A new method is described for detection of S\textsubscript{2}F\textsubscript{10} in SF\textsubscript{6} at the parts-per-billion (ppb) level. The method utilizes a gas chromatograph/mass spectrometer (GC/MS) equipped with a heated jet separator. S\textsubscript{2}F\textsubscript{10} is converted to SOF\textsubscript{2} on the hot surfaces of the low-pressure portions of the jet separator at temperatures above 150 °C by a surface-catalyzed reaction involving H\textsubscript{2}O. A consequence of this conversion, peaks corresponding to S\textsubscript{2}F\textsubscript{10} appear on single-ion chromatograms at ion masses characteristic of SOF\textsubscript{2} (m/z 48, 67, and 86) where there is little or no interference from SF\textsubscript{6} features. By this method, a direct analysis of SF\textsubscript{6} for S\textsubscript{2}F\textsubscript{10} content can be performed with greater sensitivity than conventional gas chromatographic methods and with a higher degree of reliability and in a time much shorter than required for chromatographic methods that use enrichment procedures. Problems associated with the preparation and stability of reliable S\textsubscript{2}F\textsubscript{10} reference samples are discussed.

INTRODUCTION

The ability to detect gaseous disulfur decafluoride (S\textsubscript{2}F\textsubscript{10}) at trace levels in sulfur hexafluoride (SF\textsubscript{6}) is of interest because of its known high level of toxicity (1-5) and because of recent measurements (6, 7) and calculations (8, 9) which show that S\textsubscript{2}F\textsubscript{10} can be produced during electrical discharge activity in SF\textsubscript{6}. The concern about S\textsubscript{2}F\textsubscript{10} production in SF\textsubscript{6} stems in part from the increasingly widespread use of SF\textsubscript{6} as a gaseous dielectric in high-voltage electric-power transmission systems. The Occupational Safety and Health Administration (OSHA) recently set peak exposure limits (PELs) for S\textsubscript{2}F\textsubscript{10} at 10 ppb (10). However, due to the difficulty of detecting low concentrations of S\textsubscript{2}F\textsubscript{10} in SF\textsubscript{6}, enforcement of the PELs has been stayed until the development of suitable detection techniques.

There are previous preliminary reports by Janssen (11, 12) of having achieved a detection sensitivity for S\textsubscript{2}F\textsubscript{10} in helium gas of 0.04 ppb by using a gas chromatograph (GC) equipped with an electron-capture detector. In order to achieve this level of sensitivity, however, it was necessary to employ a complex S\textsubscript{2}F\textsubscript{10} enrichment procedure requiring long analysis times (~45 min). When SF\textsubscript{6} is a major constituent of the gas in which S\textsubscript{2}F\textsubscript{10} is to be detected, the sensitivity for S\textsubscript{2}F\textsubscript{10} detection drops dramatically (to >10 ppb) despite the enrichment process. This drop in sensitivity is a consequence of increased background signal in the detector output due to the favorable electron-attracting properties of the residual SF\textsubscript{6} which interferes with the S\textsubscript{2}F\textsubscript{10} signal. Reduced sensitivity for S\textsubscript{2}F\textsubscript{10} detection in the presence of SF\textsubscript{6} also occurs when flame photometric detectors (11) or thermal conductivity detectors (13) are used.

Mass spectrometric detection, when coupled to a gas chromatograph, suffers from the specific limitation that SF\textsubscript{6} has a positive-ion mass spectrum that is very similar to that of SF\textsubscript{6}, especially at the standard electron-impact energy of 70 eV (12, 14, 15). For electron-impact energies greater than 20 eV, all of the significant ions that appear in the S\textsubscript{2}F\textsubscript{10} mass spectrum also appear in the SF\textsubscript{6} spectrum. Thus, even when chromatographic separation of S\textsubscript{2}F\textsubscript{10} from SF\textsubscript{6} is used, ions from SF\textsubscript{6} can sufficiently increase the background level to interfere with S\textsubscript{2}F\textsubscript{10} detection. Recent claims (16) of using a mass spectrometer (MS) operated at low electron-impact energies to detect trace levels of S\textsubscript{2}F\textsubscript{10} in SF\textsubscript{6} have been disputed (15).

A new method is described here in which a gas chromatograph/mass spectrometer (GC/MS) system is easily modified to allow detection of S\textsubscript{2}F\textsubscript{10} in gaseous SF\textsubscript{6} down to the ppb level without the necessity of a complex and time-consuming preenrichment procedure. With this method, a fraction of the S\textsubscript{2}F\textsubscript{10} is converted to thionyl fluoride (SOF\textsubscript{2}) in a heated jet separator at the interface between the GC and MS. Because the major ions that appear in the 70-eV mass spectrum of SOF\textsubscript{2} differ from those in the SF\textsubscript{6} spectrum, interference of SF\textsubscript{6} with the S\textsubscript{2}F\textsubscript{10} peaks in single-ion chromatograms can be avoided. Elimination of the enrichment step significantly reduces the gas analysis time and improves the reliability of the detection method.

EXPERIMENTAL SECTION

Measurement System. The analytical method proposed for sensitive detection of S\textsubscript{2}F\textsubscript{10} in SF\textsubscript{6} utilizes a GC/MS with a heated metal tube on the lower pressure side of the interface between the GC and MS. As shown in Figure 1, a jet separator serves as the heated metal tube in the GC/MS system used to obtain the results presented here. The jet separator is a standard design consisting of a stainless steel tube of 8-cm length and 5-mm diameter that is heated to a temperature of about 150 °C. As discussed later, a fraction of the S\textsubscript{2}F\textsubscript{10} undergoes thermal decomposition in the heated tube and converts to SOF\textsubscript{2}, which is detected by the mass spectrometer without interference by the ion signals from SF\textsubscript{6}. The efficiency of the conversion is not known but appears, from experiments discussed below, to depend on the length, shape, and temperature of the heated surface upon which conversion takes place. The conversion efficiency is most sensitive to the tube temperature and relatively insensitive to details of the tube geometry and material composition. A high sensitivity for S\textsubscript{2}F\textsubscript{10} detection is obtainable with a wide range of heated inlet tube configurations.

The GC/MS system used for the experiments presented here is a Hewlett-Packard 5995A with a Hewlett-Packard jet separation inlet. In this particular instrument, the jet separator is heated by the diffusion pump heater. For other systems, the conversion region may be heated externally. The GC column is similar to that described by Hanrahan and Patterson (17), namely a 24-ft × 1/8-in. Teflon tube containing 30% SP-2100 (Supelco) on 80/100 Chromosorb WAW. The column was operated with helium as the carrier gas (20-30 mL/min flow rate) that had not been predried. The GC oven temperature was maintained between 25 and 50 °C, and the sample injections were made with a gas-tight syringe. Detection sensitivities for S\textsubscript{2}F\textsubscript{10} in SF\textsubscript{6} of nearly 1 ppb were obtained with the instrument described above.

Pure SF\textsubscript{6} samples, synthesized at Clemson University, were provided to us as liquid under its own vapor pressure (~600 Torr at room temperature) in 30-mL stainless steel cylinders. Identity and purity of the sample were established by IR spectroscopy and gas chromatography/mass spectrometry analysis. Gas-phase
Reference mixtures were prepared immediately prior to use, either by injection or needle valve, in argon (99.999%) or SF₆ (99.99%) in a stainless steel vacuum manifold housed in a vented hood. The argon and SF₆ were not dried before use.

Data Acquisition and Analysis. Data acquisition was performed by using the manufacturer-supplied software, and analysis was performed by using software developed in-house. For S₂F₁₀ samples in buffer gases other than SF₆, trace amounts of S₂F₁₀ could be detected by single-ion monitoring of SF⁺⁺, SF⁺⁺, SF⁺⁺, and F⁺⁺ (m/z = 127, 108, 89, 70, and 19) produced by direct ionization of S₂F₁₀. When mixed with SF₆, sensitive S₂F₁₀ detection required the monitoring of ion signals characteristic of the SOF₂ produced by surface conversion in the heated inlet tube mentioned above. These ions include SOF⁺⁺, SOF⁺⁺, or SO⁺⁺ (m/z = 86, 67, and 48). For the data presented here, as many as eight ions could be monitored at a given time with dwell times ranging from 10 to 200 ms.

The response of the GC/MS to S₂F₁₀ is defined here to be the area under the peak identified with this species in a chromatogram. This area was computed from the GC/MS data by numerical integration after performing a background subtraction. No attempts were made to “smooth” or average data, and unless specified, the data presented here correspond to chromatograms from single sample injections. Retention time was measured from the time of sample injection.

RESULTS AND DISCUSSION

In the first subsection of this portion of the paper, we present the results of the previously described detection procedures using a commercially available GC/MS system. In the following subsection, we present results of an investigation into the pyrolysis of S₂F₁₀ on hot surfaces under vacuum that indicates the conditions for optimum conversion efficiency and that supports the hypothesis that adsorbed H₂O accounts for the conversion of S₂F₁₀ into SOF₂. The next subsection discusses the possible effects of gas-phase impurities upon the detection method, and in the final subsection, we discuss how surface decomposition of S₂F₁₀ at room temperature affects the maintenance of reliable S₂F₁₀ reference samples.

GC/MS Results and Calibration. When a gas sample containing S₂F₁₀ is injected into the column of the GC/MS in which the interface is heated, the conversion of S₂F₁₀ into SOF₂ discussed in the next section becomes evident from single-ion chromatograms at m/z = 48, 67, and 86 (SO⁺⁺, SOF⁺⁺, and SO⁺⁺). Examples of such chromatograms are shown in Figure 2 for a 500 ppm sample of S₂F₁₀ in argon. Ions produced by direct ionization of S₂F₁₀ are observed (F⁺⁺ and SF⁺⁺) as are ions from SOF₂ produced by surface conversion (SOF⁺⁺ and SO⁺⁺).

The m/z = 20 chromatogram in Figure 2 exhibits a peak at the retention time characteristic for S₂F₁₀, thus indicating that HF is also a byproduct of S₂F₁₀ decomposition in the heated tube. This peak, however, exhibits a structure that can be accounted for by interference from HF originally present as a contaminant in the sample mixture. Analysis of dilute HF mixtures showed that HF has nearly the same retention time as S₂F₁₀ for the column conditions used here. Thus, although HF may be formed by thermal decomposition of S₂F₁₀ in the heated gas inlet tube, it cannot, by itself, be relied upon to give an unambiguous indication of S₂F₁₀.

For the results shown in Figure 2, ions due to direct ionization of S₂F₁₀ are observable because no SF₆ was present in the sample. However, in the presence of SF₆, S₂F₁₀ signals in the single-ion chromatograms at m/z = 19 and 127 are obscured by the SF₆ contribution to the signal at these masses. This is demonstrated by data presented in Figure 3 from a gas sample containing 660 ppb S₂F₁₀ in SF₆. These results show the effect of SF₆ in limiting the sensitivity for S₂F₁₀ detection when conventional mass spectrometric monitoring...
that was partially decomposed in a direct-current corona discharge. It is used and clearly show the advantages of using the S$_2$F$_{10}$ conversion technique discussed here.

Figure 4 shows a chromatogram for $m/z = 86$ for an "unknown" SF$_6$ sample from a container in which the gas had been subjected to a weak electrical corona discharge. The discharge produced traces of the oxyfluorides SOF$_2$, SOF$_4$, and SO$_2$F$_2$ in addition to S$_2$F$_{10}$. It is seen that the retention times of SOF$_2$ and SOF$_4$ produced by the discharge are much shorter than for S$_2$F$_{10}$ (2.1 and 2.3 min compared to 4.0 min). The oxyfluorides are known from previous work (18) to be the major gaseous byproducts from decomposition of SF$_6$ in corona discharges. The production of S$_2$F$_{10}$ in SF$_6$ electrical discharges has only recently been verified (6, 7).

Under the conditions used to obtain the data in Figures 2 and 3, the response of the GC/MS was measured as a function of the S$_2$F$_{10}$ concentration in reference gas samples. Typical response curves obtained with known concentrations of S$_2$F$_{10}$ mixed with argon are shown in Figure 5 for the indicated $m/z$ values. The S$_2$F$_{10}$ response is compared with that for SOF$_2$, which was also added to the mixture in known concentrations. The S$_2$F$_{10}$ response curves for $m/z = 48$ and 86, corresponding to the chemical conversion of S$_2$F$_{10}$ into SOF$_4$, are seen to be distinctly nonlinear. The deviation from linearity is greatest at the highest S$_2$F$_{10}$ concentrations and indicates a saturation effect possibly associated with depletion of H$_2$O from the heated inlet separator tube surface during the conversion of S$_2$F$_{10}$ into SOF$_4$. By contrast, the S$_2$F$_{10}$ response curve for $m/z = 127$, corresponding to unreacted S$_2$F$_{10}$, is seen to be nearly linear over 5 orders of magnitude. Likewise, the responses to SOF$_2$ originally present in the sample at $m/z = 48$ and 86 are also nearly linear. The small deviations from linearity observed at low concentrations (<200 ppb) may be attributable to uncertainties in the preparation of samples by successive dilutions.

The shape and slope of the response curves for the S$_2$F$_{10}$ conversion process are quite reproducible for a given set of instrument operating conditions. Nevertheless, when attempting accurate measurements of S$_2$F$_{10}$ concentrations in SF$_6$, frequent checks on the GC/MS calibration may be necessary and reference sample concentrations should ideally be as close to the unknown sample concentration as possible.

Figure 4. Single-ion chromatogram of an "unknown" sample of SF$_6$ that was partially decomposed in a direct-current corona discharge.

The response of the present GC/MS system to S$_2$F$_{10}$ was periodically checked and found to be stable for long periods of time (typically more than a day). When performing a quantitative analysis of S$_2$F$_{10}$ content in SF$_6$, it is desirable to bracket the unknown sample injection with reference injections of comparable concentration.

It should be noted that although the response at high S$_2$F$_{10}$ concentrations shows evidence of H$_2$O removal, the surface apparently recovers to its former condition in a relatively short time (~5-10 min) as indicated by responses from successive injections of samples at high concentrations (~100 ppm). In general, the larger the quantity of S$_2$F$_{10}$ injected, the longer the surface recovery time of the inlet tube. For samples containing less than 10 ppm S$_2$F$_{10}$, the recovery time of the system used here was found to be less than the typical S$_2$F$_{10}$ retention time of 4 min.

The limit of S$_2$F$_{10}$ detection in SF$_6$ depends, of course, on the operating conditions of the GC/MS equipped with the heated inlet line. For the instrument used here, under conditions identical with those used to obtain the results shown in Figures 2-4, the limit of detection (signal-to-noise ratio = 2) was estimated to be about 2 ppb for a 2-mL injection at 200 kPa. Figure 6 shows an example of a result obtained for a 4 ppb mixture of S$_2$F$_{10}$ in SF$_6$, which gives an indication of the limit of detection sensitivity for this instrument. The single-ion chromatogram at $m/z = 86$ is an average of data from four injections each with a volume of 2 mL at a total gas pressure of 200 kPa. The S$_2$F$_{10}$ peak is statistically significant and is indicated by the vertical arrow. The presence of S$_2$F$_{10}$ in SF$_6$ at the 10 ppb level (the PEL) gives a much larger peak than that shown in Figure 6 and is easily detected when using a single injection. If necessary, additional improvements in signal-to-noise ratios needed for higher sensitivity applications can be achieved through more signal processing, (i.e., averaging of results from more injections coupled with appropriate background subtraction) or when using heated MS inlet-tube conditions that optimize the efficiency of S$_2$F$_{10}$ conversion into SOF$_4$.

Mass Spectrometric Investigation of S$_2$F$_{10}$ Pyrolysis. In order to determine the optimum operating temperature range for the heated gas inlet tube and to better understand the thermal S$_2$F$_{10}$ conversion mechanism discussed in the previous section, it was necessary to investigate the pyrolysis
of $\text{S}_2\text{F}_{10}$ on heated metal surfaces at low pressure and at different temperatures. The specific purposes of this investigation were to (1) show evidence that it is surface chemistry which is involved in the $\text{S}_2\text{F}_{10}$ conversion, (2) indicate the temperature range over which this conversion is effective, (3) demonstrate that $\text{SF}_6$ does not chemically decompose in this temperature range, and (4) provide an independent verification that $\text{SOF}_2$ is indeed one of the products of the $\text{S}_2\text{F}_{10}$ conversion process.

An Extrel quadrupole mass spectrometer was used for these measurements, and the sample gas was admitted to the MS via heated stainless steel bellows connected to a variable-leak valve. The temperature of the bellows could be varied from 20 to 300 °C, and the mass spectra could be observed as a function of the temperature of the inlet system. The gas pressure in the bellows was estimated to be lower than 1 mTorr ($\sim 0.13$ Pa), and the pressure in the MS ion source was below $5 \times 10^{-5}$ Torr.

Shown respectively in Figures 7 and 8 are mass spectra obtained from mixtures of 1500 ppm $\text{SF}_6$ and 1500 ppm $\text{S}_2\text{F}_{10}$.
in argon for different temperatures of the inlet bellows. At 30 °C, the mass spectra of SFs and SFs are seen to be nearly identical in agreement with previously published data (14, 15, 19, 20). Other than minor differences in the relative intensities of the SFs ions (x = 1–4), the only significant difference between the mass spectra of SFs and SFs is the appearance of a peak at m/z = 54 (SFs+) in the SFs spectrum that is not present in SFs spectrum. Peaks at masses 48, 64, 67, and 86 in the SFs spectrum at 30 °C are due to small impurities of SO2 and SOF2 present in the SFs sample. At 220 °C, the SFs mass spectrum remains essentially unchanged, indicating that SFs does not undergo a measurable chemical transformation in the heated inlet tube. The SFs spectrum, on the other hand, exhibits a significant change for temperatures above about 100 °C. In going from 30 to 200 °C, the ratio of the SFs+ (m/z = 89) peak to the SFs+ (m/z = 127) peak in the SFs mass spectrum increases, indicating conversion of SFs into SFs or SOF2. Peaks associated with SOF2 at m/z = 48, 67, and 86 become more prominent above 100 °C and dominate the spectrum at 270 °C, indicating that SFs is nearly completely destroyed at this temperature with SOF2 as the predominant stable byproduct.

Tests performed with different inlet tubes appear to indicate that, at any given temperature, the conversion of SFs into SOF2 becomes more efficient as the effective surface area encountered by the incoming gas is increased, e.g., a bellows gives a more complete conversion than a straight tube of the same length. This trend is consistent with chemical conversion via a surface-catalyzed reaction. There are indications that some surface materials may be more effective than others in converting SFs to SOF2; however, an extensive investigation appeared to be unwarranted in view of the relatively high efficiency achieved with commonly used stainless steel. The temperature and presence of adsorbed water appear to be more important than either surface configuration or composition.

The detailed mechanisms of SFs conversion to SOF2 on heated surfaces are not presently known. It is speculated that the process involves thermally induced dissociation of SFs along the weak sulfur–sulfur bond followed by a fast reaction of SF3 with H2O adsorbed on the surface, i.e.

\[
\text{SF}^+_6 \rightarrow \text{SF}^+_5 + \text{SF}_6
\]

\[
\text{SF}^+_6 + \text{H}_2\text{O} \rightarrow \text{SOF}^+_2 + 2\text{HF} + \text{F}
\]

Previous work (21–23) has shown that SFs is thermally unstable in the gas phase at temperatures above 100 °C. The thermal unimolecular gas-phase decomposition rate at high pressures (23) has a temperature (T) dependence given by

\[
k = 3 \times 10^{19} \exp\left(-46400/RT\right)
\]

which is based on reaction data (21) obtained in the temperature range 435–454 K (RT is given in units of cal and k in s⁻¹). Assuming this expression applies at room temperature, the half-life of SFs in the gas phase is predicted to be about 10⁷ years. The half-life drops dramatically to 10⁵ s at 475 K. However, the SFs decomposition rate implied by the present mass spectrometric results is significantly higher than predicted by the above gas-phase rate and unlikely to apply at the low pressures typically encountered here in the heated inlet tube, further supporting the likelihood of a surface-catalyzed reaction mechanism.

An indirect indication of the role of adsorbed water was obtained from measurements made with the quadrupole mass spectrometer under conditions where the inlet line temperature was allowed to rise relatively rapidly after the Ar/SF10 mixture was introduced. The mass spectra obtained in this way differ from those shown in Figure 8, which correspond to equilibrated conditions achieved after keeping the inlet line at the indicated temperatures for many minutes. The results obtained from monitoring selected ions as a function of time under the “transient” conditions of continuous rising inlet-line temperature are shown in Figure 9. Presented in this figure are time-dependent peak intensities for ions at m/z = 86 and 67, which are indicators of SOF2; m/z = 127, indicator of SFs; and m/z = 89, indicator of SFs. Unlike the results given in Figure 8, the yield of SOF2 is seen to go through a maximum at a time of 6 min, which corresponds to a temperature of 160 °C. The data for m/z = 127 indicate that SFs is nearly completely decomposed at this temperature, i.e., the intensity for this ion ceases to decrease significantly beyond this temperature. The m/z = 127 signal that appears at higher temperatures is undoubtedly associated with SFs, which can be a product of SFs decomposition. As noted by Herron (23) (see also ref 24), SF6 and SFs can be formed in the gas phase by the disproportionation reaction

\[
\text{SF}_6 + \text{SF}_6 \rightarrow \text{SF}_4 \rightarrow \text{SF}_6
\]

As the temperature increases, the m/z = 89 signal does not fall off quite as rapidly as the m/z = 127 signal, thus suggesting formation of SFs, whose primary electron impact ion is SFs+. The increase in SOF2 production with time can be attributed to an increase in the decomposition rate of SF10 and an increase in the surface hydrolysis rate of the decomposition products as the surface temperature is increased. However, as the amount of water adsorbed on the surface decreases due to heating, the rate of SFs conversion into SOF2 drops. It should be noted that at the highest temperatures the production of SOF2 has decreased with no corre-
sponding increase in any of the other compounds that are being monitored. This suggests that at high temperatures S$_2$F$_{10}$ or its byproducts are being converted into compounds that are presently unidentified.

Although there is evidence (25) that SOF$_2$ hydrolyzes slowly in the gas phase at 300 K and may react with H$_2$O on surfaces, little is known about its decomposition at higher temperatures. These results indicate that there is an optimum temperature range at which conversion of S$_2$F$_{10}$ into SOF$_2$ is most efficient. If the temperature is too low, the conversion rate is low, and if the temperature is too high, SOF$_2$ itself may be destroyed.

**Gas-Phase Impurities.** It should be realized that if gaseous species are present in the unknown sample that could react with S$_2$F$_{10}$, or its decomposition products at temperatures above 150 °C, uncertainties can be introduced in the quantitative analysis for S$_2$F$_{10}$ by the method proposed here if the reference sample does not also contain these species in nearly the same amounts. It is known (26–29) that S$_2$F$_{10}$ can react at high temperatures with numerous gases such as NO, NO$_2$, NO$_3$, NOCl, (CF$_3$)$_2$NONO, CH$_2$ONONO, Fe(CO)$_5$, ICl, CH$_3$Hg, CH$_2$Hg, (CH$_3$)$_2$NH, BCl$_3$, and NH$_3$. If it is suspected that gases may be present in the unknown sample that can react with S$_2$F$_{10}$ at temperatures above 150 °C, then care must be taken to assess the influence of these gases on the GC/MS response to S$_2$F$_{10}$. Ideally the reference sample should have the same, or nearly the same, composition as the unknown sample. It was found here that the response of the GC/MS to S$_2$F$_{10}$ was not significantly influenced by the presence of the oxyfluorides SOF$_2$, SOF$_3$, and SOF$_4$, which are commonly formed together with S$_2$F$_{10}$ during decomposition or oxidation of SF$_6$.

Of particular importance is the presence of water vapor as a contaminant in a sample. The gas-phase water vapor present in the sample can affect the amount of adsorbed water on the inlet tube surface at any given time and thus the S$_2$F$_{10}$-to-SOF$_2$ conversion efficiency. Low-water vapor concentrations in gas samples did not show significant effects. However, it was observed that the addition of excessive amounts of water vapor to an S$_2$F$_{10}$ sample can noticeably decrease the amount of SOF$_2$ detected from S$_2$F$_{10}$ conversion at surface temperatures above about 120 °C. This is not understood but may be due to mechanisms that either inhibit the conversion if gas-phase water is present or increase the rate of SOF$_2$ decomposition (for example, by hydrolysis (29)) at elevated temperatures. The reactivities of gas-phase S$_2$F$_{10}$ and SOF$_2$ toward water vapor at temperatures above 100 °C are presently unknown and require more investigation.

**Reference Sample Stability.** Surface conversion of S$_2$F$_{10}$ into SOF$_2$ also occurs at room temperature, although at a much slower rate than observed at elevated temperatures. This decomposition raises questions about the long-term reliability of reference gas samples containing known amounts of S$_2$F$_{10}$ that are needed for calibration of the GC/MS. In order to assess the stability of S$_2$F$_{10}$ in reference samples, a series of tests were performed to monitor the content of S$_2$F$_{10}$-containing cylinders over relatively long periods of time. Preliminary reports of these tests have already been given (7, 20).

It was found that the rate of S$_2$F$_{10}$ decomposition depended on such factors as temperature, cylinder material, surface-to-volume ratio, and moisture content. Data indicating the temperature and moisture content dependencies of S$_2$F$_{10}$ decomposition in 150-mL stainless steel cylinders are shown respectively in Figures 10 and 11. Shown in these figures are measured S$_2$F$_{10}$ concentrations in argon as a function of time after mixture preparation. The measurements were performed by using the gas chromatography/mass spectrometry method described above, and the “aged” samples were compared with reference samples prepared immediately prior to the measuremen. The “wet” sample (H$_2$O added) results in Figure 11 were obtained from a sample prepared by injecting 1 mL of liquid water into the cylinder under vacuum prior to introducing the Ar/S$_2$F$_{10}$ gas mixture. The data presented in Figures 10 and 11 clearly demonstrate that the S$_2$F$_{10}$ decomposition rate increases with increasing temperature and moisture content.

The products of the S$_2$F$_{10}$ decomposition were found to include SOF$_2$ and SF$_6$, and thus, it is speculated that the decomposition process involves a surface-catalyzed reaction with adsorbed H$_2$O that may be similar to that observed at higher temperatures in the heated MS gas inlet tube. The SOF$_2$ produced from S$_2$F$_{10}$ also appears to react slowly on the stainless steel surface and convert to other products that have yet to be identified. Once S$_2$F$_{10}$ disappears from the gas, SOF$_2$ will also eventually disappear (30). From analyses of the decomposed gas using mass spectrometry and gas chromatography/mass spectrometry, it has not been possible to account for all of the sulfur originally present in S$_2$F$_{10}$. The only identified gaseous compound resulting from S$_2$F$_{10}$ decomposition that contains sulfur and exhibits long-term stability is SF$_6$. Generally, less than 15% of the sulfur can be accounted for by this product.

On the basis of the tests that were conducted, long-term storage of S$_2$F$_{10}$ reference samples in the gas phase cannot be recommended. It was found that samples stored under even the most favorable conditions exhibited significant decomposition over sufficiently long periods of time. It is recommended that reference samples be prepared immediately prior to gas analysis, under conditions that are as dry as possible and in cylinders that are as large as possible.

Preliminary tests of commercial-grade SF$_6$ (98.8% purity) have indicated that S$_2$F$_{10}$ does not readily decompose in SF$_6$-filled cylinders when compressed into the liquid phase. Analysis showed that S$_2$F$_{10}$ was present as an impurity at a level of about 40 ppb in a 12-year-old sample. It should be noted that S$_2$F$_{10}$ is a possible byproduct from the commercial production of SF$_6$ and can be present as a trace liquid impurity.
in the liquified SF₆ that exists in pressurized cylinders. The results of analyzing SF₆ stored as a liquid suggest that significant improvements might be achieved in maintaining sample stability by compressing reference samples into the liquid phase.

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