

## PROCEDURE FOR MEASURING TRACE QUANTITIES OF $S_2F_{10}$ , $S_2OF_{10}$ , AND $S_2O_2F_{10}$ IN $SF_6$ USING A GAS CHROMATOGRAPH-MASS SPECTROMETER

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### INTRODUCTION

The compounds  $S_2F_{10}$ ,  $S_2OF_{10}$ , and  $S_2O_2F_{10}$  are formed by decomposition of gaseous sulfur hexafluoride ( $SF_6$ ) in electrical discharges.<sup>1,2</sup> The species  $S_2F_{10}$  is known to be highly toxic to humans,<sup>3</sup> and there is recent evidence that  $S_2O_2F_{10}$  may also be very toxic.<sup>4</sup> There is, therefore, an interest in having analytical methods to detect these compounds in compressed  $SF_6$  at trace levels down to 10 parts in  $10^9$  by volume (10 ppb<sub>v</sub>). Two chromatographic methods have been used to detect these compounds at the 10 ppb<sub>v</sub> level or lower. The first method developed by Sauers and coworkers<sup>5</sup> is based on a cryogenic enrichment procedure first proposed by Janssen,<sup>6</sup> and uses a gas chromatograph with an electron-capture detector. The second method, which is the focus of the present work, utilizes a gas chromatograph-mass spectrometer (GC/MS) with a thermal-chemical converter.<sup>7</sup>

The purposes of the present work are: 1) to define a procedure for using the GC/MS method to make fast, reliable measurement of trace  $S_2F_{10}$ ,  $S_2OF_{10}$ , and  $S_2O_2F_{10}$  in pressurized  $SF_6$ ; 2) to discuss the major sources of error that can be encountered in using the method; and 3) to discuss the factors that limit the sensitivity such as interference from other compounds.

### MEASUREMENT SYSTEM

The GC/MS measurement system, shown diagrammatically in Fig. 1, has previously been described in detail by Olthoff and coworkers.<sup>7</sup> The gas chromatograph connects to a quadrupole mass spectrometer through a jet separator that is heated to a temperature of about 180 °C. A significant fraction of the  $S_2F_{10}$  that enters the jet separator tube from the GC column is converted to  $SOF_2$  by a surface-catalyzed reaction with  $H_2O$  adsorbed on the walls of the separator. Peaks therefore appear in

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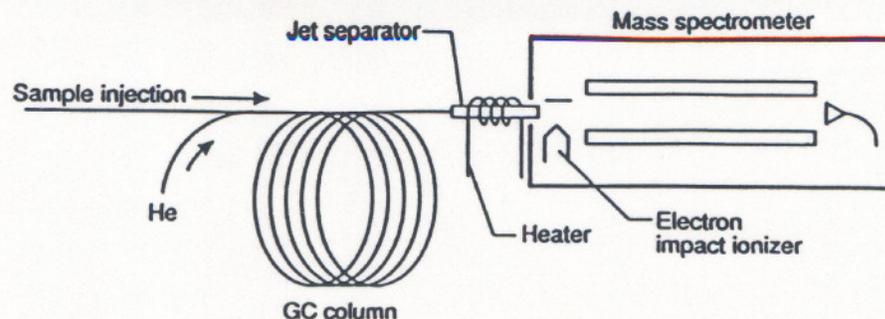


Figure 1. Diagram of the gas chromatograph-mass spectrometer system.

Table 1. Mass-to-charge ratios of ions in atomic units (u) selected for observing  $S_2F_{10}$ ,  $S_2OF_{10}$ , and  $S_2O_2F_{10}$  and typical GC-column retention times.

	$S_2F_{10}$	$S_2OF_{10}$	$S_2O_2F_{10}$
Ions observed ( $m/z$ )	(86,67,48)	(86,48)	(121,102,86,67)
Column retention time (min)	4.48	3.99	5.72

the "single-ion" chromatograms at mass-to-charge ratios ( $m/z$ ) of 48, 67, and 86 u (characteristic of the  $SOF_2$  mass spectrum) at the time that  $S_2F_{10}$  elutes from the column. The conversion to  $SOF_2$  avoids the interfering effects of  $SF_6$  on the  $S_2F_{10}$  signal and enormously enhances the sensitivity of detection. The interference of  $SF_6$  is a consequence of the fact that it has a mass spectrum identical to that of  $S_2F_{10}$  at the standard 70 eV electron-impact ionization energy.<sup>8</sup> This method allows  $S_2F_{10}$  to be detected in  $SF_6$  down to the 1 ppb<sub>v</sub> level.

It is not necessary for the species  $S_2OF_{10}$  and  $S_2O_2F_{10}$  to undergo a chemical conversion in the jet separator in order to detect them with high sensitivity, because the predominant ions in their mass spectra are different from those in the  $SF_6$  mass spectrum. The observed GC-column retention times for  $S_2F_{10}$ ,  $S_2OF_{10}$ , and  $S_2O_2F_{10}$  and the  $m/z$  values of the ions that were used to detect these compounds are given in Table 1.

The retention times given in Table 1 apply to a 7.3 m Chromosorb WAW column<sup>†</sup> operated at room temperature (20–23 °C). No attempt has yet been made to determine the lowest concentrations of  $S_2OF_{10}$  and  $S_2O_2F_{10}$  that can be detected with this system.

## ANALYTICAL PROCEDURE

A quantitative analysis of  $SF_6$  gas using the GC/MS method to determine the concentrations of  $S_2F_{10}$ ,  $S_2OF_{10}$ , and  $S_2O_2F_{10}$  at trace levels is most accurately performed by making immediate comparisons with reference gas samples that contain known concentrations of these compounds. Using the programmable features of the GC/MS, it is possible to make a sequence of sample injections that give responses which appear

<sup>†</sup>Certain commercial equipment, instruments, or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

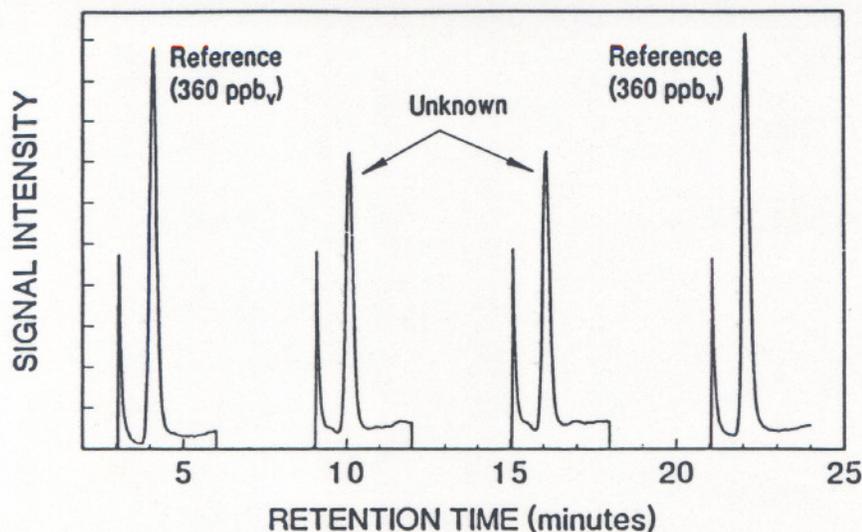


Figure 2. Single-ion chromatogram for  $m/z = 86$  u showing responses from a sequence of four 1.0 ml injections: two unknowns and two references containing the indicated amount of  $S_2F_{10}$  in 300 kPa  $SF_6$ .

on one single-ion chromatogram as shown in Fig. 2. In obtaining the chromatogram displayed in Fig. 2, the mass spectrometer was not operated for the first three minutes following the injection of a sample into the GC column. This is the time during which most of the  $SF_6$  elutes from the column. Deactivation of the mass spectrometer during this time reduces the background and inhibits exposure of the detector to the large ion flux associated with  $SF_6$ .

In following this procedure, it is desirable to bracket one or more injections from the unknown sample with at least two injections from a reference containing a known concentration of the species of interest. In this way, it is possible to eliminate errors due to drift in the GC/MS response such as associated with GC-column conditioning effects, changes in the jet separator surface composition, and variations in the electron-impact source conditions. It is also desirable to use the same injection size (quantity of gas) for both the reference and the unknown and to adjust the concentration of the reference to give a response (peak height) that closely matches that of the unknown. These precautions reduce the errors associated with nonlinearities in the response which tend to be more of a problem with  $S_2F_{10}$  than with the other species.<sup>7</sup> The results of analysis for  $S_2F_{10}$  content shown in Fig. 2 were obtained using a 1.0 ml  $\times$  300 kPa injection size. The unknown concentration is determined from the ratio of the average responses from the unknown and reference injections based on either peak heights or areas under the peaks. If there are no interference effects associated with other compounds or with previous injections, the area and peak-height determinations should yield the same result to within the normal statistical variability which will tend to increase as the response (concentration) decreases. Interference from preceding injections can usually be eliminated by appropriate adjustment of the sample monitoring times (MS on) in the injection sequence, which is 3.0 min for the case shown in Fig. 2. Before setting up the injection sequence, it is desirable to make a single "long-time" chromatogram from the unknown sample to determine the possible presence of other peaks at times longer than that for the species of interest.

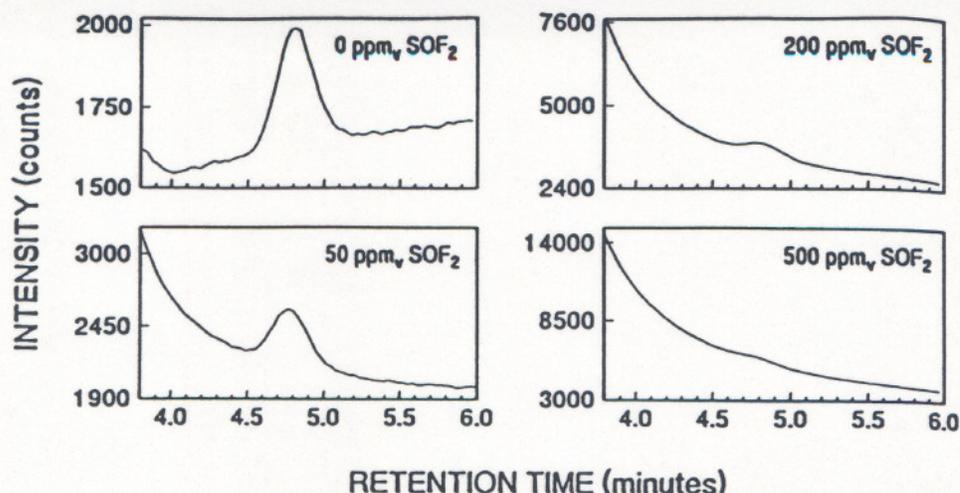


Figure 3. Single-ion chromatograms at  $m/z = 86$  u that show the effect of  $\text{SOF}_2$  on the detection of 20 ppb<sub>v</sub>  $\text{S}_2\text{F}_{10}$  in 200 kPa  $\text{SF}_6$ . Shown are the concentrations of  $\text{SOF}_2$  that were present and the peak for  $\text{S}_2\text{F}_{10}$  that appears at a retention time of about 4.8 min.

## SOURCES OF ERROR

### Interference Effects

When the GC column is operated under "normal conditions" at a temperature of 20 °C and a helium carrier gas flow rate of 20 to 30 ml/min at atmospheric pressure (100 kPa), the compounds  $\text{S}_2\text{F}_{10}$ ,  $\text{S}_2\text{OF}_{10}$ , and  $\text{S}_2\text{O}_2\text{F}_{10}$  are sufficiently well separated in time that they do not interfere with each other. It is thus possible to observe all three species on a single chromatogram for the common ion at  $m/z = 86$  u (see Table 1). The compound  $\text{SOF}_2$  has a retention time of less than 2.4 min under the conditions that give the results listed in Table 1; therefore it is sufficiently well separated from the compounds of interest that it does not ordinarily cause significant interference. On the other hand, if its concentration greatly exceeds that of the compounds of interest, particularly  $\text{S}_2\text{F}_{10}$ , it can have the effect of increasing the background level enough to reduce the detection sensitivity. This is illustrated by the results displayed in Fig. 3. Shown in this figure are the responses for samples that all contain 20 ppb<sub>v</sub>  $\text{S}_2\text{F}_{10}$  and differing amounts of  $\text{SOF}_2$  from 0 to 500 parts in  $10^6$  by volume (ppm<sub>v</sub>). It is seen that the  $\text{S}_2\text{F}_{10}$  detection sensitivity is reduced to about 20 ppb<sub>v</sub> when the  $\text{SOF}_2$  concentration reaches the 500 ppm<sub>v</sub> level. Over this range of  $\text{SOF}_2$  concentrations, the lowest concentration of  $\text{S}_2\text{F}_{10}$  in ppb<sub>v</sub> that can be detected is estimated from the data to be  $(2.0 + 3.6 \times 10^{-2}[\text{SOF}_2])$  where  $[\text{SOF}_2]$  is in ppm<sub>v</sub>.

Of the contaminants that are often present in commercial  $\text{SF}_6$ , it was found that the compound  $\text{CCl}_2\text{F}_2$  can be a source of interference in the detection of  $\text{S}_2\text{F}_{10}$  under some conditions. This is because it has a retention time that is only 0.10 min shorter than that for  $\text{S}_2\text{F}_{10}$ . In most cases it is possible to distinguish  $\text{CCl}_2\text{F}_2$  from the  $\text{SOF}_2$  formed from  $\text{S}_2\text{F}_{10}$  by examination of the mass spectrum for the feature attributed to  $\text{S}_2\text{F}_{10}$ . The relative abundances of the major ions that appear in the mass spectra of both  $\text{SOF}_2$  and  $\text{CCl}_2\text{F}_2$  for  $m/z \geq 50$  u are given in Table 2. Interference from  $\text{CCl}_2\text{F}_2$

Table 2. Relative abundances of ions in the mass spectra of  $\text{SOF}_2$  and  $\text{CCl}_2\text{F}_2$  for  $m/z \geq 50$  u.

$m/z$ (u)	Abundances		$m/z$ (u)	Abundances	
	$\text{SOF}_2$	$\text{CCl}_2\text{F}_2$		$\text{SOF}_2$	$\text{CCl}_2\text{F}_2$
50	0.012	0.118	70	0.017	0.002
51	0.036	0.001	85	0.000	1.000
66	0.000	0.036	86	0.556	0.010
67	1.000	0.000	87	0.005	0.326
68	0.010	0.012	101	0.000	0.087
69	0.046	0.000	103	0.000	0.057

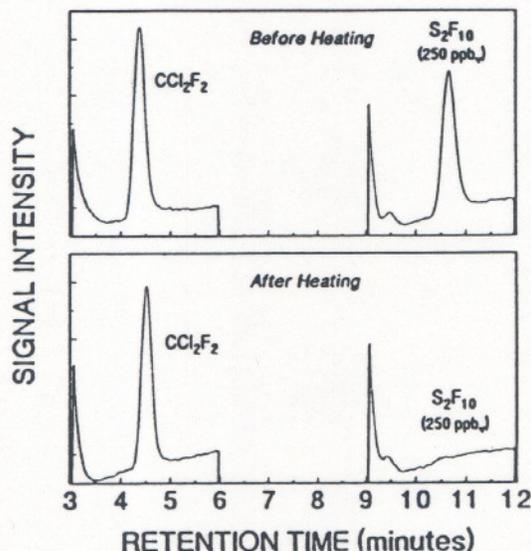


Figure 4. Single-ion chromatograms at  $m/z = 86$  u from two different  $\text{SF}_6$  gas samples containing either  $\text{CCl}_2\text{F}_2$  or  $\text{S}_2\text{F}_{10}$  before and after heating at  $250^\circ\text{C}$  for 30 min.

is only a problem if the mass spectrometer is slightly detuned to enhance the detection sensitivity at  $m/z = 86$  u. Under conditions where the mass resolution is insufficient to allow complete separation of the adjacent ions at  $m/z = 85, 86, 87$  u, the  $\text{CCl}_2\text{F}_2$  interference can become significant. However, even with poor mass resolution,  $\text{CCl}_2\text{F}_2$  can usually be distinguished from  $\text{SOF}_2$  at  $m/z = 67$  u.

Independent of how the mass spectrometer is operated, it is possible to perform a pyrolysis test to confirm that the observed peak in the chromatogram is due to  $\text{S}_2\text{F}_{10}$ . This is illustrated by the chromatograms shown in Fig. 4 that were obtained from two different  $\text{SF}_6$  gas samples, one containing  $\text{CCl}_2\text{F}_2$  at an unknown trace level and one containing 250 ppb  $\text{S}_2\text{F}_{10}$ . Indicated in this figure are the chromatograms that were obtained before and after these samples were heated for 30 min at a temperature of  $250^\circ\text{C}$  in a  $150\text{ cm}^3$  stainless-steel cylinder. It is seen that the  $\text{CCl}_2\text{F}_2$  feature remains unchanged after heating, whereas the  $\text{S}_2\text{F}_{10}$  disappears, presumably by the same process that converts it into  $\text{SOF}_2$  in the heated jet separator of the GC/MS. The compound  $\text{S}_2\text{O}_2\text{F}_{10}$  is also thermally unstable at  $250^\circ\text{C}$  and will disappear from the sample after heating as illustrated by the results shown in Fig. 5. It is also seen from this figure that  $\text{S}_2\text{OF}_{10}$  is unaffected by the heating. This compound is relatively more stable than either  $\text{S}_2\text{O}_2\text{F}_{10}$  or  $\text{S}_2\text{F}_{10}$ , and is frequently observed to be a contaminant in commercial  $\text{SF}_6$ .

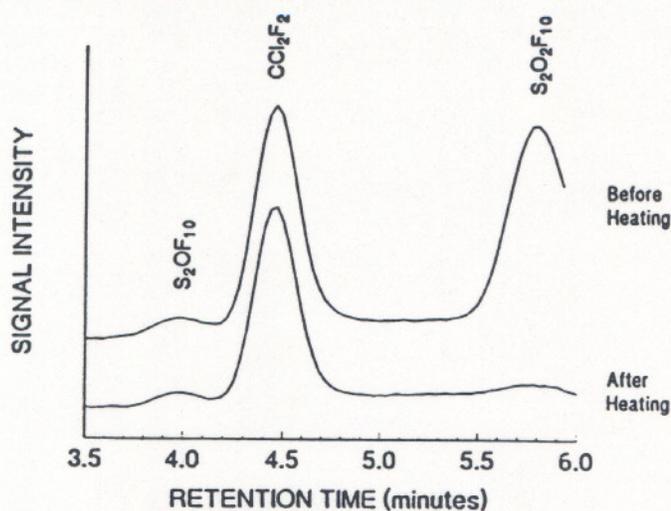


Figure 5. Single-ion chromatograms at  $m/z = 86$  u before and after heating an  $SF_6$  gas sample containing trace amounts of  $CCl_2F_2$ ,  $S_2OF_{10}$ , and  $S_2O_2F_{10}$ .

#### Reference Sample Preparation

The most significant source of error in using a GC/MS to measure the content of  $S_2F_{10}$ ,  $S_2OF_{10}$ , and  $S_2O_2F_{10}$  in  $SF_6$  is likely to occur in the process of preparing reference samples. The decomposition of  $S_2F_{10}$  and  $S_2O_2F_{10}$  that occurs at temperatures above  $180^\circ C$  also occurs at room temperature at a slower rate. This decomposition process can introduce errors in determining and controlling the concentration of  $S_2F_{10}$  or  $S_2O_2F_{10}$  in a reference sample.

The usual procedure in preparing a reference sample is to inject a known quantity of the trace gas of interest into a sample cylinder under vacuum and then introduce the  $SF_6$  to the desired pressure. In the process of doing this, the trace gas is usually retained initially in tube of relatively small diameter. In the case of  $S_2F_{10}$ , some of the gas will decompose during this retention time as illustrated by the chromatogram shown in Fig. 6. The data in this figure correspond to a sequence of injections made after pure  $S_2F_{10}$  was introduced into a 0.6 cm diameter stainless-steel tube under vacuum. It can be seen that a significant decay of the sample occurs in a matter of minutes. There are two precautions that can be taken to minimize the error due to  $S_2F_{10}$  decay during sample preparation. The first, is to remove as much  $H_2O$  as possible from the surfaces of the sample cylinder and associated tubing, either by direct heating or by flushing with a gas that readily hydrolyzes such as  $SF_4$ . The second is to minimize the time that the sample container is under vacuum by introducing the diluent gas ( $SF_6$ ) immediately after the  $S_2F_{10}$  is injected into the system. Generally it is better to start by preparing a sample that contains a relatively high concentration of  $S_2F_{10}$  ( $\geq 1000$  ppm<sub>v</sub>) and then use successive dilutions with  $SF_6$  to reduce the concentration down to the desired level.

It has been found<sup>7</sup> that the rate of  $S_2F_{10}$  decomposition in a reference sample increases with decreasing  $S_2F_{10}$  concentration, total gas pressure, and sample cylinder size. It also increases with increasing temperature and water vapor content. These factors must be considered in maintaining reference samples. To avoid problems of sample decay, it is advisable to prepare a new reference each time that an analysis is to be performed.

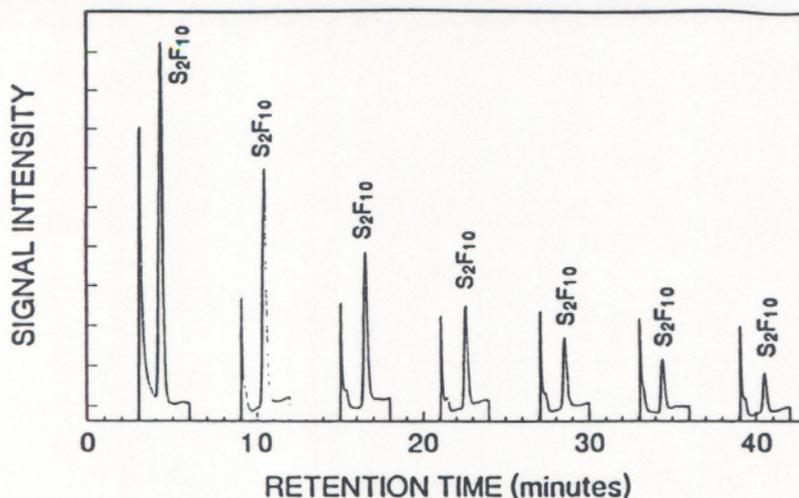


Figure 6. Chromatogram showing the decay of  $S_2F_{10}$  after being injected into a 0.6 cm diameter stainless-steel tube under vacuum at room temperature.

#### ACKNOWLEDGMENTS

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## DISCUSSION

L. NIEMEYER: I understand you have a couple of decay channels for  $S_2O_2F_{10}$  and one of them is thermal. We know how thermal decay of  $S_2F_{10}$  works. Are you able to state how it would work for  $S_2O_2F_{10}$  - do you know the appropriate binding energies that would need to be overcome thermally to decompose it?

R. J. VAN BRUNT: Unfortunately I do not know the answer to that question because that compound has not been studied very thoroughly. There is much less known about this compound than  $S_2F_{10}$  and we are not aware of any published data on thermal decay of  $S_2O_2F_{10}$ . We now have evidence that  $S_2O_2F_{10}$  spontaneously decomposes at a low rate at room temperature (300 K). From our preliminary tests, it appears that one of the decomposition products is  $SO_2F_2$ . At the present time, for example, we know nothing about the mechanism responsible for the decomposition whether it is a gas-phase or a surface reaction.

I. SAUERS: I would like to point out that we also observed the thermal instability and decay of  $S_2O_2F_{10}$  to be similar to the situation with  $S_2F_{10}$ . Also, from preliminary work done by Dr. Guy Griffin at Oak Ridge National Laboratory on the toxicity of  $S_2O_2F_{10}$  using cell culture bioassays, it appears that the toxicity of  $S_2O_2F_{10}$  approaches that of  $S_2F_{10}$ , i.e. it is less toxic than  $S_2F_{10}$  but more toxic than the other  $SF_6$  by-products studied ( $SOF_2$ ,  $SO_2F_2$ ,  $SF_4$ ,  $SO_2$  and HF). No other toxicity data are currently available in the literature.

S. W. ROWE: In switchgear insulating spacers will constitute a quasi-permanent source of humidity even if a filter is fitted. This is because the humidity must diffuse through the gas to reach the filter and a local high humidity zone will probably build up at the spacer-gas interface. What sort of reactions with  $S_2F_{10}$  and  $S_2OF_{10}$  would be expected under these conditions? Would decay be promoted with respect to an "all-metal" situation? Would any catalytic type reactions be expected with the diverse components of the spacer?

R. J. VAN BRUNT: We have evidence that the rate of  $S_2F_{10}$  decomposition in  $SF_6$  at room temperature (300 K) is increased when cast epoxy materials are introduced. Presently there is no evidence that the mechanism of  $S_2F_{10}$  decomposition on epoxy surfaces is any different from that which occurs on metal surfaces. The enhancement in  $S_2F_{10}$  decomposition rate when epoxy is present may simply be due to the fact epoxy is more efficient than metals in adsorbing  $H_2O$ .

H. MORRISON: The probable source of  $CCl_2F_2$  (Freon 12) in commercial  $SF_6$  is a leak from the cooling compressors used by the manufacturers in the production of  $SF_6$ . As well,  $CCl_2F_2$  has been used by some GIS manufacturers and some utilities as a tracer to test for pressure leaks.

R. J. VAN BRUNT: It should be noted that  $CCl_2F_2$  generally appears at trace levels (less than 200 ppb) in nearly all commercial-grade  $SF_6$  that we have analyzed.

J. CASTONGUAY: You did try to condition the internal surface of your small introduction tube to limit the surface conversion of  $S_2F_{10}$ . Was this effective?

R. J. VAN BRUNT: We have found that predrying of the sample cylinder, either by heating under vacuum or by introducing  $SF_4$  that readily reacts with  $H_2O$  to form HF and  $SOF_2$ , helps to reduce the rate of  $S_2F_{10}$  decomposition in gas mixtures that are subsequently introduced into that cylinder. We would recommend the heating method for drying. The formation of HF from  $SF_4$  could have undesirable side effects.