DETECTION OF S_2F_{10} PRODUCED BY ELECTRICAL DISCHARGE IN SF_6

R. J. Van Brunt[†], J. K. Olthoff[†], I. Sauers[*], H. D. Morrison[‡], J. R. Robins[‡], and F. Y. Chu[‡]

[†]National Institute of Standards and Technology, Gaithersburg, MD, USA

[*]Oak Ridge National Laboratory, Oak Ridge, TN, USA

[‡]Ontario Hydro Research Division, Toronto, Ontario, Canada

INTRODUCTION

The production of disulfurdecafluoride (S_2F_{10}) in SF_6 by electrical discharges is of concern because of its known high level of toxicity and because SF_6 is widely used as an insulating gas in electric-power systems. This work presents recent progress at the Oak Ridge National Laboratory, the National Institute of Standards and Technology and the Ontario Hydro Research Division on the development of three different methods for detecting S_2F_{10} in SF_6. These methods are applied to the detection of S_2F_{10} produced from SF_6 subjected to corona and power arc discharges.

CHROMATOGRAPH-ENRICHMENT METHOD

A cryogenic enrichment procedure similar to that used previously [1,2] has been adopted for improved detection sensitivity of S_2F_{10} in SF_6. The technique, based on the earlier work of Gutbier and Luy [3] and Hanrahan and Paterson [4] utilizes a pre-trapping of S_2F_{10} in which a substantial portion of the SF_6 in the sample is removed prior to chromatographic analysis. The apparatus consists of four basic components: 1) a cryogenically controlled pre-trap where a gas sample entrained in a helium carrier gas stream is selectively trapped in order to enrich the S_2F_{10} component; 2) a cryogenically controlled injector where the sample emerging from the pre-trap is retrapped; 3) a cryogenically controlled gas chromatograph (GC) where the components of the sample are separated in real-time, and 4) the detection system, including an electron capture detector (ECD) for sensitive detection of S_2F_{10} and a flame photometric detector (FPD) for monitoring the large SF_6 component of the original gas sample. These components are shown schematically in Fig. 1. The GC (Varian, Model 3600)[1] houses the analytical column which is a 50 m long, 0.25 mm ID fused silica capillary with an inside 0.6 μm coating of SPB-1 (Supelco, Inc.)[1] phase. This column is similar in characteristics to the OV-101 capillary column used in the KEMA work [1,2]. The pre-trap is a 3.175 mm ($\frac{1}{8}$ inch) diameter stainless steel tube filled with Porapak Q over a length of 2.54 cm. A septum programmable injector, (SPI) permits direct injection of samples into the GC column. In the enrichment procedure, the gas sample is introduced from the pre-trap through tubing connected via multiple port gas sampling valves (not shown in the figure) to the SPI. A gas sample exiting the SPI can be directed (via a 4-port gas sampling valve) either to the analytical column and on to the ECD or to the FPD (by-passing the column) and vented to an exhaust system. A discussion of factors influencing S_2F_{10} detection sensitivity is found in ref. 5.
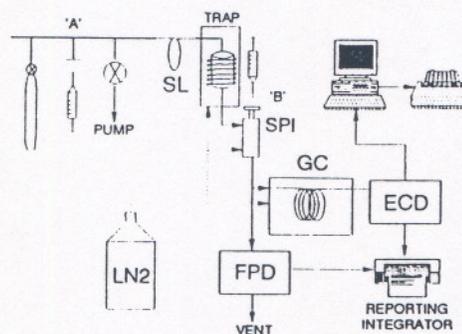
Figure 1. Schematic diagram of cryogenic enrichment gas chromatography system: SL, sample loop; SPI, septum programmable injector; GC, gas chromatograph; ECD, electron capture detector, FPD, flame photometric detector, LN2, liquid nitrogen. 'A' and 'B' refer to sample injection ports respectively with and without trapping. Multiport switching valves are not shown.

Gas samples with volumes ranging from 0.5 to 10 ml are introduced by syringe into a manifold sample loop having a 0.25 or 2 ml volume. A fraction of this sample is then injected into the pre-trap, operated at -35° C. In the first enrichment stage, the effluent of the trap is swept directly to the FPD, by-passing the column. The pre-trap, operated in this manner, is purged of the SF_6 component for about 10 min. Before beginning the analysis stage, the SPI temperature is lowered to T=-182° C. During the analysis stage the pre-trap is heated to 100° C, sending the trapped components to the SPI where they are frozen. Desorption of the gas sample at the SPI (for a temperature increase rate of 300° C/min) then commences, whereupon the sample flows through the analytical column to the ECD. Figure 2 shows chromatograms of 0.5 ml samples of SF_6 containing S_2F_{10} produced in a corona discharge. Under these conditions, S_2F_{10} elutes at t=700 s. The large peak (clipped at the top) represents residual SF_6 remaining in the sample despite the purge/enrichment process.

GAS CHROMATOGRAPH-MASS SPECTROMETER

This approach employs a GC/MS with a chemical conversion technique [6] as shown in Fig. 3. Gas samples extracted with a gas-tight syringe are injected into the GC-column. After passing through the column, S_2F_{10} is converted to SOF_2 by reaction with water adsorbed on the surface of a jet separator heated to a temperature of about 180° C. The SOF_2 is ionized by electron impact at 70 eV and detected with a quadrupole mass spectrometer tuned to ions with a mass-to-charge ratio of 86 corresponding to the ion SOF_2^{+}. This method achieves a high sensitivity (~2 ppb) for detection of S_2F_{10} in SF_6 because it eliminates the background interference from ions associated with SF_6 [6,7].

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[1]Certain commercial equipment and materials are identified to adequately specify the measurement procedures used. Such identifications do not imply recommendation or endorsement by the laboratories involved with this work nor do they imply that they are necessarily the best available for the purpose.
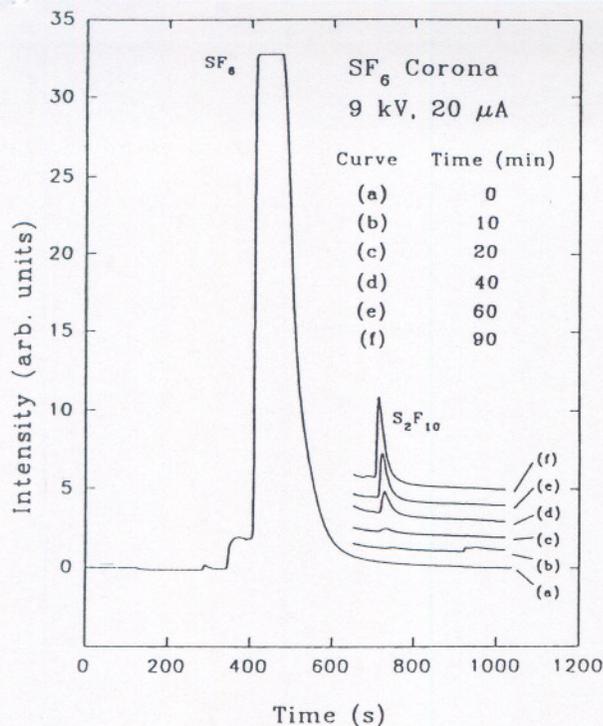
Figure 2. Chromatograms of samples of pure and decomposed SF_6 taken from corona discharge cell at times t=0, 10, 20, 40, 60 and 90 min of discharge. Curves (b)-(f) have been offset for clarity.
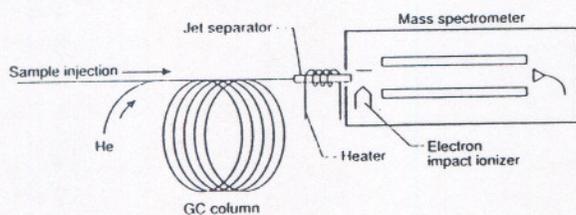
Figure 3. Gas chromatograph mass spectrometer system used to detect S_2F_{10} in SF_6 [6]. The S_2F_{10} is converted to SOF_2 in the heated jet separator.

Figure 4 shows examples of two single-ion chromatograms indicating the quantity of S_2F_{10} initially present in SF_6 cylinders as background. Shown in each of these chromatograms are the responses from five sequential injections made during a period of 30 minutes. The mass spectrometer is turned off during those times when SF_6 elutes from the column to avoid damage to the ion detector and to reduce the background level.

For the data shown in Fig. 4, the peaks designated as "Ref." correspond to a reference sample containing 140 ppb S_2F_{10} in compressed SF_6. Each injection was made with a 2 ml syringe containing gas at absolute pressure of 300 kPa ($\sim$3 atm). For the chromatograms in the lower part of Fig. 4, the reference sample also contained about 680 ppb of S_2OF_{10}, known to be a possible contaminant. The sensitivity for S_2OF_{10} detection is considerably below that for S_2F_{10}. It is interesting to note that commercially prepared SF_6 can contain widely varying amounts of S_2F_{10} as a trace contaminant (from 7 to 235 ppb as indicated by the data in Fig. 4). This initial concentration of S_2F_{10} must be considered in the measurement of S_2F_{10} production rates from electrical discharges.
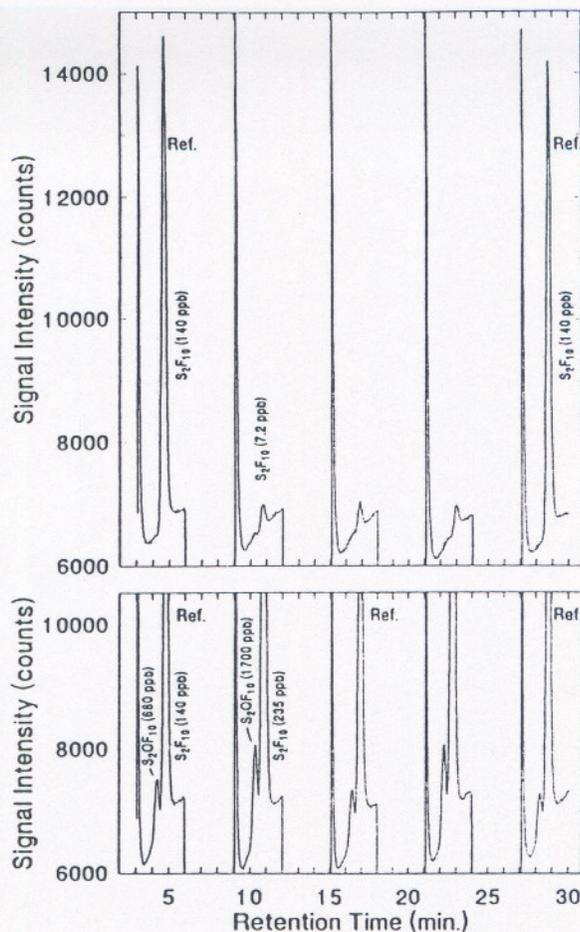
Figure 4. Chromatograms for two 30 minute injection sequences showing responses for five separate injections from commercial SF_6 gas cylinders containing the different indicated trace amounts of S_2F_{10} and S_2OF_{10}. The samples containing 140 ppb S_2F_{10} are "references".

INFRARED (IR) ANALYSIS SYSTEM

The application of an infrared absorption technique to detect SF_6 decomposition products is described in [8]. For detection, two windows, the 825 cm^{-1} (ν_6 band) and the 545 cm^{-1} (ν_8 band) regions, have been found to be relatively free of interference from SF_6 and other dominant discharged products such as SOF_2, SO_2F_2 and SF_4. Reference spectra of these discharged products have been obtained to aid the identification of S_2F_{10} in arced SF_6. All infrared analyses were carried out with an FT-IR spectrometer (Bruker model IFS66)[1] using 0.1 cm^{-1} resolution. An attempt was made to use a diode laser with a line width of 0.001 cm^{-1} to resolve the individual vibration-rotational transitions of S_2F_{10}. However, the lines are so closely spaced (on the order of 10^{-4} cm^{-1}) that the present work is based on using the whole absorption band profile. Pressures in the range of 1.3 to 6.7 kPa in 10 and 20 cm cells fitted with KBr and NaCl windows were employed. The estimated sensitivity of the IR technique for S_2F_{10} detection is about 100 ppm with a 10 cm absorption path length which could be improved to 0.5 ppm with a 20 m path length. Figure 5-A shows the spectra obtained from 1% S_2F_{10} and 2% SOF_2 in SF_6. The S_2F_{10} peaks at 825 cm^{-1} together with the SOF_2 (808 cm^{-1}) peak are shown.

FORMATION OF S_2F_{10} BY CORONA DISCHARGE

All three methods have been applied to the detection of S_2F_{10} in
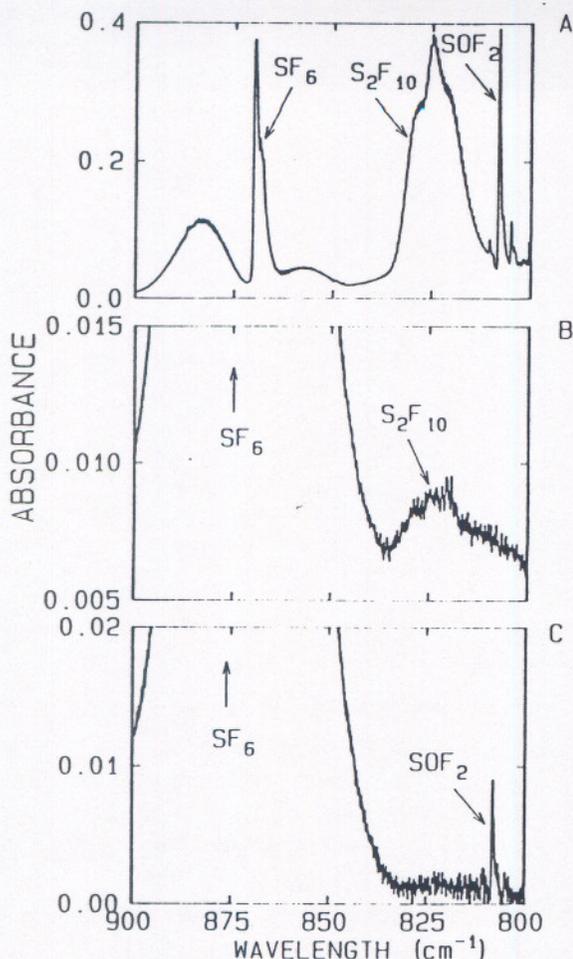
Figure 5. A – Spectra of a mixture of 1% S_2F_{10}, 2% SOF_2 and the remainder SF_6 (10 cm cell, 4.75 kPa gas pressure, 0.1 cm^{-1} resolution). B – Spectrum of SF_6 that has undergone corona discharge (10 cm cell, 2.13 kPa gas pressure, 0.1 cm^{-1} resolution). C – Spectrum of SF_6 from the high current arc experiment #2. The SOF_2 peak at 808 cm^{-1} is clearly visible (10 cm cell, 2.53 kPa pressure, 0.1 cm^{-1} resolution).

SF_6 following exposure of SF_6 to a corona discharge. The SF_6 samples that produced the chromatograms shown in Fig. 2 using the cryogenic enrichment method were extracted from a 1.1 liter stainless-steel cell where a negative-corona discharge was generated using a point-to-grounded plane electrode geometry in 100 kPa SF_6. The corona current and voltage were 20 μA and 9 kV respectively. Curves (a)-(f) are chromatograms of SF_6 at discharge times t=0, 10, 20, 40, 60 and 90 min respectively, showing the increase in S_2F_{10} concentration. The S_2F_{10} feature in curve (f) corresponds to a concentration of 11 ppm.

Similar measurements were performed using the IR method for negative corona generated in a 1.3 liter chamber with 200 kPa SF_6 at a constant current of 100 μA. The IR spectrum of the gas shown in Fig. 5-B corresponds to 85 ppm of S_2F_{10} formed after 4 hours.

The GC/MS method was used to measure the S_2F_{10} production rates from negative point-plane SF_6 corona discharges in a 3.7 liter cell with stainless-steel electrodes as previously described [9–11]. Examples of measured S_2F_{10} yields in micromoles versus net charge, Q, transported in millicoulombs are shown in Fig. 6 for different discharge currents and for a gas pressure of 200 kPa. The transported charge is given by $Q = It$, where I is the discharge current and t is
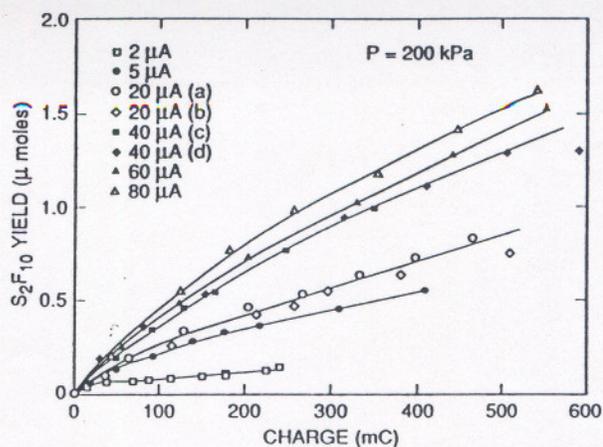
Figure 6. Measured yields of S_2F_{10} versus net charge transported from negative corona discharges in 200 kPa SF_6 at the indicated constant discharge currents. The data designated (a) and (b) at 20 μA and (c) and (d) at 40 μA were obtained from separate experiments performed at different times.

the time during which the discharge has been operated.

The data shown in Fig. 6 indicate that the charge rate-of-production, $d[S_2F_{10}]/dQ$, decreases with decreasing current, especially for $I < 40\mu$A. Above 40μA, the slopes of the $[S_2F_{10}]$-versus-Q curves are nearly parallel consistent with previously reported results [11]. The data obtained from two different experiments performed at widely separated times for both 20 and 40 μA are seen to be in good agreement thus demonstrating that the results are reproducible.

For $Q < 100$ mC, $d[S_2F_{10}]/dQ$, drops significantly from its initial value with increasing Q and eventually approaches a limiting constant value. This initial nonlinear behavior in the S_2F_{10} production has been attributed to increases in the rate of catalytic destruction of S_2F_{10} on the point electrode surface during the initial conditioning of the polished surface [10].

It is encouraging that the results for the S_2F_{10} yields from the three different methods give comparable rates of production consistent with earlier work [9,11].

S_2F_{10} FORMATION IN POWER ARCS

Two experiments (Table 1) were carried out to measure the concentration of S_2F_{10} produced in a power arc similar in energy-per-unit volume of gas to the most energetic arcs likely to be encountered in gas-insulated switchgear. The arcs were initiated with a trigger wire between the conductor and the enclosure in an aluminum co-axial chamber. Gas samples were drawn from the chamber after each arc for analysis by the infrared, GC and GC/MS techniques described above. In the IR analysis, no S_2F_{10} absorption peak was detected at 824.9 cm^{-1} or 545 cm^{-1}, but a strong peak at 808 cm^{-1} (SOF_2) was observed (Figure 5-C). The lower concentration of SOF_2 in the second experiment can be explained by the lower initial moisture

Table 1. Observed conditions from two power-arc tests

Arc	#1	#2
SF_6 Pressure (kPa)	158	210
Water Content (ppm)	>800	100
Current (kA)	9.5	7.8
Energy deposited per unit volume (kJ/liter STP)	1.5	0.97
SOF_2 concentration (ppm)	106,000	4100
SO_2F_2 concentration (ppm)	19	<2

content in the SF_6. A significant quantity of SF_4 was found in the second arc experiment by IR analysis.

Analyses of the arc-decomposed SF_6 were made about 4 to 19 days after the experiments using the GC and GC/MS techniques described above. Evidence was seen of S_2F_{10} content at concentrations below about 10 ppm by both methods. Precise determinations of the S_2F_{10} concentrations were not made by GC/MS because of interference from SOF_2 produced by the arc which significantly increases the background level. In this case, the cryogenic enrichment method provided better resolution of the S_2F_{10} and improved sensitivity over the other methods.

DISCUSSION

Three different methods of detecting S_2F_{10} in SF_6 have been described. Each has its advantages and disadvantages with respect to sensitivity and ease of use. For example, the GC/MS method achieves very high sensitivity with relatively short analysis time but has a significant loss of sensitivity when SOF_2 is present at high concentrations. The infrared absorption technique has lower sensitivity but is amenable to in situ measurements with very short analysis times and relatively low interference from SOF_2.

The data presented show again that S_2F_{10} is readily produced from relatively "cold" corona-type discharges in SF_6. The reproducibility of S_2F_{10} yields from corona suggest the possibility of using this type of discharge to generate "reference" gas samples that contain known quantities of S_2F_{10} in SF_6.

Questions remain about the production of S_2F_{10} from power arcs. Results from this type of discharge are more difficult to quantify. Janssen [2] reported that the concentration of S_2F_{10} was about 50-100 ppb during an arc experiment (40 kA/0.8s). However, the results in Fig. 4 show that S_2F_{10} can be present in commercial grade SF_6 at these levels even before SF_6 is subjected to an arc.

Results from the two types of discharges indicate that the formation rate of S_2F_{10} in an arc is significantly lower than that in corona. This and the observation of large amounts of SF_4 in the arced gas supports the hypothesis that thermodynamic equilibrium conditions in the arc favour formation of SF_4 which eventually combines with moisture to form SOF_2. Also, because S_2F_{10} is thermally unstable above about 200° C [12], it is likely to be formed only during the "cool-down" phase of the arc and therefore its contribution to SF_6 decomposition by-products is expected to be relatively small. Previous measurements of the S_2F_{10} yield in spark discharges [11] indicate that the S_2F_{10}-to-SOF_2 concentration ratio is between that found for corona (high ratio) and arcs (low ratio).

While the data presented here suggest that S_2F_{10} could be produced from low-level corona or partial discharges in practical gas-insulated systems, its formation rate in arcs is much smaller than that for the other by-products. The formation rate of S_2F_{10} in short duration discharges such as produced during disconnecter operations remains to be investigated.

ACKNOWLEDGEMENTS

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