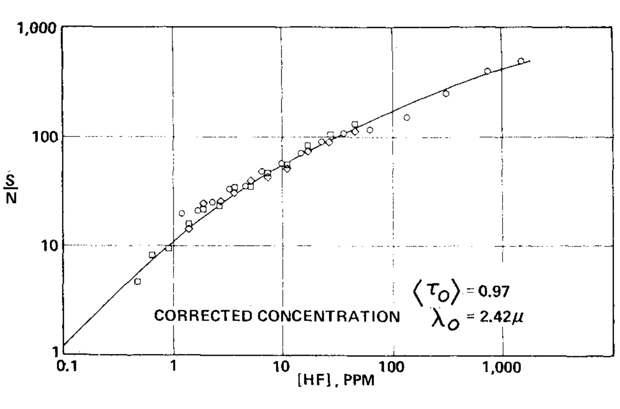

Fig. 6 Sensitivity of laboratory GFC instrument for detecting HF.

Table 2 Specificity of laboratory GFC instrument

Interfering gas	Maximum expected concentration (ppm)	Concentration (ppm) required to give $\lvert S/N \rvert \approx 0.25$ ppm HCl	Concentration (ppm) required to give $\lvert S/N \rvert \approx 0.1$ ppm HF
Ammonia	500	10^3*	350
Carbon dioxide	1,000	$>10^6$	3,000
Carbon monoxide	1,500	$>10^6$	4,000
Hydrazine	30	400*	4,000
Methane	3	100	250
Hydrogen sulfide	200	$>10^6$	1,200
Nitrous oxide	55	10^4	750
Monomethyl hydrazine	10	50*	2,500
Sulfur dioxide	30	$>10^6$	13,000
Unsymmetrical dimethyl hydrazine	100	250*	4,300
Water vapor	100% RH	>20% RH	>20% RH

Similar experiments were conducted for the other potential interfering gases. In all cases, the individual gases were placed in the sample cell at 100% concentrations or diluted with He to obtain a pressure of 1 atm. Mixtures of HCl, He, and other gases were attempted but, in general, not used due to difficulties with chemical reactions that occurred when they were confined in the sample cell. The results of the specificity experiments are summarized in Table 2, column 3.

For the results given, a $S/N = 1$ is the threshold detection limit for [HCl] = 0.25 ppm. The concentrations marked by * do not give any positive correlation, but instead give a negative correlation (signal in the opposite direction of the signal due to HCl). But, in any event, it is clear that concentrations of interfering gases far greater than expected to be present are required before they would affect the instrument's ability to measure HCl concentrations quantitatively.

Similar specificity evaluations were made for the instrument operating in the HF detection mode. The results are given in Table 2, column 4. No negative correlation signals were observed, but the indicated interferences are greater than expected. Two possibilities may explain this. One, residual HF remained adsorbed on the sample cell walls, and the interfering gases displaced them to give a signal which appeared to be due to the interfering gas but in reality was due to HF; this is the most likely explanation. Two, the optical bandpass filter, which has a specified transmission $\leqslant 1.0\%$ outside the band, may allow leakage in the wings and permit radiation at spectral intervals that should have been eliminated; if this is the problem, a better optical filter would solve it.

Discussion and Conclusions

Experimental results obtained using the laboratory GFC instrument demonstrate that HCl and HF may be monitored in the presence of other gases and vapors that may be in the atmosphere.

Indicated threshold sensitivities are about 0.25 and 0.10 ppm for HCl and HF, respectively. This appears to be about the best that can be achieved with the present laboratory instrument. However, sensitivity could be improved significantly by using either a more rugged optical system, a longer optical path, a higher source temperature, a longer data integration time ($\Delta t > 10$ sec), or a more sensitive detector (or a combination of the preceding). Penalties are paid by increasing the sensitivity by these methods. For example, if the sensitivity is increased, a field instrument would be more costly, require more frequent maintenance and calibration, and become more complex and probably more bulky.

As pointed out earlier, wall adsorption effects are particularly troublesome when trying to analyze mixtures of HCl, HF, and hydrazines. Not only do the HCl and HF tend to adsorb on the sample cell walls, leading to erroneous indicated concentrations, but chemical reactions also occur. Some additional experimental observations regarding wall adsorption phenomena follow.

In the case of HCl wall adsorption, it was found that the walls becomes saturated after the sample cell is thoroughly soaked overnight with 0.25% HCl and 99.75% N_2. When pure N_2 was purged through the system, a signal equivalent to approximately 1 ppm HCl resulted. After thoroughly baking and pumping out the cell, no signal resulted when N_2 was purged through. However, it was observed that if He is used as the purge gas, no signal resulted. For this reason, He was used as a dilutent for final experiments.

In HF wall adsorption, two problems occurred: considerable uncertainty arose in preparing test gas mixtures with known HF concentrations; and for the HF sensitivity tests, corrections had to be applied by running He blanks before and after each sensitivity test.

In the case of hydrazine wall adsorption, even more serious effects are encountered. For example, when helium-diluted mixtures of HCl are admitted to the sample cell after MMH has been placed in and pumped out of the sample cell, an extremely fast reaction between the residual MMH on the cell wall and the HCl occurs, destroying the HCl so that no signal is observed by the instrument. The adsorbed MMH and/or the reaction products are very difficult to remove. Evacuating the cell to less than 10^{-4} mm Hg and simultaneously baking is not effective. The only way we were able to eliminate the after-effects of placing MMH in the sample cell was to thoroughly soak the cell with high-concentration HCl mixtures until the effects were neutralized. Similar observations were made for UDMH and N_2H_4.

For an operating field instrument, this effect could cause serious problems if a sample cell is employed to analyze for HCl, or HF in the presence of hydrazines. Although our laboratory type instrument (using a sample cell) will discriminate spectroscopically, it, and in fact any type of instrument, will encounter the wall adsorption effects observed. It is possible that the sample cell could be lined with Teflon or some other material having a low absorptivity. But it appears that any instrument using any closed container to sample atmospheres containing HCl, HF, and hydrazines would be subject to wall reactions, and thus could not accurately measure HCl or HF at ppm concentrations. However, for a GFC instrument there is no real need to use a sample cell during field operation. All that is required for monitoring a polluted atmosphere containing HCl, HF, and hydrazines is the source, chopper, two instrument cells, and the detector. Such an instrument would not be subject to wall adsorption effects. Calibration could be accomplished in the field by temporarily placing a temperature-controlled cell (or cells) in the optical path; the calibration cells would have been loaded in the laboratory with test gas mixtures containing known HCl and HF, concentrations.

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