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ADSORPTION–DESORPTION GAS CHROMATOGRAPHIC–INFRARED DETERMINATION OF TRACE DISULFUR DECAFLUORIDE IN SULFUR HEXAFLUORIDE

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SUMMARY

Disulfur decafluoride (S_2F_{10}) is a highly toxic potential impurity which may appear during the manufacture or electrical stress of sulfur hexafluoride (SF_6), a commonly used dielectric. To monitor S_2F_{10}, a rapid procedure was developed for its determination to at least 1 ppm by an adsorption–desorption gas chromatography–infrared procedure. Typically, a 1-l (vapor) sample of SF_6 is passed through a cryogenic trap whereby S_2F_{10} is preferentially and quantitatively adsorbed. Subsequent heating of the trap desorbs the S_2F_{10} into a gas chromatograph for quantitation and thence to an on-line infrared spectrophotometer for identification.

INTRODUCTION

As a result of the extensive use of sulfur hexafluoride (SF_6) as a dielectric, there is reason to monitor its potentially toxic impurities produced during manufacture or electrical stress. One such impurity, disulfur decafluoride (S_2F_{10}), is regarded as more toxic than phosgene[1]. It may appear in SF_6 during the production process[2] and can also be generated by subjecting oxygen-contaminated SF_6 to electrical discharges[3]. Collection of S_2F_{10} and $S_2F_{10}O$ from gaseous SF_6 on activated alumina, followed by desorption, recondensation, dissolution in carbon tetrachloride and gas chromatographic (GC) analysis has been described[4]. During manufacture, routine quality control for overall toxicity has involved the 16–20-h exposure of mice to SF_6–oxygen (4:1) with an acceptability criterion of no visible effects on the animals[5]. In this communication, we describe a rapid determination of S_2F_{10} in SF_6 at levels down to at least 1 ppm by a procedure involving adsorption–desorption GC and infrared (IR) spectroscopy.

EXPERIMENTAL

Materials and apparatus

The S_2F_{10} used was obtained from PCR Research Chemicals (Gainesville, Fla., U.S.A.), pure SF_6 and sulfuryl fluoride (SO_2F_2) from Allied Chemical Corp. (Morris-

town, N.J., U.S.A.) and Porasil A silica beads from Waters Assoc. (Milford, Mass., U.S.A.).

GC separations were performed on a Hewlett-Packard 5750B series gas chromatograph equipped with a thermal-conductivity detector and a manual six-port linear Microtek gas-sampling valve. For enhanced sensitivity, a GOW-MAC (Bound Brook, N.J., U.S.A.) Model 10-700 thermistor-bead cell was connected via minimum lengths of 1/8-in. O.D. copper tubing to the exit ports of the thermal-conductivity cell, thereby providing a tandem detector arrangement. Its power was supplied by a GOW-MAC Model 40-002 power supply control unit. Simultaneous chromatograms from the two detectors were obtained on a Hewlett-Packard 7128A dual-pen recorder. Peak areas were measured by planimeter or derived from the product of peak height and width at half height. GC conditions are listed in Table I.

TABLE I

GAS CHROMATOGRAPHIC CONDITIONS FOR ANALYSIS OF S_2F_{10} IN SF_6

Column	6.1 m (20 ft.) × 6.25 mm (¼ in.) O.D.; copper; 30% of silicone oil SF-96 on Chromosorb W AW		
Helium flow-rate (ml/min)	(1) 55; (2) 40		
Column temperature (°C)	Isothermal, 22°		
Injector temperature (°C)	22°		
Detector No. 1	Thermal conductivity		
Temperature (°C)	100		
Bridge current (mA)	260		
Detector No. 2 (optional)	Thermistor bead		
Temperature (°C)	22		
Bridge current (mA)	7.5		
Approximate elution times (min)		*(1)*	*(2)*
	SF_6	4.5	5.0
	SO_2F_2	Covered by SF_6	6.5
	$S_2F_{10}O$	7.5	10.5
	S_2F_{10}	8.5	12.0

A U-tube was fashioned from a 5-in. length of 1/4-in. O.D. copper tubing, and each end was fitted with 1/4-in. copper Swagelok nuts and ferrules. The tube was filled with 80–100 mesh Porasil A porous silica beads held in place by small plugs of silane-treated glass wool. The beads were conditioned for 1 h at 125° under a flow of helium; no further conditioning was required for subsequent analyses. By means of Swagelok reducing unions (1/4–1/8 in.), the U-tube was connected to the sample-loop ports of the gas-sampling valve via short (8–10 in.) lengths of 1/8-in. copper tubing; the U-tube was so positioned that it was accessible for immersion in a cooling or heating bath.

The cooling bath consisted of a 60 × 110 mm Dewar flask filled with a liquid nitrogen–chloroform (−63°) slush[6]. The heating bath consisted of a 600-ml beaker of water maintained at *ca.* 85° by a heating mantle. A small lab-jack served to raise the baths into position.

Sample cylinders of liquified SF_6 were connected to a purge port of the gas-sampling valve by means of 1/8-in. copper tubing. In addition to a cylinder shut-off valve, a metering valve (Hoke, Model No. 1315G4B) was installed in the sampling

line as close as possible to the shut-off valve. Liquid SF_6 was allowed to expand and vaporize slowly through the metering valve into the delivery system at a controlled rate (measured by a flowmeter situated at the exit purge port of the gas-sampling valve); this afforded a measure of the total volume of SF_6 scrubbed.

At a convenient point along the line between the metering valve and the gas-sampling valve, a 1/8-in. Swagelok tee-piece was installed. A GC injection-port septum was positioned in the stem of the tee-piece and held in place with a 1/8-in. Swagelok nut. This allowed for the introduction (by gas syringe) of known small amounts of contaminant gases into the SF_6 stream. A diagram of the adsorption–desorption system is shown in Fig. 1.

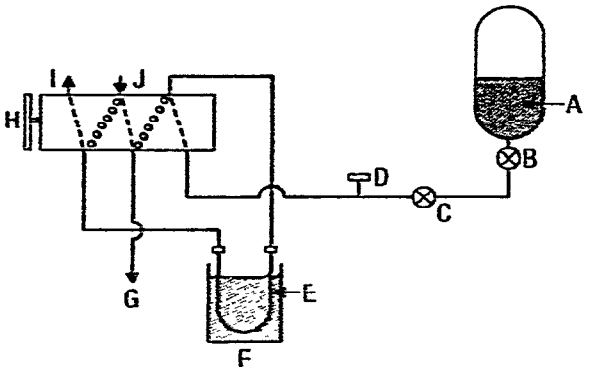

Fig. 1. Adsorption–desorption system for determination of S_2F_{10} in SF_6. A = Liquid SF_6; B = shut-off valve; C = metering valve; D = tee-piece and septum; E = U-tube containing Porasil A; F = cooling or heating bath; G = to gas chromatograph; H = six-port gas-sampling valve; I = to flow-meter; J = helium source. ———, Adsorption mode; ○○○, desorption mode.

The IR spectroscopic identification was made with a Wilks Scientific Corp. (now Foxboro Analytical, S. Norwalk, Conn., U.S.A.) Model 11A GC–IR spectrophotometer attached directly to the exit port of the chromatograph detector by 1/8-in. stainless-steel tubing; the connecting lines and vapor-phase light cells were maintained at room temperature.

A leak-tight manifold system equipped with bellows seal valves (Hoke 4550 Series Monel), a Wallace & Tiernan (Belleville, N.J., U.S.A.) 0–800 mm pressure gauge (Serial No. FA 145-RR10860), and a Welsh Duo-Seal vacuum pump were required in order to provide controlled access to known amounts of contaminant gases. All manifold lines were constructed of 1/4-in. copper tubing with soldered joints (at the valves) and Swagelok fittings. A 1/4-in. Swagelok nut with septum was included in the system whereby syringe samples were withdrawn. The manifold system is depicted in Fig. 2.

Adsorption–desorption GC–IR procedure

With the gas-sampling valve in the fill mode, the Porasil A trap was cooled to −63°. The SF_6 cylinder was connected to the sampling–scrubbing system so that the liquid phase could expand slowly through the metering valve to produce a steady vapor flow-rate of *ca.* 50 ml/min. After 1 l of vapor had been scrubbed, the SF_6

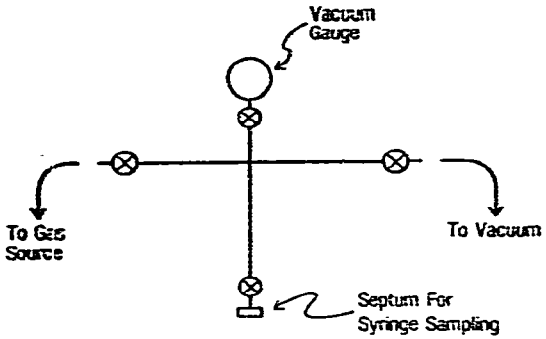

Fig. 2. Schematic diagram of vacuum manifold for syringe sampling of gases at reduced pressure.

flow was stopped and the gas-sampling valve was set to the inject mode. This allowed helium to flow through the scrubber (for 5 min) and remove most of the residual SF_6 by venting it through the chromatographic column. On completion of the helium flush, the slush bath was removed from the scrubber and immediately replaced by the hot (85°) water bath. The recorder was started, and a chromatogram was taken of the desorbed scrubber contents. Incidental to the analysis of one sample was the detection of two other impurities, later shown to be SO_2F_2 and $S_2F_{10}O$. Typical chromatograms are shown in Fig. 3.

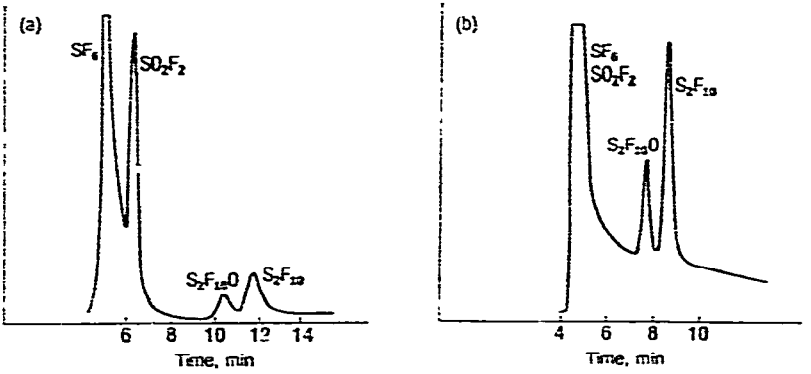

Fig. 3. Gas chromatograms (thermal-conductivity detector) of impurity concentrates from SF_6. (a) helium flow 40 ml/min; (b) helium flow 55 ml/min.

By scrubbing a 4-l sample of the contaminated SF_6 and passing each eluted peak into the solenoid-valved light cell of the Wilks spectrophotometer, a vapor-phase IR spectrum was obtained of each "captive" species. A separate scrub–GC run was made for the initial IR identification of each compound, because the short time between eluted compounds precluded successive IR scanning on a single run.

S_2F_{10} and SO_2F_2 were identified by comparing their GC retention times and vapor-phase IR spectra with those obtained from the authentic compounds. S_2F_{10} was identified by comparing its vapor-phase IR spectrum with that from the literature[3]. The IR spectra are shown in Fig. 4.

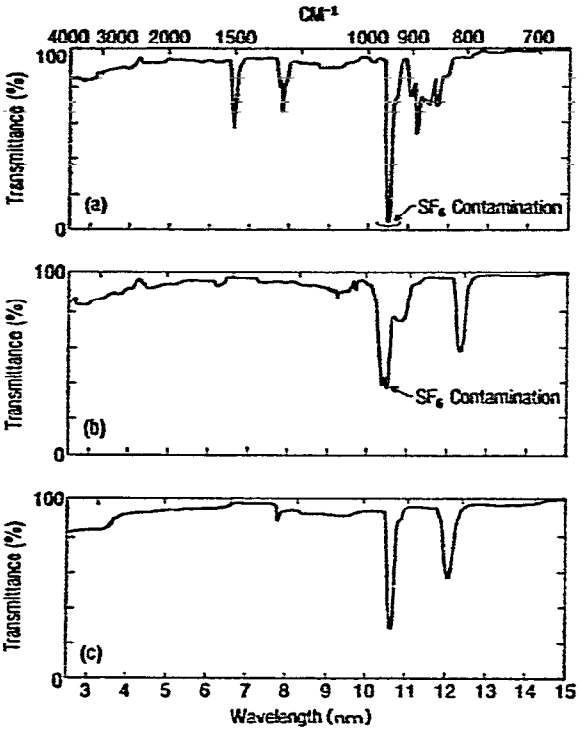

Fig. 4. Vapor-phase IR spectra of impurities recovered from SF_6. (a) SO_2F_2; (b) $S_2F_{10}O$; (c) S_2F_{10}.

Scrubber efficiency (concentration and desorption) was established by "doping" the vapor stream of known pure SF_6 with small-volume syringe injections of pure S_2F_{10}. By means of the vacuum manifold system, an absolute pressure of 190 mmHg of S_2F_{10} was established. By using a Precision Sampling (Baton Rouge, La., U.S.A.) 100-μl gas-tight syringe, 10 μl of S_2F_{10} was withdrawn through the septum after flushing the syringe several times into the manifold. The syringe was removed from the manifold, and its volume was brought to *ca.* 50 μl in order to afford a greater working range of the syringe and to provide further mixing of air and S_2F_{10} (air has no adverse effect on the analysis). The entire contents of the syringe were injected into the vapor stream of a pure SF_6 sample during the first moments of a 1-l scrubbing run. The peak area obtained for S_2F_{10} by this procedure was equivalent to 2.5 ppm (v/v) based on 1 l of SF_6 vapor at 760 mmHg. In order to ascertain how much of the "doping" S_2F_{10} was recovered, the peak areas were compared with those obtained from the same amounts of S_2F_{10} injected by syringe into the gas chromatograph via the injection port. Finally, the reproducibility of syringe sampling of small amounts of "doping" S_2F_{10} was established by making multiple injections into the chromatograph via the injection port and measuring peak areas thus obtained. No recovery efficiencies or quantitation for SO_2F_2 and S_2F_{10} were performed in this work.

RESULTS AND DISCUSSION

The choice of a suitable scrubber material for selective adsorption of S_2F_{10} from SF_6 was based on the GC screening of potential scrubbing materials by using them as column packings. By comparing elution times and peak shapes of SF_6 and S_2F_{10} at various isothermal temperatures (*i.e.*, room temperature and higher) on such columns, the potential usefulness of each material as a scrubber could be reasonably predicted. Although some initial investigation of porous polymer beads and conventional GC packings as potential scrubbers was performed, it was believed that porous glass beads would perform best because of their independence from such temperature effects as glass transition, crystallization and bleed.

Consequently, Porasil A was chosen after comparing it with analogous materials of lower surface area (Porasils B and C). As the surface area decreased, the separation of SF_6 and S_2F_{10} decreased. Therefore, Porasils D, E and F (which have even lower surface areas) were not evaluated.

The liquid nitrogen–chloroform slush bath produced a temperature (—63°) at which S_2F_{10} was quantitatively retained on the scrubber, but most of the SF_6 passed through. When solid CO_2–acetone was tried as a bath, the SF_6 apparently condensed (sublimation temperature —63.9°) and subsequently plugged the scrubber.

The peak-area reproducibility for 2 and 10 ppm (v/v) of S_2F_{10} using 1-l scrubs was ± 3–4% of the mathematical mean of the area. Both SO_2F_2 and $S_2F_{10}O$ exhibited similar reproducibility in the one sample in which they appeared.

The S_2F_{10} recovered from pure SF_6 "doped" by syringe via the septum in the sample flow-line was found to have at least 95% of the peak area obtained from identical injections of S_2F_{10} via the injection port. The reproducibility of repeated injections of small amounts (*e.g.*, 10 μl) of S_2F_{10} via the injection port was 98–99%. Thus, the quantitative reliability of syringe "doping" and scrubber adsorption–desorption was established.

Although unavailable to us at the time of this work, the application of a Fourier-transform GC–IR system would be of distinct advantage in subsequent analyses because of its greater sensitivity and scanning speed. However, once a GC retention time is established for S_2F_{10}, its IR spectrum need not be recorded in every analysis.

Approximately $5 \cdot 10^{-7}$ moles of a gaseous compound was found to afford an easily identifiable IR spectrum. Thermal-conductivity detection afforded convenient sensitivity to at least 1 ppm (v/v) of S_2F_{10} for a 1-l scrub; thermistor-bead detection was some eight times better.

Vacuum sampling of pure S_2F_{10} was used in the calibration procedure because (1) the S_2F_{10} was supplied in a valved metal cylinder, (2) it permitted the withdrawal of very small "spiking" samples, and (3) it afforded minimal exposure to an extremely toxic compound.

REFERENCES

1 L. A. Greenberg and D. Lester, *Arch. Ind. Hyg. Occup. Med.*, 2 (1950) 350.
2 W. C. Schumb, J. G. Trump and G. L. Priest, *Ind. Eng. Chem.*, 41 (1949) 1348.
3 W. Becher and J. Massonne, *Elektrotech. Z., Ausg. A*, 91 (1970) 605.
4 H. Gutbier and H. Luy, *Z. Anal. Chem.*, 231 (1967) 329.
5 Kirk-Othmer, "*Encyclopedia of Chemical Technology*", Vol. 9, Wiley, New York, 2nd ed., 1966, p. 670.
6 R. E. Rondeau, *J. Chem. Eng., Data*, 11 (1966) 124.