

Detection of Trace Disulfur Decafluoride in Sulfur Hexafluoride by Gas Chromatography/Mass Spectrometry

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A new method is described for detection of S_2F_{10} in SF_6 in the parts-per-billion (ppb) level. The method utilizes a gas chromatograph/mass spectrometer (GC/MS) equipped with a heated jet separator. S_2F_{10} is converted to SOF_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_2O . As a consequence of this conversion, peaks corresponding to S_2F_{10} appear on single-ion chromatograms at ion masses characteristic of SOF_2 ($m/z = 48, 67, \text{ and } 86$) where there is little or no interference from SF_6 features. By this method, a direct analysis of SF_6 for S_2F_{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_2F_{10} reference samples are discussed.

INTRODUCTION

The ability to detect gaseous disulfur decafluoride (S_2F_{10}) at trace levels in sulfur hexafluoride (SF_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_2F_{10} can be produced during electrical discharge activity in SF_6 . The concern about S_2F_{10} production in SF_6 stems in part from the increasingly widespread use of SF_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_2F_{10} at 10 ppb (10). However, due to the difficulty of detecting low concentrations of S_2F_{10} in SF_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_2F_{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_2F_{10} enrichment procedure requiring long analysis times (~45 min). When SF_6 is a major constituent of the gas in which S_2F_{10} is to be detected, the sensitivity for S_2F_{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-attaching properties of the residual SF_6 , which interferes with the S_2F_{10} signal. Reduced sensitivity for S_2F_{10} detection in the presence of SF_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 S_2F_{10} has a positive-ion mass spectrum that is very similar to that of SF_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_2F_{10} mass spectrum also appear in the SF_6 spectrum. Thus, even when chromatographic separation of S_2F_{10} from SF_6 is used, ions from SF_6 can sufficiently increase the background level to interfere with S_2F_{10} detection. Recent claims (16) of using a mass spectrometer (MS) operated at low electron-impact energies to detect trace levels of S_2F_{10} in SF_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_2F_{10} in gaseous SF_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_2F_{10} is converted to thionyl fluoride (SOF_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_2 differ from those in the SF_6 spectrum, interference of SF_6 with the S_2F_{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_2F_{10} in SF_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 180 °C. As discussed later, a fraction of the S_2F_{10} undergoes thermal decomposition in the heated tube and converts to SOF_2 via surface-catalyzed wall reactions with H_2O . SOF_2 can then be detected by the mass spectrometer without interference by the ion signals from SF_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_2F_{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 5992A 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 \times 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_2F_{10} in SF_6 of nearly 1 ppb were obtainable with the instrument described above.

Pure S_2F_{10} 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

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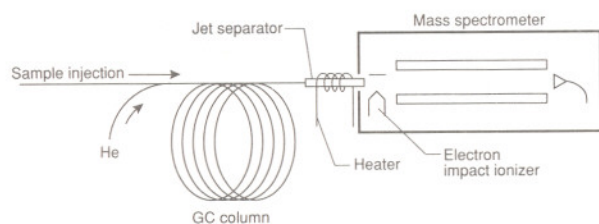


Figure 1. Schematic diagram of the GC/MS system with a heated jet separator between the GC column and the ion source of the mass spectrometer. Heating of the interface between the GC and MS is essential for the sensitive detection of S_2F_{10} in the presence of SF_6 .

reference mixtures were prepared immediately prior to use, either by injection or needle valve, in argon (99.999%) or SF_6 (99.99%) in a stainless steel vacuum manifold housed in a vented hood. The argon and SF_6 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 S_2F_{10} samples in buffer gases other than SF_6 , trace amounts of S_2F_{10} could be detected by single-ion monitoring of SF_5^+ , SF_4^+ , SF_3^+ , SF_2^+ , and F^+ ($m/z = 127, 108, 89, 70$, and 19) produced by direct ionization of S_2F_{10} (15). When mixed with SF_6 , sensitive S_2F_{10} detection required the monitoring of ion signals characteristic of the SOF_2 produced by surface conversion in the heated inlet tube mentioned above. These ions include SOF_2^+ , 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 S_2F_{10} 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 S_2F_{10} on hot surfaces under vacuum that indicates the conditions for optimum conversion efficiency and that supports the hypothesis that adsorbed H_2O accounts for the conversion of S_2F_{10} into SOF_2 . 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 S_2F_{10} at room temperature affects the maintenance of reliable S_2F_{10} reference samples.

GC/MS Results and Calibration. When a gas sample containing S_2F_{10} is injected into the column of the GC/MS in which the interface is heated, the conversion of S_2F_{10} into SOF_2 discussed in the next section becomes evident from single-ion chromatograms at $m/z = 48, 67$, and 86 (SO^+ , SOF^+ , and SOF_2^+). Examples of such chromatograms are shown in Figure 2 for a 500 ppm sample of S_2F_{10} in argon. Ions produced by direct ionization of S_2F_{10} are observed (F^+ and SF_5^+) as are ions from SOF_2 produced by surface conversion (SOF_2^+ and SO^+).

The $m/z = 20$ chromatogram in Figure 2 exhibits a peak at the retention time characteristic for S_2F_{10} , thus indicating that HF is also a byproduct of S_2F_{10} 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 S_2F_{10} for the column conditions used here. Thus, although HF may be formed by thermal decomposition

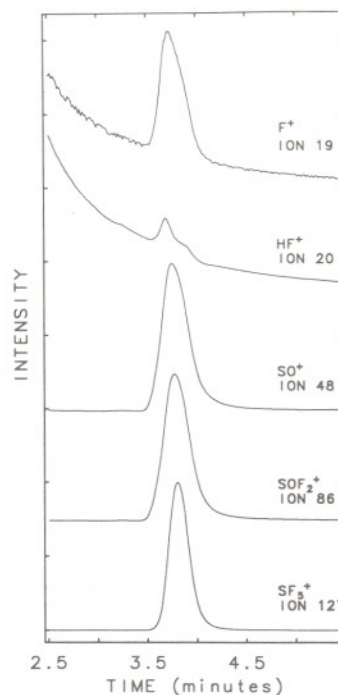


Figure 2. Chromatograms of representative ion signals due to ions from direct ionization of S_2F_{10} and from ionization of surface conversion products for a 500 ppm sample of S_2F_{10} in 100 kPa of argon buffer gas.

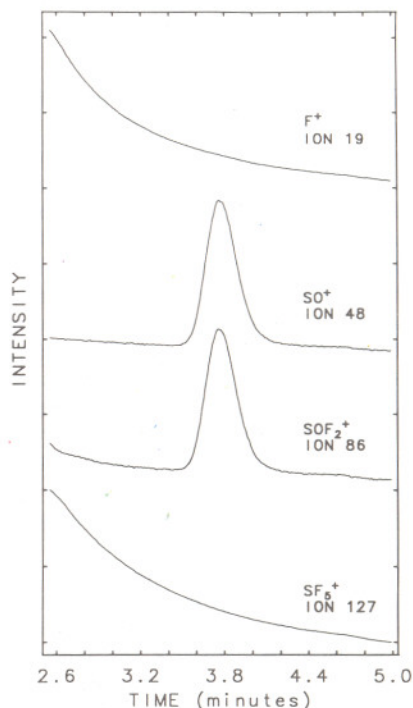


Figure 3. Single-ion chromatograms of a 660 ppb S_2F_{10} sample in 200 kPa of SF_6 buffer gas.

of S_2F_{10} in the heated gas inlet tube, it cannot, by itself, be relied upon to give an unambiguous indication of S_2F_{10} .

For the results shown in Figure 2, ions due to direct ionization of S_2F_{10} are observable because no SF_6 was present in the sample. However, in the presence of SF_6 , S_2F_{10} signals in the single-ion chromatograms at $m/z = 19$ and 127 are obscured by the SF_6 contribution to the signal at these masses. This is demonstrated by data presented in Figure 3 from a gas sample containing 660 ppb S_2F_{10} in SF_6 . These results show the effect of SF_6 in limiting the sensitivity for S_2F_{10} detection when conventional mass spectrometric monitoring

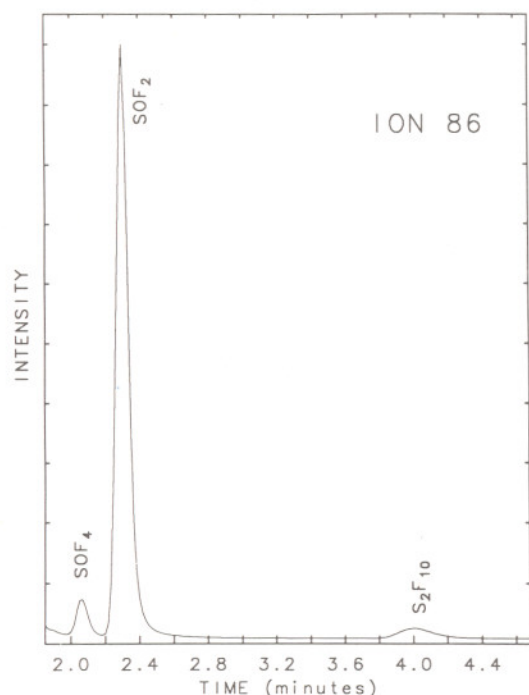


Figure 4. Single-ion chromatogram of an "unknown" sample of SF_6 that was partially decomposed in a direct-current corona discharge.

is used and clearly show the advantages of using the S_2F_{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 trace amounts of the oxyfluorides SOF_2 , SOF_4 , and SO_2F_2 in addition to S_2F_{10} . It is seen that the retention times of SOF_2 and SOF_4 produced by the discharge are much shorter than for S_2F_{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_2F_{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_2F_{10} concentration in reference gas samples. Typical response curves obtained with known concentrations of S_2F_{10} mixed with argon are shown in Figure 5 for the indicated m/z values. The S_2F_{10} response is compared with that for SOF_2 , which was also added to the mixture in known concentrations. The S_2F_{10} response curves for $m/z = 48$ and 86, corresponding to the chemical conversion of S_2F_{10} into SOF_2 , are seen to be distinctly nonlinear. The deviation from linearity is greatest at the highest S_2F_{10} concentrations and indicates a saturation effect possibly associated with depletion of H_2O from the heated jet separator tube surface during the conversion of S_2F_{10} into SOF_2 . By contrast, the S_2F_{10} response curve for $m/z = 127$, corresponding to unreacted S_2F_{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_2F_{10} conversion process are quite reproducible for a given set of instrument operating conditions. Nevertheless, when attempting accurate measurements of S_2F_{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.

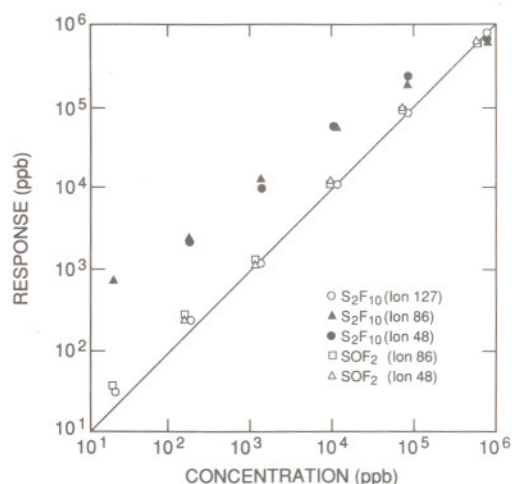


Figure 5. Detection response curves for various concentrations of S_2F_{10} and SOF_2 in argon using the Chromosorb GC column discussed in the text. Open symbols represent detection of S_2F_{10} and SOF_2 by direct ionization, while closed symbols represent detection of S_2F_{10} by ionization of SOF_2 produced by surface catalysis. The measured responses were normalized to the observed responses of a reference sample containing 750 ppm S_2F_{10} and 750 ppm SOF_2 in argon (upper right-hand corner). Similar response curves are obtained for samples diluted in SF_6 .

The response of the present GC/MS system to S_2F_{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_2F_{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_2F_{10} concentrations shows evidence of H_2O 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_2F_{10} injected, the longer the surface recovery time of the inlet tube. For samples containing less than 10 ppm S_2F_{10} , the recovery time of the system used here was found to be less than the typical S_2F_{10} retention time of 4 min.

The limit of S_2F_{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_2F_{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_2F_{10} peak is statistically significant and is indicated by the vertical arrow. The presence of S_2F_{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_2F_{10} conversion into SOF_2 .

Mass Spectrometric Investigation of S_2F_{10} Pyrolysis.

In order to determine the optimum operating temperature range for the heated gas inlet tube and to better understand the thermal S_2F_{10} conversion mechanism discussed in the previous section, it was necessary to investigate the pyrolysis

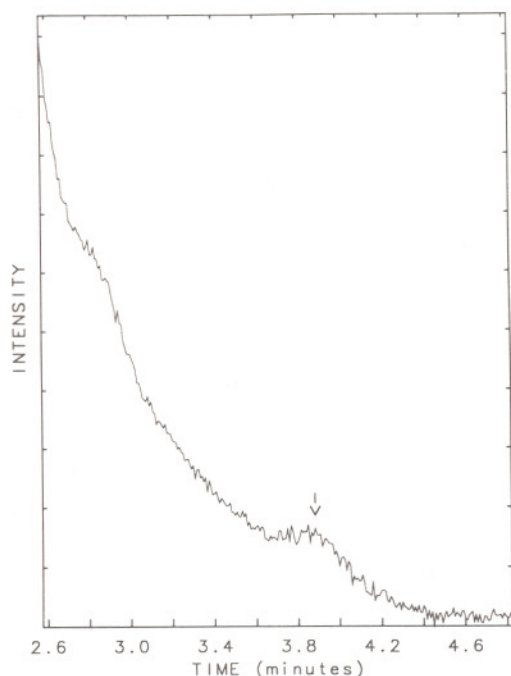


Figure 6. Single-ion chromatogram (ion 86) of 4 ppb S_2F_{10} in 200 kPa of SF_6 .

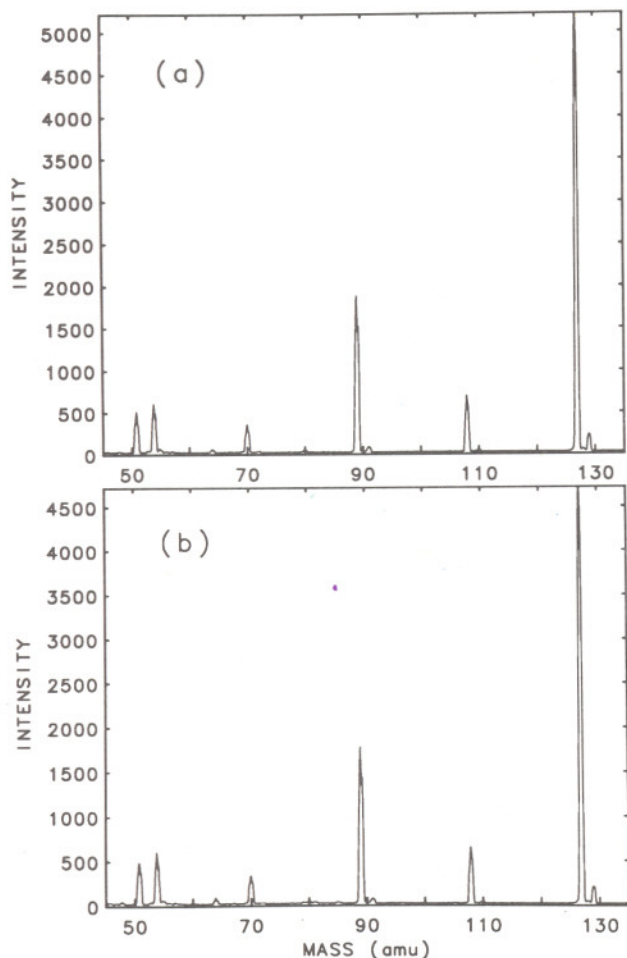


Figure 7. Electron-impact mass spectra of 1500 ppm SF_6 in argon buffer gas at (a) 30 and (b) 220 °C.

of S_2F_{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 S_2F_{10} conversion, (2) indicate the temperature range over which this conversion is effective, (3)

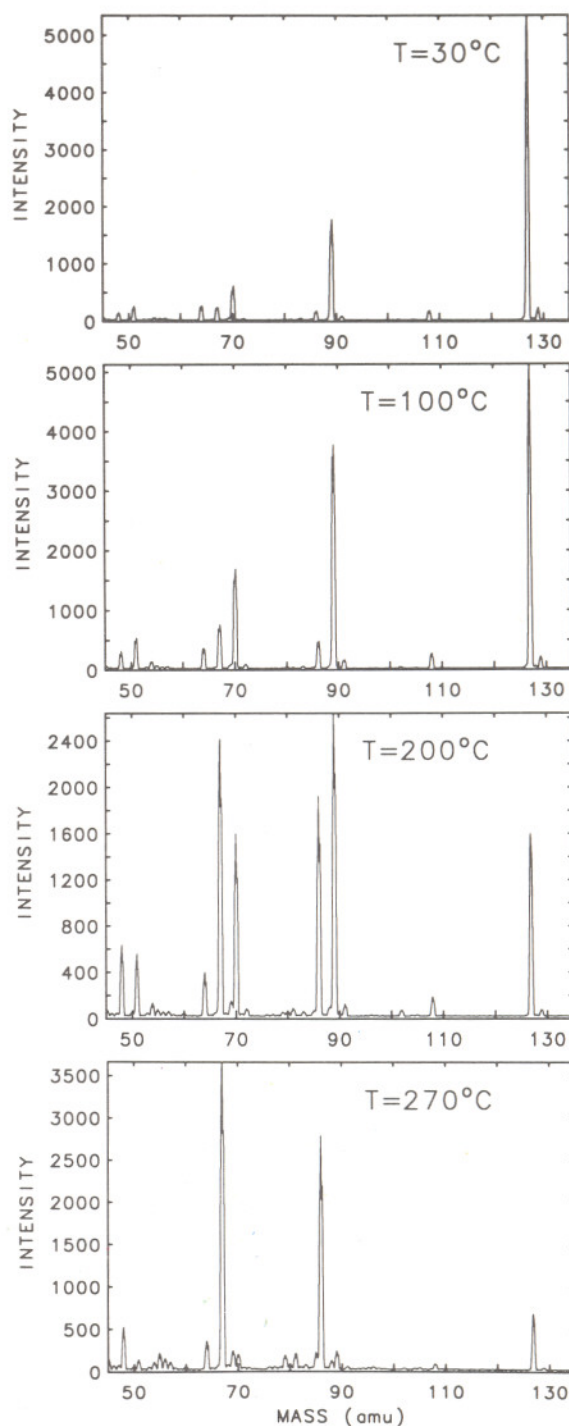


Figure 8. Electron-impact mass spectra of 1500 ppm S_2F_{10} in argon buffer gas at various temperatures.

demonstrate that SF_6 does *not* chemically decompose in this temperature range, and (4) provide an independent verification that SOF_2 is indeed one of the products of the S_2F_{10} conversion process.

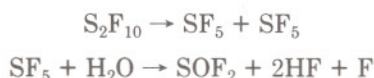
An Extrel quadrupole mass spectrometer was used for these measurements, and the sample gas was admitted to the MS via heated stainless steel bellows connected to a variable-leak valve. The temperature of the bellows could be varied from 20 to 300 °C, and the mass spectra could be observed as a function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

Shown respectively in Figures 7 and 8 are mass spectra obtained from mixtures of 1500 ppm SF_6 and 1500 ppm S_2F_{10}

in argon for different temperatures of the inlet bellows. At 30 °C, the mass spectra of S_2F_{10} and SF_6 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 SF_x^+ ions ($x = 1-4$), the only significant difference between the mass spectra of S_2F_{10} and SF_6 is the appearance of a peak at $m/z = 54$ (SF_4^{2+}) in the SF_6 spectrum that is not present in S_2F_{10} spectrum. Peaks at masses 48, 64, 67, and 86 in the S_2F_{10} spectrum at 30 °C are due to small impurities of SO_2 and SOF_2 present in the S_2F_{10} sample. At 220 °C, the SF_6 mass spectrum remains essentially unchanged, indicating that SF_6 does not undergo a measurable chemical transformation in the heated inlet tube. The S_2F_{10} 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 SF_3^+ ($m/z = 89$) peak to the SF_5^+ ($m/z = 127$) peak in the S_2F_{10} mass spectrum increases, indicating conversion of S_2F_{10} into SF_4 or SF_5 . Peaks associated with SOF_2 at $m/z = 48, 67$, and 86 become more prominent above 100 °C and dominate the spectrum at 270 °C, indicating that S_2F_{10} is nearly completely destroyed at this temperature with SOF_2 as the predominant stable byproduct.

Tests performed with different inlet tubes appear to indicate that, at any given temperature, the conversion of S_2F_{10} into SOF_2 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 S_2F_{10} to SOF_2 ; 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 S_2F_{10} conversion to SOF_2 on heated surfaces are not presently known. It is speculated that the process involves thermally induced dissociation of S_2F_{10} along the weak sulfur-sulfur bond followed by a fast reaction of SF_5 with H_2O adsorbed on the surface, i.e.



Previous work (21-23) has shown that S_2F_{10} 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

$$k = 3 \times 10^{19} \exp(-46400/RT)$$

which is based on reaction data (21) obtained in the temperature range 435-454.5 K (RT is given in units of cal and k in s^{-1}). Assuming this expression applies at room temperature, the half-life of S_2F_{10} in the gas phase is predicted to be about 10^7 years. The half-life drops dramatically to 10^2 s at 475 K. However, the S_2F_{10} 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/S_2F_{10} 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

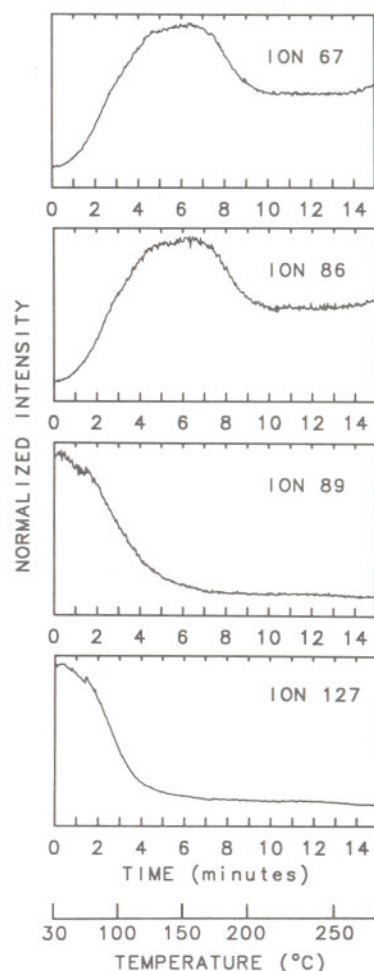


Figure 9. Signal intensity of several selected ions from a 1500 ppm S_2F_{10} sample in argon as a function of time as the inlet temperature is rapidly increased from room temperature to 270 °C.

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 SOF_2 ; $m/z = 127$, indicator of S_2F_{10} and SF_6 ; and $m/z = 89$, indicator of S_2F_{10} , SF_6 , and SF_4 . Unlike the results given in Figure 8, the yield of SOF_2 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 S_2F_{10} 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 SF_6 , which can be a product of S_2F_{10} decomposition. As noted by Herron (23) (see also ref 24), SF_4 and SF_6 can be formed in the gas phase by the disproportionation reaction



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 SF_4 whose primary electron impact ion is SF_3^+ . The increase in SOF_2 production with time can be attributed to an increase in the decomposition rate of S_2F_{10} 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 S_2F_{10} conversion into SOF_2 drops. It should be noted that at the highest temperatures the production of SOF_2 has decreased with no corre-

spending increase in any of the other compounds that are being monitored. This suggests that at high temperatures S_2F_{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_2O 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_2F_{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_2F_{10} or its decomposition products at temperatures above 150 °C, uncertainties can be introduced in the quantitative analysis for S_2F_{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_2F_{10} can react at high temperatures with numerous gases such as NO , NO_2 , NO_2Cl , $(CF_3)_2NONO$, CH_3ONO , $Fe(CO)_5$, ICl , C_6H_6 , C_2H_4 , $(CH_3)_2NH$, BCl_3 , and NH_3 . If it is suspected that gases may be present in the unknown sample that can react with S_2F_{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_2F_{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_2F_{10} was not significantly influenced by the presence of the oxyfluorides SOF_2 , SO_2F_2 , and SOF_4 , which are commonly formed together with S_2F_{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_2F_{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_2F_{10} sample can noticeably decrease the amount of SOF_2 detected from S_2F_{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 (25)) at elevated temperatures. The reactivities of gas-phase S_2F_{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_2F_{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_2F_{10} that are needed for calibration of the GC/MS. In order to assess the stability of S_2F_{10} in reference samples, a series of tests were performed to monitor the content of S_2F_{10} -containing cylinders over relatively long periods of time. Preliminary reports of these tests have already been given (7, 30).

It was found that the rate of S_2F_{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_2F_{10} decomposition in 150-mL stainless steel cylinders are shown respectively in Figures 10 and 11. Shown in these figures are measured S_2F_{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 mea-

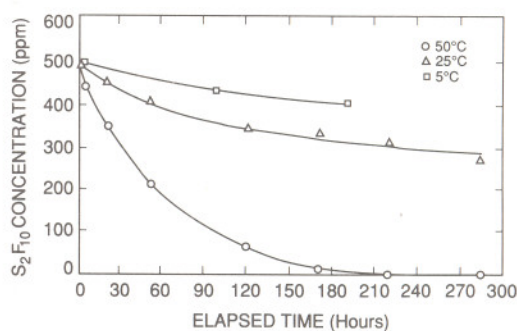


Figure 10. Low-temperature dependence for the decomposition of 500 ppm S_2F_{10} samples in argon stored in 150-mL stainless steel cylinders.

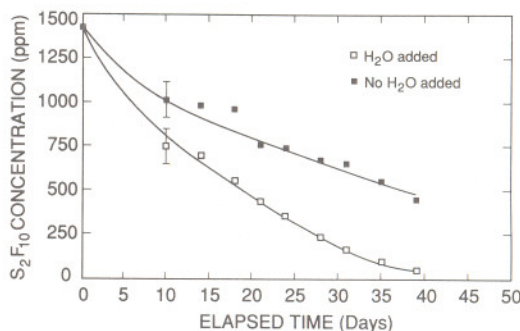


Figure 11. Decomposition of S_2F_{10} as a function of time for two 1400 ppm, S_2F_{10} samples in 1 atm of Ar in 150-mL stainless steel cylinders. For one sample (\square), 1 μ L of liquid water was injected into the cylinder prior to filling with gas.

surements. The "wet" sample (H_2O added) results in Figure 11 were obtained from a sample prepared by injecting 1 μ L of liquid water into the cylinder under vacuum prior to introducing the Ar/ S_2F_{10} gas mixture. The data presented in Figures 10 and 11 clearly demonstrate that the S_2F_{10} decomposition rate increases with increasing temperature and moisture content.

The products of the S_2F_{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_2O that may be similar to that observed at higher temperatures in the heated MS gas inlet tube. The SOF_2 produced from S_2F_{10} also appears to react slowly on the stainless steel surface and convert to other products that have yet to be identified. Once S_2F_{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_2F_{10} . The only identified gaseous compound resulting from S_2F_{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_2F_{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 (99.8% purity) have indicated that S_2F_{10} does not readily decompose in SF_6 -filled cylinders when compressed into the liquid phase. Analysis showed that S_2F_{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_2F_{10} is a possible byproduct from the commercial production of SF_6 and can be present as a trace liquid impurity

in the liquified SF_6 that exists in pressurized cylinders. The results of analyzing SF_6 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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