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SIMPLE CHEMICAL ASSAYS FOR PRESENCE OF S_2F_{10} IN DECOMPOSED SF_6

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INTRODUCTION

Disulfur decafluoride (S_2F_{10}; also referred to as sulfur pentafluoride) is a highly toxic gas which can be produced by electrical discharges in SF_6.[1,2] It would be very useful, both for safety in handling decomposed SF_6 and for diagnosis of fault conditions, to have a convenient, rapid and sensitive field assay for the presence of S_2F_{10}. A number of different assays for S_2F_{10} with varying levels of sensitivity have been developed in the course of a CRADA initiative "Investigation of S_2F_{10} Production and Mitigation in Compressed SF_6-Insulated Power Systems."[3] These techniques include GC-MS[4], cryogenic GC enrichment[5] and IR absorption.[6] Although all of these procedures have been shown to have utility in detecting S_2F_{10}, and some have great sensitivity (GC-MS and cryogenic enrichment), they do not, in general, lend themselves to rapid field analyses. Ideally, one might wish to have an assay modeled after the "Draeger Tubes," where a gas sample is drawn through some chemical compound, and the resulting color change can be used to quantify the gas of interest. Disulfur decafluoride had been rather extensively studied in World War II as a candidate chemical warfare agent[7], and along with biological studies of its toxicity, chemical detection techniques had also been developed.[8] Of the chemical assays described, two were particularly promising, one involving reaction of S_2F_{10} with NaI to produce free I_2 which could be titrated with sodium thiosulfate, and the other involving reaction of S_2F_{10} with p-phenylenediamine to produce a pink/red color. This second assay appeared to hold some promise, and accordingly, experiments were carried out to see if this assay could be useful for detecting S_2F_{10} in electrically decomposed SF_6 samples.

METHODS AND MATERIALS

The standard procedure by which various gas samples were analyzed by colorimetric assay was as follows. Filter paper discs (Whatman 3MM) were wet with 100 μl of the test chemical in appropriate solvent, and the filter papers were then

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immediately inserted into a 10 ml glass vacutainer tube (Becton-Dickinson 6441) by removing the rubber septum sealing the tube. The rubber septum was <u>immediately</u> replaced (to avoid evaporation of solvent from the filter paper), and the pressure inside the sealed vacutainer was reduced to below atmospheric, by using a plastic syringe and needle (the syringe was used to sequentially remove three 10 ml aliquots of the gas from inside the vacutainer). The gas sample of interest was then introduced into the tube using a needle and syringe. Usually, 8 ml of the gas was drawn into the tube by the reduced pressure in the tube. For dilute gas samples, an attempt was made to introduce the needle directly over the filter paper, so that as the gas entered the tube, it would impinge directly onto the moist paper. The color change on the filter paper as a whole or in a linear region of the paper over which the gas flowed, was observed. When p-phenylenediamine was used for the assays reported in Table 2, the assay solution was 5% (w/v) of p-phenylenediamine in acetone.

For spectrophotometric assays of absorption bands due to reactions of gases with the assay chemical, the colored material was either eluted from the paper using the same solvent the chemical was originally dissolved in, or a 1.0 ml aliquot of the chemical solution was placed in a 10 ml vacutainer tube, and the gas sample introduced as explained above. In this case, the gas sample was mixed with the chemical in solution by vigorous mixing and inversion. Absorption spectra were determined using an IBM Spectrophotometer, model 9420. Fluorescence measurements were made using a Perkin-Elmer LS50B Luminescence Spectrometer.

Analysis of individual gas mixtures was by mass spectrometry and/or gas chromatography[9]. Individual gases were from the following sources: SiF_4, HF, SF_4, and SO_2, Matheson Gas Products; SO_2F_2, Union Carbide, Linde Division; SOF_2, Columbia Organic Chemicals Co.; SOF_4, S_2F_{10} and $S_2O_2F_{10}$ were synthesized and provided by Dr. D. DesMarteau, Clemson University.

All solvents used were reagent grade and from standard laboratory supply companies. The p-phenylenediamine (1, 4-phenylenediamine) used was from Aldrich (catalog #27, 515-8), 99+% purity, sublimed, and zone-refined. It was important to use this high quality p-phenylenediamine in the assay, as experiments with lower purity grades of this chemical were not as satisfactory. Suppliers for other chemicals used were Aldrich (melamine, phenylhydrazine, diphenylamine, 2,4,6-triaminopyridine, 4-nitroaniline, and 2,4-dinitrophenylhydrazine), Fluka (benzidine), Eastman Kodak (3-aminoquinoline) and Fisher Scientific (catechol).

RESULTS AND DISCUSSION

World War II era attempts[8] to develop a chemical assay included development of an analytical method based upon oxidation of NaI to I_2 by S_2F_{10}, and subsequent titration of the free iodine using thiosulfate. This assay, however, was found to be not nearly as sensitive as the reaction of S_2F_{10} with p-phenylenediamine, which was recommended as a qualitative test for the presence of S_2F_{10}. About 30 easily oxidizable organic compounds had been tested as possible detectors for S_2F_{10}. Based upon the range of compounds used in this old report, we selected a variety of organic compounds which we felt might serve as suitable detectors for S_2F_{10}, and tested them for visual evidence (i.e., a colored product or a color change) of a reaction with S_2F_{10}, when the compound, dissolved in suitable solvent and spotted onto white filter paper, was exposed to a stream of gas containing S_2F_{10}. The concentration of S_2F_{10} used in these studies varied from 100 to 500 ppm. It was felt that no evidence of reaction with these concentration ranges of S_2F_{10} precluded the compound from being a useful indicator of the presence of S_2F_{10}. Table 1 shows the results of these studies. It is clear that of the compounds tested, only p-phenylenediamine showed any real promise as an S_2F_{10} indicator compound. The color change seen upon reaction of S_2F_{10} with p-phenylenediamine was observed to have the following characteristics. The solution of the high purity compound in acetone was a very light tan color when freshly prepared (upon standing, air oxidation produced progressive darkening until the solution became black after ~24 hrs). Upon spotting on filter paper, the fresh solution did not noticeably color the filter paper at all. When a stream of gas containing S_2F_{10} impinged on the paper, a red color developed as a line along the paper, indicative of the direction of gas flow. The intensity (and hue) of this colored product varied with the concentration of S_2F_{10} in the gas stream (see below for further discussion). Certain of the compounds in Table 1 (i.e. p-phenylenediamine and diphenylamine) were investigated as the basis for a fluorimetric assay for S_2F_{10}. In this case, the fluorescence excitation and emission spectra of the compounds was determined in various solvents, and after reaction of a solution with S_2F_{10}, the spectra were re-examined for any changes which might be indicative of a reaction between the S_2F_{10} and the indicator chemical. No consistent change in fluorescence spectra could be discerned following treatment with S_2F_{10}.

Table 1. List of Chemicals Tested for Suitability as a Detector of S_2F_{10}

Chemical	Solvent*	Reaction with S_2F_{10}**
p-Phenylenediamine	Acetone	+
Catechol	Ethanol	-
Benzidine	Ethyl Acetate	-
Diphenylamine	Ethyl Acetate	-
3-Aminoquinoline	Ethyl Acetate	-
4-Nitroaniline	Ethyl Acetate	-
Melamine	Ethyl Acetate	-
2,4,6-Triaminopyrimidine	Dimethyl Sulfoxide	-
Phenylhydrazine	Ethanol	-
2,4-Dinitrophenylhydrazine	Methanol	-

*A solution of 4 or 5% (w/v) of compound in appropriate solvent was made up in each case.
**+ = visible colored product on filter paper; - = no evidence of a color change

Using the p-phenylenediamine reagent, a number of studies were made to see if other decomposition products of SF_6 might react with this reagent, and to determine what the approximate limit of detection (LOD) of various decomposition products might be. Table 2 gives the results of these experiments. The p-phenylenediamine reagent proved to be a quite sensitive indicator of S_2F_{10}. Concentrations of S_2F_{10} in the range of 20-50 ppm produced a definite pink to pink-red line on the filter paper. The limit of detection for an 8 ml sample of gas containing S_2F_{10} was approximately 6 ppm of S_2F_{10} in SF_6. A rather faint pink band appeared at this concentration which required about 30 to 60 sec. to reach its final intensity. Nevertheless, the band was very discernible against the white background of the paper.

This chemical detection technique for S_2F_{10} had originally been developed for detecting the use of S_2F_{10} in air as a chemical warfare agent, and it was therefore not of any particular importance to detect S_2F_{10} in the presence of numerous other sulfur or sulfoxy-fluor compounds. The chemical detection of S_2F_{10} in decomposed SF_6, however, demands a considerable degree of specificity, since a variety of other closely related compounds are produced by electrical decomposition of SF_6.

As can be seen from Table 2, neither SF_6 nor many of the common decomposition products of SF_6 (e.g. HF, SO_2, SO_2F_2, SOF_4 and SiF_4) produced any visible reaction with the color reagent, even at relatively high concentrations (thousands of ppm). Thionyl fluoride, SOF_2, produces a yellow color, totally different from the color produced by S_2F_{10}. Furthermore, the reaction of SOF_2 with p-phenylenediamine is different from that with S_2F_{10} in two respects. First, the reaction of the reagent with SOF_2 is considerably less sensitive than that with S_2F_{10}($LOD \cong 50$ppm for SOF_2). Second, the yellow color produced by the reaction of SOF_2 with the color reagent takes considerable time (minutes) to develop, and this development time lengthens as the concentration of SOF_2 decreases. In contrast, the color of the S_2F_{10} reaction product develops almost instantaneously, even at very low (near LOD) concentrations of S_2F_{10}. In fact when a mixture of S_2F_{10}/SOF_2 (250/475 ppm) was tested with the reagent, the red color due to S_2F_{10} was seen immediately, and eventually the filter paper turned an orange-yellow color, as the SOF_2 reacted. We therefore believe that SOF_2, even when present in fairly high concentrations, may not be a hinderance to detecting S_2F_{10} by this method. Of course many more trials using mixtures would need to be carried out before one could validate the limit of detection of S_2F_{10} in the presence of SOF_2.

Sulfur tetrafluoride (SF_4), on the other hand, produces a color with p-phenylenediamine which is indistinguishable from the color produced by S_2F_{10}. Spectrophotometric analysis of the colored solutions eluted from filter papers reacted with SF_4 and S_2F_{10} revealed the absorption spectra to be indistinguishable. Thus SF_4 could certainly interfere with the detection of S_2F_{10}. Since SF_4 is one of the primary breakdown products produced by electrical discharge in SF_6[9], its presence is certainly a possibility in various SF_6 samples. It should be noted that the LOD of SF_4 is much higher than S_2F_{10}.

Sulfur tetrafluoride is rapidly hydrolyzed by trace moisture to SOF_2 and HF[10], so the amount of SF_4 remaining in a particular sample is very dependant upon conditions within the electrical apparatus, sampling procedures, etc. Whether the presence of SF_4 would preclude detection of S_2F_{10} would depend in part, upon absolute concentrations of both components. Possible strategies to eliminate SF_4 (e.g. exposure of samples to moist atmospheres) might also be successful.

Table 2. Reaction of p-Phenylenediamine with Various Gases

Compound	Description of Reaction- Approximate Limit of Detection (LOD) or Highest Concentration Tested Giving No Reaction
S_2F_{10}	Red to Pink (higher to lower concentrations) LOD ≅ 6 ppm (faint pink) 20 ppm - immediately discernible pink
SOF_2	Yellow to Pale Yellow (higher to lower concentrations) LOD ≅ 50 ppm (pale yellow which develops only after a delay of several minutes)
SF_4	Red to Pink (higher to lower concentrations) LOD ≅ 100 ppm (faint pink)
$S_2O_2F_{10}$	Very faint reddish tan at 333 ppm*
HF	No Reaction-5,000 ppm
SO_2F_2	No Reaction-2,000 ppm
SOF_4	No Reaction-2,000 ppm
SO_2	No Reaction-2,000 ppm
SiF_4	No Reaction-2,000 ppm
SF_6	No Reaction-100%

*Preliminary Results

The compound $S_2O_2F_{10}$ also produced a reddish color in the color assay. This is a very preliminary result, however, as only one assay (3 different concentrations) was performed, and we are unsure of the purity of the compound, which had to be custom-synthesized for us.

The preliminary results to date suggest that this colorimetric assay may have some utility in assaying for the presence of S_2F_{10} in decomposed SF_6 samples. This colorimetric assay is unlikely to be able to detect S_2F_{10} at its TLV (0.01 ppm), approximately three orders of magnitude below our current LOD. On the other hand, the LOD listed in Table 2 of 6 ppm is based upon a gas sample of ~8-9 mls total volume. Preliminary experiments have indicated that concentrations of S_2F_{10} lower than 6 ppm (i.e. ~1 ppm) can be detected, if the sample volume of gas passed over the filter is increased. The color reaction appears to be accumulative; that is, color develops as a function of total amount of S_2F_{10} reacting on the filter paper surface. If S_2F_{10} is present in the gas in lower concentrations, then more gas volume must flow over the reactive surface, than if it is present at higher concentrations. We therefore feel that the LOD of the colorimetric reaction for S_2F_{10} could be lower than indicated in Table 2. The assay procedure would have to be modified, however, to incorporate larger gas volumes. Even though this colorimetric assay may not be sensitive enough to detect S_2F_{10} at TLV levels, it may serve a useful purpose as a screening assay for evidence of potentially hazardous levels of certain highly toxic SF_6 decomposition products (e.g. SF_4 and S_2F_{10}, with TLV's of 0.1 and 0.01 ppm respectively).[11,12] The speed and simplicity of the assay both recommend it for this purpose. Use of this colorimetric assay in the field will require further development, however. One potential problem is the instability of the p-phenylenediamine in acetone. The organic compound oxidizes rapidly (overnight) to produce a black solution, of no use for assay purposes. The reagent solution would need to be stabilized, or perhaps made freshly before an assay.

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