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DEPARTMENT of
APPLIED
SCIENCE

SUMMARY REPORT OF THE BROOKHAVEN EXPLOSIVE TAGGING PROGRAM

Russell N. Dietz, Coordinator
Robert W. Goodrich, James D. Smith, William Vogel

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BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973

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NOTICE

This report was prepared as an account of work sponsored by the United States Government through an Interagency Agreement (No. LEAA-J-IAA-011-4) awarded to the U. S. Energy Research and Development Administration by the Law Enforcement Assistance Administration, U. S. Department of Justice.

ABSTRACT

Tagging explosives, and in particular, blasting caps, with a volatile electronegative gas could make possible the detection of such explosives in close proximity and remote monitoring scenarios. The use of sulfur hexafluoride as the taggant gas was explored by determining existing ambient levels, evaluating barrier materials to the detection of the gas, selecting substances for the absorption of the volatile SF_6, determining how long such absorbed sources would last, assessing the compatibility with the blasting cap manufacturing methods, exploring detection methods for SF_6, and demonstrating the feasibility by detecting sources in suitcases. Background levels of 0.5 to 1.0 ppt only limit detection in large volume scenarios. Only tightly closed materials (such as paint cans) are effective barriers to the SF_6. Fluoropolymers were found to be the most effective absorbers of SF_6 holding as much as nine percent by weight. Projected indications were that such tagged sources should last for 10 or more years in suitcase sniffing scenarios. Monitoring instruments commercially available did not have the sensitivity required in continuous mode sampling. But instrument developments at Brookhaven indicated that continuous detection down to as low as a few parts of SF_6 in 10^{14} parts of air should be possible. Other electronegative compounds with at least two orders of magnitude lower ambient levels are needed for large volume detection.

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SUMMARY

Detection of explosives in large volume areas such as at airport environments can be achieved with only the most sensitive of instrumentation. The candidate system in this program is the electron capture detection of sulfur hexafluoride which capabability has been demonstrated at concentrations as low as 0.2 parts per trillion (ppt) and two orders of magnitude lower with preconcentration techniques. Preliminary experiments showed that SF_6 could be absorbed into a polymer substrate which could then be permanently incorporated into blasting caps for subsequent remote detection. Program tasks included determination of existing ambient levels of SF_6, evaluation of barrier materials to the detection of the gas, selection of substrate materials for absorption of the volatile SF_6 and a measure of the potential useful life of such a taggant combination, assessment of the compatibility of the method with current blasting cap manufacturing procedures, exploration of various SF_6 detection methods, examination of the possibility of using electronegative taggants other than SF_6, and demonstration of the feasibility of explosive detection by this method.

Background SF_6 concentrations were measured in St. Louis (0.7 ppt); New York City vicinity airports (1.0 ppt); and Aiken, So. Carolina (0.55 ppt). Rural SF_6 concentrations

were estimated to be 0.26 to 0.33 ppt based on aircraft samples from the upper troposphere. Since the ultimate detector for SF_6 tagged blasting caps will be a dual detector instrument (SF_6 taggant measured relative to the ambient level), no significant interference is anticipated from background SF_6.

SF_6 sources contained in barrier materials such as wrappings (paper, foil, plastic, etc.) and containers (bottles, cans, pipes, etc.) were tested in a flow system for rate of emission of SF_6 through the barrier. Classifications ranged from ineffective to severe barriers. All types of wrapped enclosures were completely ineffective; SF_6 was detected at the same intensity as in the absence of any wrapping. The effectiveness of heat sealed polyethylene bags varied by more than an order of magnitude (from ineffective to slight) indicating that the seal or closure on any container material was the important parameter. Certain items such as paint cans and capped pipes were severe barriers to the detection of SF_6 only if no holes for wires were present and only if the closures were of highest integrity. Several barrier materials should be tested in bomb configurations.

Many substrate materials for the absorption of adequate amounts of SF_6 and slow release of the taggant gas were examined. To detect the taggant gas by sniffing near the seam of a suitcase or box suspected of containing a bomb, a release rate of about 1 ng per minute was adequate. Thus for a ten year supply only 5 mg was needed and at least that much should be contained within no more than 0.5 g of substrate for use as an end plug on blasting caps. Absorption of SF_6 was generally achieved by exposing the substrate to the gas at its vapor pressure (~ 300 psig) for 10 to 100 hours. Many materials such as polyvinylchloride, polyethylene and nylon could not absorb sufficient SF_6. Several materials such as silicone rubber and one type of polyethylene initially absorbed as much as 20 to 50 mg/g but very quickly (1 month or less) lost most of the SF_6.

Only fluoropolymers were found to absorb sufficient quantities of SF_6 and retain the gas for a relatively long period of time. Several types (CTFE, E-CTFE, ETFE) had low capacity (< 5mg/g), but others (TFE, FEP, PFA) had substantial absorptive capacity (60 to 80 mg/g). Correlation of the loss of SF_6 as a function of time (by electrobalance weight loss and SF_6 electron capture chromatography measurements) showed that 0.5 g TFE Teflon pieces, originally loaded with 65 mg/g SF_6, still retained 12 mg/g after 1 year and 6 mg/g after 5 years. A ten year old tagged blasting cap should still retain a sufficient SF_6 release rate for detection in a suitcase.

Absorption of the SF_6 was a function of time and pressure of SF_6 applied. Negligible absorption occurred at low pressures of SF_6. The amount of SF_6 absorbed at 300 psig was found to be still increasing even after 146 hours of impregnation time. That full penetration of SF_6 into a 1/4-inch diameter by 1/2-inch long piece was not attained was demonstrated by sectioning and measurement of SF_6 by EC chromatography. Higher initial loadings and still longer lifetimes should be possible by hydraulic loading of the SF_6 at elevated pressures (> 1000 psig). Loss of SF_6 after loading was not accelerated by evacuation but the rate of loss was increased an order of magnitude, by baking at $140^{\circ}F$ (an unlikely situation for a blasting cap). Residual SF_6 response of a 0.1 g FEP Teflon piece after baking at $140^{\circ}F$ for 1 1/2 months was equivalent to a six year old piece maintained at room temperature, i.e., still adequate for detection. Initial loss of SF_6 may be less than our present projections when tagged discs of Teflon are swaged in the ends of blasting caps.

The method of incorporating a disc or short rod (< 1/2-inch in length) appears to be compatible with the current manufacturing method for electric blasting caps. The manufacturers present end closure would be retained since the Teflon disc would not be a leak-tight seal. An SF_6 source within the blasting cap is not practical since tests have shown that the gas will not penetrate the presently used end closures. Methods to prevent removal of externally added, SF_6 tagged plugs must be examined with the manufacturers.

A number of commercially available chromatographs for the continuous detection of SF_6 do exist but the limits of detection are no better than 3 parts in 10^9 parts of air. At Brookhaven, we have developed a semi-continuous instrument with a detection limit of 3 parts in 10^{13} parts of air and are working on several completely continuous prototypes.

There are other electronegative compounds which could be used in place of SF_6 with possible advantage. Since SF_6 is presently used (e.g., as an electrical insulating gas in high voltage equipment) and released to the environment, the possibility of false detection of a tagged explosive always would exist but would be minimized by the dual detector scheme. However, most other electronegative compounds do not have the ultimate sensitivity to EC detection that applies to SF_6, many are toxic or of unknown toxicity (the non-toxicity of SF_6 is well established), many contain halogen atoms potentially hazardous to the ozone layer although consumption of taggant would be only 10 tons/year compared to 10^5 tons/year or more of refrigerants (fluorine atoms are not harmful to the ozone layer), and semi-continuous methods for these other compounds have not been demonstrated. Potential candidates to replace SF_6 are the cyclic perfluorocarbons. Methods for continuously detecting the perfluorocarbons are being developed since background concentrations are several orders of magnitude less than that of SF_6.

Demonstration of the SF_6 taggant technique has been done in the laboratory using a $2\frac{1}{2}$ year old tagged dummy blasting cap. Two hours after placing the blasting cap within an attache case, concentrations measured at the seam of the case were two orders of magnitude greater than ambient and concentration within the case was 3.5×10^{-10} - three orders above ambient. Laboratory ambient was 5×10^{-13}.

Complete details of the results of the explosives tagging program at Brookhaven are included in this Summary Report. Sufficient experience and positive results to date warrant continued laboratory studies and some preliminary field evaluation studies using the Brookhaven semi-continuous portable detectors. Methods to increase the SF_6 loading in the substrate are possible, the use of perfluorocarbons needs to be examined, commercial fabrication of tagged blasting caps and detection in various scenarios should be performed, and development of continuous sniffers with appropriate sensitivity should be hastened. The method of incorporating taggant sources in blasting caps has been submitted for patenting by ERDA.

I. INTRODUCTION

The growing awareness and concern with the number of unexplained explosions throughout the United States, as well as the increasing number of airplane hijackings that have occurred, motivated several governmental agencies to examine various technical approaches to the seeding of explosives for detection and tracing purposes. Originally only a concern of police departments, other government agencies connected with transportation (Federal Aviation Administration of the Department of Transportation), mail (U.S. Post Office), illegal trafficking of explosives (Bureau of Alcohol, Tobacco, and Firearms of the Treasury Department), and criminal justics (U. S. Department of Justice) have become equally concerned. A considerable number of explosives detection and identification methods have been examined since no one method is likely to be without deficiences. Determent of bombing incidences by fear of detection or by identification and prosecution through positive identification techniques is an important reason to explore as many techniques as possible.

A. Detection and Identification Techniques

Two basic procedures have been used for detection of explosives - methods requiring close proximity to the explosive material and those based on analysis of airborne vapors.

Identification procedures are primarily aimed at determining the source or manufacturer of explosive materials following a bombing incident.

1. Detection in large volumes

A substantial amount of research has been conducted on detection of inherent vapors from explosives(1-4) for determining the presence of explosives at great distances from the source - e.g., in a room or the cargo compartment of an airplane.(5) The addition of volatile gas, sensitive to detection by electron capture chromatography, was indicated to be a more sensitive and specific method(6) and was the purpose of the research described in this report.

2. Close proximity detection

Many methods have been proposed for the screening of luggage to determine if explosives were contained therein.(7-9) Recent methods include thermal neutron activation of unseeded explosives(10) as well as seeded with gadolinium and cadmium(10,11) for detection of prompt gamma rays and with dysprosium(11) for detection of delayed gamma rays, fast neutron activation of explosives seeded with barium and cerium,(11) and x-ray fluorescence for detection of rare earth seeds(11) and detection of lead in bullets(12) in addition to vapor detection methods.

3. Post explosion identification

As an aid to law enforcement agencies, post explosion identification and tracing of unexplained explosions would be exceptionally useful. Westinghouse(13a) has developed an identification procedure based on the addition of small (200 micron) chips containing uv-excitable spotting phosphors (66%) and about 2 percent of a combination coding phosphor. The coding phosphors were 99 percent inert with about one percent of a combination of rare earth oxides (the code). Following an explosion, a uv-lamp has been successfully used to spot the residue of chips and identification of the relative amounts of the rare earth codes has been achieved using laser excited optical fluorescence techniques.

The 3M Company(13b) has devised two approaches to identification - elemental analysis of coded 50-micron micro-spheres and visual (microscope) determination of color-coded polyethylene micro sandwiches. In the former case, recovery of the micro-spheres was facilitated by the use of a hand held magnet above the debris (the spheres contained magnetic iron) and analysis was performed by an electron microprobe. The Ames Laboratory of Iowa State University has added rare earth elements in coded amounts for identification by x-ray excited optical fluorescence. Collection following explosions was with alcohol-saturated cotton swabs. A critical evaluation of these three techniques (performed by Lawrence Livermore Laboratory) indicated that only the Westinghouse technique could be successfully implemented.(13c)

B. Tagging and Detection with Sulfur Hexafluoride

The low vapor pressure of commercial explosives and the normal vapor dilution remote from the source impose requirements for sensitivity and selectivity in the part per trillion (ppt) and sub-ppt range. Recent developments in analytical instrumentation indicate the possibility of obtaining the desired detection capability, but an extensive continued research effort is still required.

The possibility of using easily detectable taggants warranted investigation since it would provide a faster development for an explosives detection system. The extreme sensitivity for detection of sulfur hexafluoride, a few parts in 10^{13} parts of air without preconcentration, indicated that SF_6 as a taggant offered the best current approach for predetonation vapor phase detection. Preliminary experiments at Brookhaven showed that SF_6 might readily be absorbed into a fluoropolymer material which, when incorporated in blasting caps, would slowly desorb at a rate sufficient for detection in suitcases for up to ten years after tagging.

Since as many as 80 percent or more of unexplained explosives have been shown to be started with electric blasting caps and only three manufacturers of blasting caps account for over 90 percent of the caps in the United States, tagging blasting caps during manufacture should give a reasonably good chance for detecting an illicit bomb.

To evaluate the application of the SF_6 taggant approach, certain important areas needed a more thorough study. Background ambient levels of SF_6 would play an important role in whether the technique could be successfully employed. The degree by which the vapors of SF_6 could be shielded from detection by a barrier material such as a plastic bag also was important. Possible methods for containing the tagging gas on the blasting cap were examined as well as consideration of the ease of incorporation into the manufacturing step.

II. SF_6 BACKGROUND MEASUREMENTS

Brookhaven has the capability of measuring SF_6 concentrations by either collecting air samples from the environment in evacuated steel canisters for subsequent analysis back in the laboratory or directly determining SF_6 in air using the Brookhaven developed semi-continuous SF_6 sniffer. The laboratory technique has been used to measure SF_6 concentrations as low as 0.1 ppt and the semi-continuous method at about 0.5 ppt. Although the explosives detection scheme would ultimately require a continuous monitoring system - e.g., at airport passenger and baggage check-in locations, in baggage carriers, or on board airplanes, the evacuated cannister method was much easier to adapt to sampling at various locations in the United States.

A. Sampling Regions

1. St. Louis. During the end of July and early August of 1974, samples of background ambient air were collected in the St. Louis area and analyzed in the laboratory. A typical calibration curve for the laboratory chromatograph procedure, which did not involve any pre-concentration steps, is shown in Figure 2-1. Complete details of the analytical procedure have been published earlier.(14) The averaged results of duplicate analyses of eight bottles samples are shown in Table 2-1. In six of the samples the SF_6 concentration was 0.5 ppt or less. Only 2 bottles contained concentrations greater than 1 ppt. An average background concentration of 0.7 ppt SF_6 in St. Louis was calculated.

2. New York City vicinity airports. Samples were collected on Long Island, New York, on November 1, 1974 at Islip (MacArthur) Airport (45 miles east from mid-town New York City), November 4 at Brookhaven Airport (57 miles east from New York City), and November 21 at La Guardia Airport (5 miles east from mid-town). On all three days the wind was coming approximately from the west. As shown in Table 2-2, the background SF_6 was usually less than

1.5 ppt and averages 1.0 ppt. The limit of detection was about 0.2 ppt and duplicate bottle samples generally agreed to within 15 percent.

Sulfur hexafluoride is used extensively as an electrical insulator in electrical switching and transformer equipment · especially high voltage devices used at electric generating power plant sites. New York City has a large number of power plants, yet there was no trend with increasing proximity to the mid-town area. La Guardia Airport samples 53 and 54 were taken almost directly downwind from the Ravinswood electric power plant and samples 55 and 56 were taken less than 500 feet from a bank of transformers yet the SF_6 concentrations were equal to or below the average.

3. New York City samples. The Health and Safety Laboratory (HASL) of the Energy Research and Development Administration from their location in New York City have been measuring the concentration of SF_6 in the city air for the past two years. As shown in Table 2-3, with the exception of some high readings in June and July of 1973, the average SF_6 concentration was found to be 2.3±1.3 ppt for January 1973 to December 1974. The high concentrations in the summer of 1973 had a wide degree of variability indicating a very good possibility of a local source that was emitting an unusually large amount.

4. Savannah River Plant samples. During comparative meteorological tracer studies in conjunction with the National Oceanic and Atmospheric Administration,(17) background concentrations of SF_6 were measured in Aiken, South Carolina. The results, shown in Table 2-4, can be used to determine an average value of 0.55±0.18 ppt.

5. Stratospheric samples. The Health and Safety Laboratory, since the fall of 1973, has been measuring the SF_6 content of the lower stratosphere using aircraft sampling techniques. The results of their analyses(14) are summarized in Table 2-4. A few of the samples were obtained from the upper troposphere which is considered to have uniform mixing ratios for conservative trace gases. The results indicated the background tropospheric SF_6 concentration was 0.26 to 0.33 ppt.

B. Conclusions

The rural ground level concentration of SF_6 is predicted to be between 1.4 and 1.3 of a part per trillion and measurements in urban (New York City, 2.3 ppt; St. Louis, 0.7 ppt), near-urban (NYC area airports, 1.0 ppt) and rural (Aiken, S.C., 0.55 ppt) areas are not significantly greater than the ultimate background concentration. That the HASL measurements in the lower stratosphere are indicative of the global tropospheric SF_6 background has been confirmed by us based on our analysis of several of the HASL samples for N_2O as well as SF_6. Nitrous oxide has been to have a uniform mixing ratio(15) up to lower stratosphere. Since the N_2O content of the HASL samples (cf. Table 2-5) was essentially the same as the ground level concentration, the global tropospheric SF_6 concentration was established at 0.26 to 0.33 ppt. The precision of our analyses shown in Table 2-6 for the sub-ppt SF_6 concentrations was achieved by using a 13X molecular sieve concentration with 80 cm^3 sample aliquots.

The background SF_6 concentration in urban areas was only about 2 to 4 times the global tropospheric concentration indicating that the sources of SF_6 were dispersed and rapidly diluted. Since the ultimate detector for SF_6 tagged blasting caps will be a dual detector instrument (SF_6 measured relative to the ambient level), no significant interference is anticipated from background SF_6.

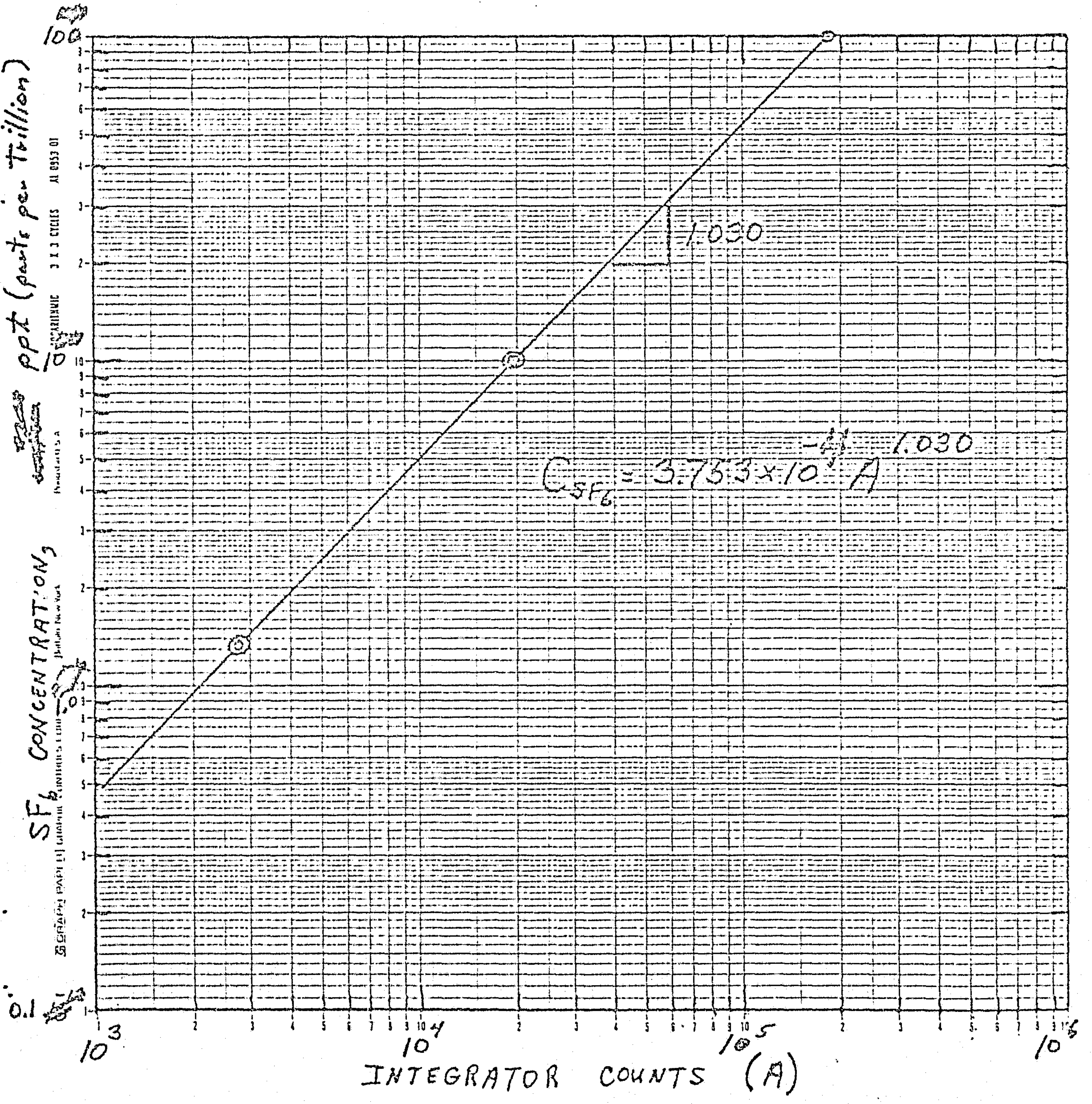
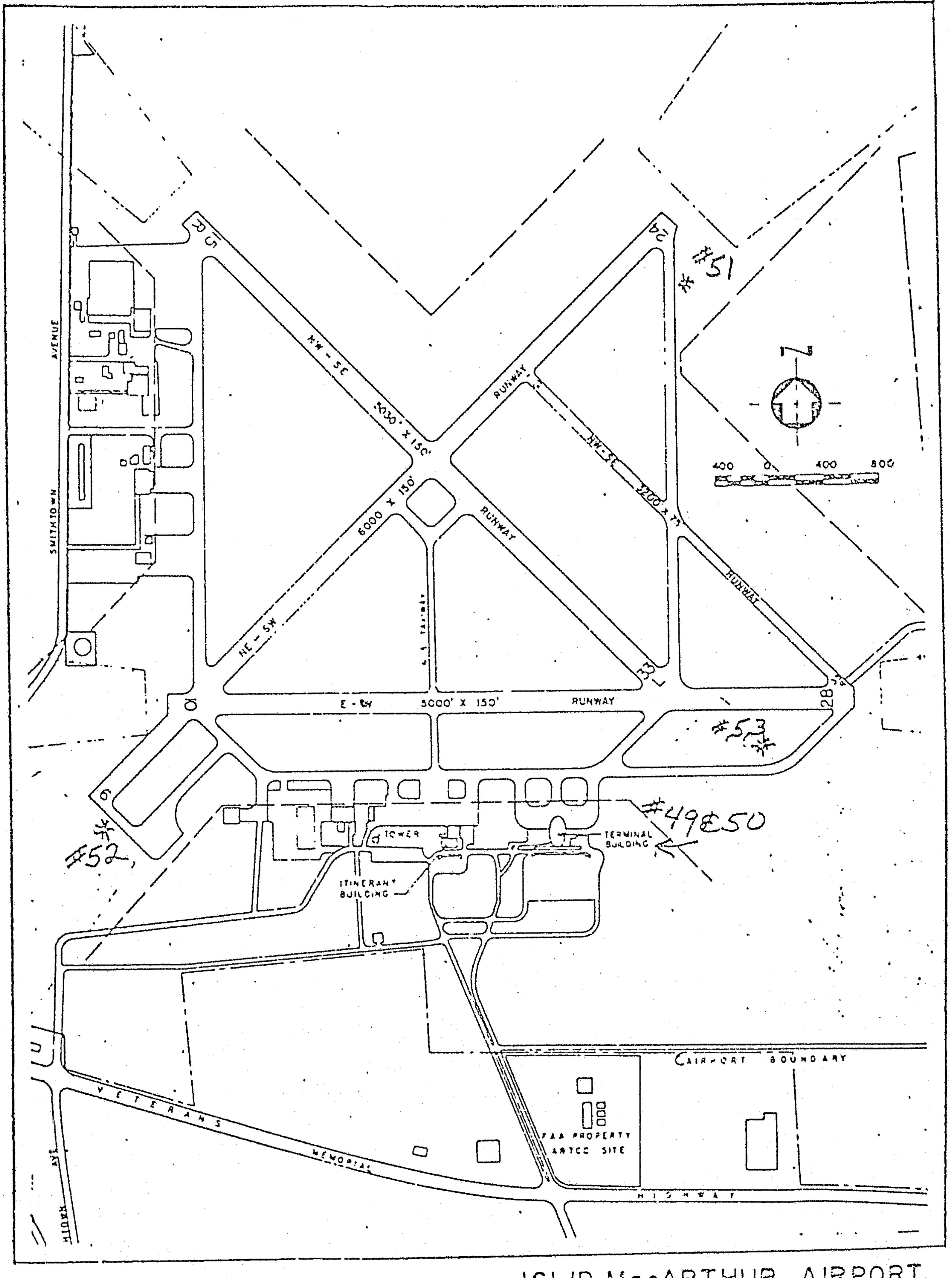


Figure 2-1. Laboratory Chromatograph Calibration Curve

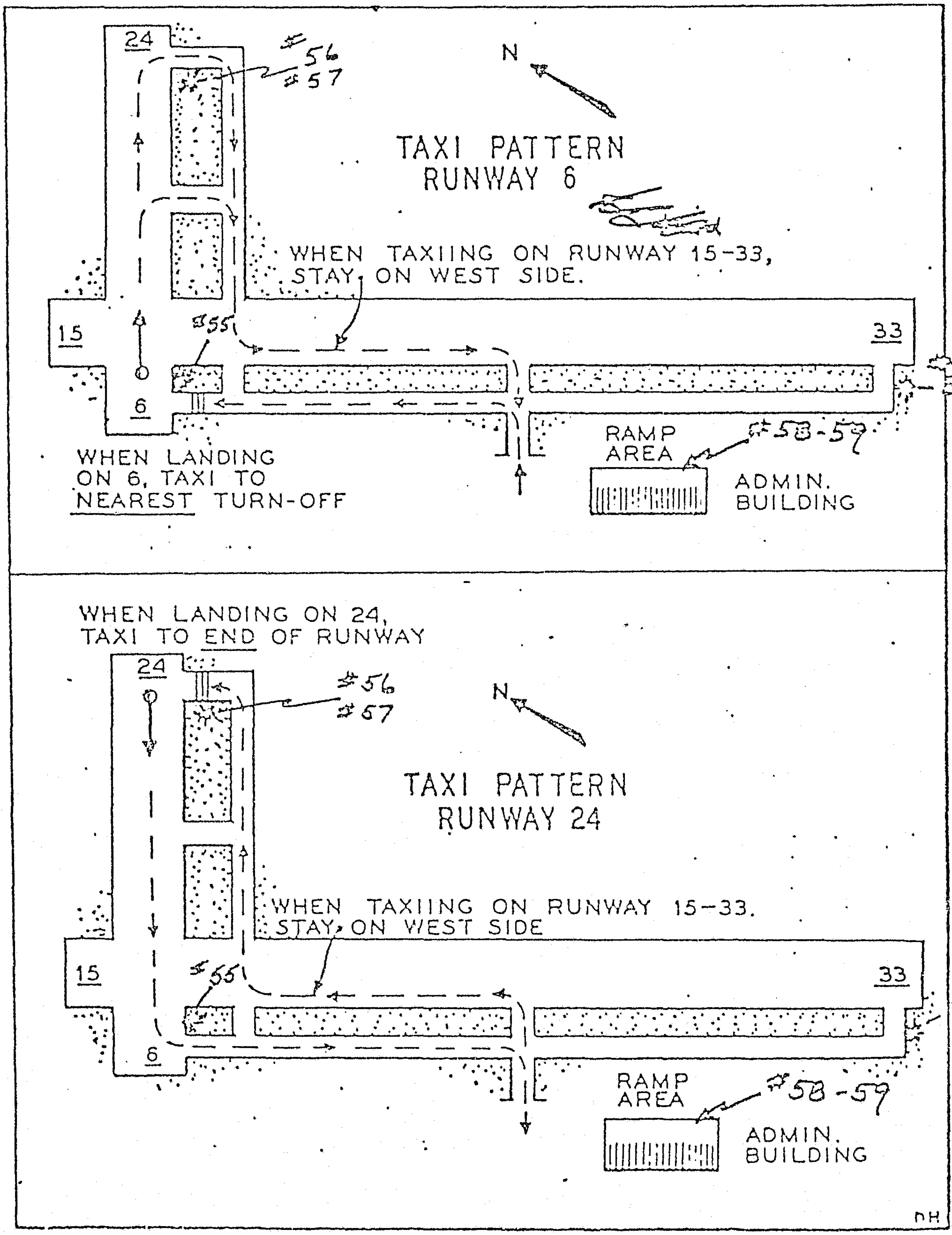
Figure 2-2. Plan of Islip (Mac Arthur) Airport



ISLIP MacARTHUR AIRPORT

BROOKHAVEN AIRPORT

Figure 2-3. Plan of Brookhaven Airport



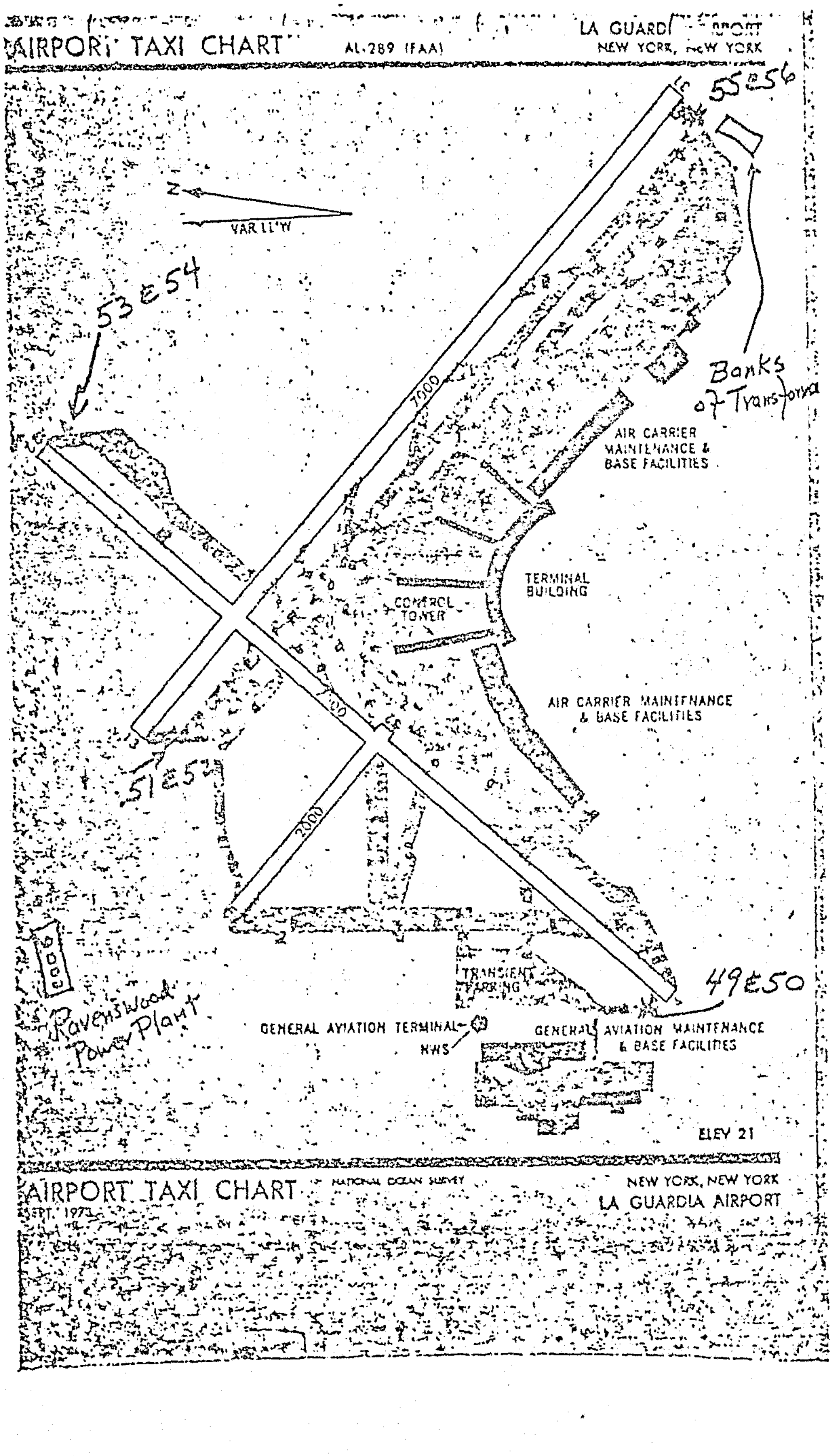


Figure 2-4. Plan of La Guardia Airport

TABLE 2-1

SF_6 IN ST. LOUIS AMBIENT AIR

Bottle samples, 7/29-8/9/74

Sample No.	SF_6 Concentration, ppt
B-70	0.2
B-34	1.5
B-46	2.6
L-15	0.2
L-16	<0.2
B-35	<0.2
B-23	0.4
D	0.5

average = 0.7 ± 0.9

TABLE 2-2

SF_6 BACKGROUND MEASUREMENTS AT NEW YORK CITY VICINITY AIRPORTS

Location	Sample Bottle Nos.[c]	SF_6 Concentration, ppt[b] First Bottle	Duplicate Bottle
Islip[a]	49, 50	1.0±0.2	1.0±0.1
(MacArthur)	51	1.1±0.2	
(cf. Fig. 2-2)	52	1.4±0.1	
	53	1.6±0.1	
Brookhaven	54	0.9±0.2	
(cf. Fig. 2-3)	55	1.0±0.1	
	56, 57	0.7±0.1	0.8±0.2
	58, 59	1.4±0.2	1.0±0.1
La Guardia	49, 50	1.3±0.1	1.2±0.1
(cf. Fig 2-4)	51, 52	0.5±0.1	0.8±0.1
	53, 54	1.0±0.2	1.0±0.1
	55, 56	0.3±0.1	0.5±0.1
	57, 58	1.4±0.1	1.5±0.2

---

[a] The locations of each of the bottle sampling points are shown in the respective Figures 2-2 to 2-4.

[b] Each bottle was analyzed 3 times.

[c] Sample bottles 49, 50 (Islip), 58, 59 (Brookhaven), and 57, 58 (La Guardia) were used inside the respective terminals.

TABLE 2-3

SF_6 BACKGROUND MEASUREMENTS[a] AT NEW YORK CITY HASL BUILDING[b]

Date		SF_6 Concentration, ppt
1973:	Jan.	1.1 ± 0.1
	Feb.	4.9 ± 1.0
	Mar.	1.9 ± 0.4
		1.1 ± 0.1
	Apr.	2.1 ± 0.1
		1.4 ± 0.4
	May	2.4 ± 0.4
		3.0 ± 0.1
	June	11.8 ± 3.2
	July	13.6 ± 7.3
	Aug.	2.5 ± 0.3
	Sept.	1.4 ± 0.1
1974:	Feb.	1.1 ± 0.1
	Apr.	1.5 ± 0.5
	May	<0.3
	Sept.	5.3 ± 0.5
	Oct.	3.9 ± 1.0
	Nov.	2.1 ± 0.6
	Dec.	2.0 ± 0.6

---

[a] Samples and analyses by the Health and Safety Laboratory of the U. S. Energy Research and Development Administration.

[b] Sampling performed on the 12 story roof of the HASL Building

TABLE 2-4

SAVANNAH RIVER PLANT

BACKGROUND SF_6 CONCENTRATION

Loc.	Bottle No.	SF_6 CONC., ppt[a] 1st Anal.	2nd Anal.	Date	Orifice	Time
1	26	0.41	0.34	9-22-75	10 min	7:45-7:55 EDT
2	28	0.45		9-26-75	10 min	10:55-11:05 EDT
2	31[b]	5.87	5.88	9-26-75	5 min	10:55-11:00 EDT
3	35	0.42		10-01-75	5 min	10:38-10:43 EDT
3	32	0.75		10-01-75	5 min	10:31-10:35 EDT
4	27	0.59	0.58	10-01-75	5 min	11:15-11:20 EDT
4	30	0.53		10-01-75	5 min	11:21-11:26 EDT
5	36	0.39		10-01-75	5 min	11:57-12:02 EDT
5	33	0.46		10-01-75	5 min	11:51-11:56 EDT
6	29	0.93		10-01-75	10 min	10:35-10:45 EDT
Blank	34	0.04				
Blank	25	0.04				

---

[a] Analyzed by a concentration procedure using 40 cm^3 samples

[b] Sample bottle leaked

TABLE 2-5

LOWER STRATOSPHERE SF_6 MEASUREMENTS[a]

Date	Altitude km	Latitude	SF_6 Conc., ppt
Nov. 1973	14	30-40°N	0.19-0.32
Feb. 1974	14-15	40-50°N	0.20-0.21
Apr. 1974	13-19	60°N-20°S	0.14-0.26
Oct. 1974	12-19	35-75°N	0.12-0.27

---

[a] Samples and analyses by the Health and Safety Laboratory of the U. S. Atomic Energy Commission (from ref. 14).

TABLE 2-6

COMPARISON OF LOWER STRATOSPHERE N_2O AND SF_6 CONTENT[a]

HASL Sphere No.	Latitude	Altitude, km	Measured Concentrations HASL SF_6, ppt	Brookhaven SF_6, ppt	Brookhaven N_2O, ppm[b]
M 150	50-52°N	19.1	0.16	0.168	0.240
N 3126	1-6°N	18.3	0.29	0.287	0.278
E 0691	0-5°N	15.3	0.32	0.326	0.295
N 2455	12-15°N	19.2	0.28	0.260	0.264

---

[a] Samples were collected by the Health and Safety Laboratory of ERDA.

[b] Ground level N_2O is typically 0.270 to 0.285 ppm.

III. BARRIER EFFECTS EVALUATION

Another important part of this program was to estimate the degree to which taggant SF_6 could be prevented from reaching a monitoring instrument if a bomb containing a tagged blasting cap were placed in various shielding materials such as a paper bag, a cardboard box, a metal can, and so forth. Such barriers would reduce the projected ability to determine the presence of tagged blasting caps as well as limit the ability of any other vapor phase detection scheme (e.g., direct detection of inherent explosive vapors). For the latter type vapors, evaluation of barriers with SF_6 would provide a lower limit of barrier effectiveness since adsorption and chemical reaction of the explosive vapors with certain barrier materials would further enhance the barrier effectiveness factor.

A. Procedure

A flow system was designed, constructed, and utilized to quantitatively measure the barrier capability of various enclosures (cf. Figure 3-1). One-half gram Teflon pieces were impregnated with SF_6 at three different loadings ranging from 3 to 60 mg SF_6/gram Teflon. A piece was placed in the type of barrier to be evaluated (e.g., paper bag, plastic bottle, aluminum foil, etc.), about 1 cubic inch in volume, and the package then enclosed in a one quart metal can through which a flow of about 0.5 to 1.0 ℓ/min of compressed air was passed. Follow-up experiments were performed with a few of the more severe barrier materials in larger sizes (about 100 cubic inches) using a 5-gallon metal drum. The effluent SF_6 concentration was monitored with an electron capture gas chromatograph using a 6 foot molecular sieve column and a 1 cm^3 sample loop (this apparatus had 1/15 the sensitivity of the instrument described in Chapter II). A digital integrator was used to quantitatively measure the SF_6 peaks; precision was about 2% from 10^{-11} to greater than 10^{-8} cm^3/cm^3 (integrator counts were 120,000 for a 10^{-9} concentration).

The rate at which the concentration changed in the effluent from the can was initially given by

$$\frac{dc}{dt} = kc_e \qquad (1)$$

where c_e was the concentration of the effluent SF_6 in the absence of the barrier. Solving over the time limits from zero to time, t, gave

$$c' = kt \qquad (2)$$

where c' was the SF_6 concentration as a percentage of the equilibrium concentration at infinite time (i.e, the concentration in the absence of the barrier).

B. Results with Various Barrier Materials

Equation 2 suggested that plots of c' versus time should give straight lines with slopes k. In addition, the diffusion rate of SF_6 from the Teflon piece should not affect the value determined for k; only the type of barrier material should be reflected in k. Both conclusions were substantiated by the results shown in Figure 3-2. The barrier in that case was an "Excedrin" plastic bottle with a snap-cap; although the SF_6 release rates from the Teflon pieces were different by a factor of 14.5, the rate constants expressed as percent per hour were identical in the two runs.

The results for a number of barrier materials are shown in Figures 3-3 through 3-6 and complete lists are given in Tables 3-1 and 3-2. Figure 3-3 contains the results obtained with a cellulose acetate bottle which was closed with the snap-cap provided (highest curve) and, in a later run, with a cork stopper (lowest curve). Figure 3-4 demonstrates the barrier capability of a heat-sealed polyethylene bag in 3 separate runs.

Clearly, it is not the barrier materials but rather the effectiveness of the closure which is really the controlling factor.

The rate constants, k, from equation 2 were determined from the slopes in the linear region (less than 50% approach to equilibrium) from a least-mean-square fit using a Hewlett-Packard computer-calculator and are listed in Table 3-1. The average relative standard deviation (an indication of the precision) was found to be 5 ± 3 percent. A qualitative effectiveness was assigned to each barrier material according to the following definitions:

Barrier Capability	Time to 10%, minutes*
ineffective	< 10
negligible	10-30
slight	30-180
moderate	180-900
severe	> 900

As a result of these tests, the last three materials (the brass pipe capped with Teflon tape on the threads, a polyethylene bottle, and a glass vial) were found to severely limit the effusion of SF_6; of moderate barrier capability were another three materials (a glass volumetric flask, a 1/2 pint paint can, and a plastic "Excedrin" bottle). Those latter six materials were tested over a longer time base (5 to 10 days) in the

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*From equation 2, time to 10% was 10/k.

present size and then in a size large enough to contain a bomb (cf. Table 3-2). For three of the barrier materials - a cardboard carton, a polyethylene bottle, and a paint can, there was little change between the small and the large size. The cardboard carton was still an ineffective barrier; the poly bottle, moderate; and the paint can, slight to moderate.

Two materials which were previously classified as very severe barriers, a glass jar and a brass pipe, were found to be only slightly to moderately effective in the larger size. Only one item, the polyethylene zip-lock bag, exhibited a significantly greater barrier capability in the larger size. Most probably the smaller zip-lock bag had either a defective seal or a pin-hole in the plastic.

C. Conclusions

The tests performed in this phase showed conclusively that the barrier capability of the material in question was not dependent on the type of barrier material used, but rather, on the type of closure. For example, those materials which were simply wrapped around the source of SF_6 presented almost no barrier capability (e.g., aluminum foil, cardboard box, plastic wrap, etc.). The sulfur hexafluoride vapors rapidly diffused through the spaces between adjacent layers of the wrappings.

When, for example, the same plastic was used as a heat-sealed plastic bag instead of just a wrap, the barrier capability was increased by as much as a factor of 150. In fact, the three runs with the heat-sealed polyethylene bag, shown in Figure 3-4 (also, cf. Table 3-1), had barrier effectiveness vary by a factor of 150. Clearly, the degree of perfection of producing the heat-seal joint played the key role in establishing the barrier capability. Thus, materials such as metal paint cans, glass jars with ground glass stoppers, and brass pipes with taped and threaded end caps would be expected to provide greater sealing capacity than just plain wrapping.

Even though a paint can lid was an effective seal, the barrier capability of the seal was measurable by the technique employed and was found to decrease in effectiveness as the size increased. This was true for most of the barrier materials studied, indicating that as the size of the seal increased, the chance for leakage also increased.

If a moderately strong SF_6 source is eventually used to tag blasting caps, it is reasonably certain that barrier materials with a rate constant greater than 1 percent per hour should not present any significant problem to detection. A moderately strong SF_6 source is one with an elution rate of 0.3 nanoliter per minute or greater which can be met with either the adsorbed on Teflon or microencapsulated sources described later. The last five barrier materials in Table 3-2 should be checked for effectiveness in an actual suitcase sniffing feasibility demonstration.

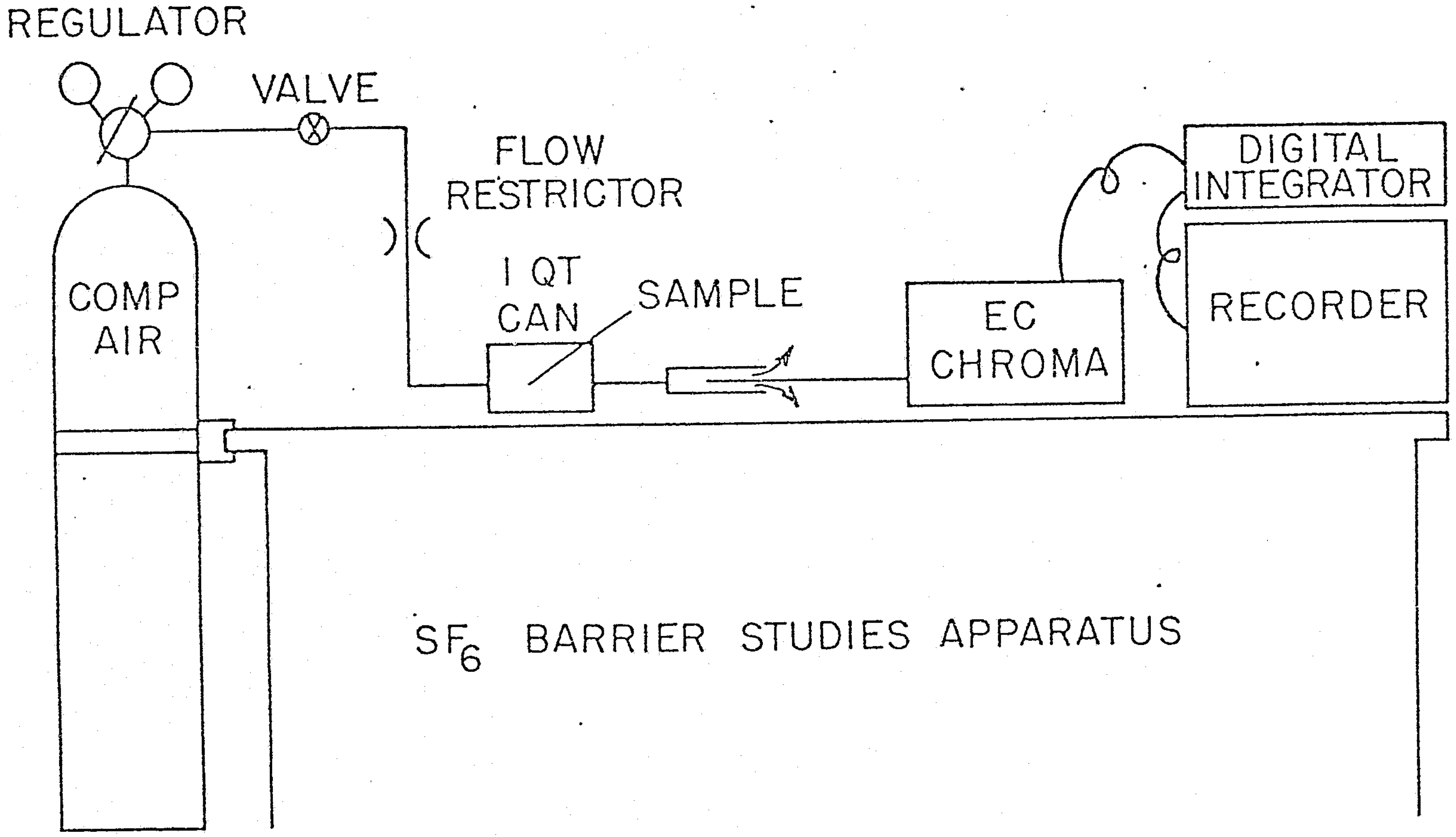

Figure 3-1.

SF$_6$ Barrier Studies Apparatus

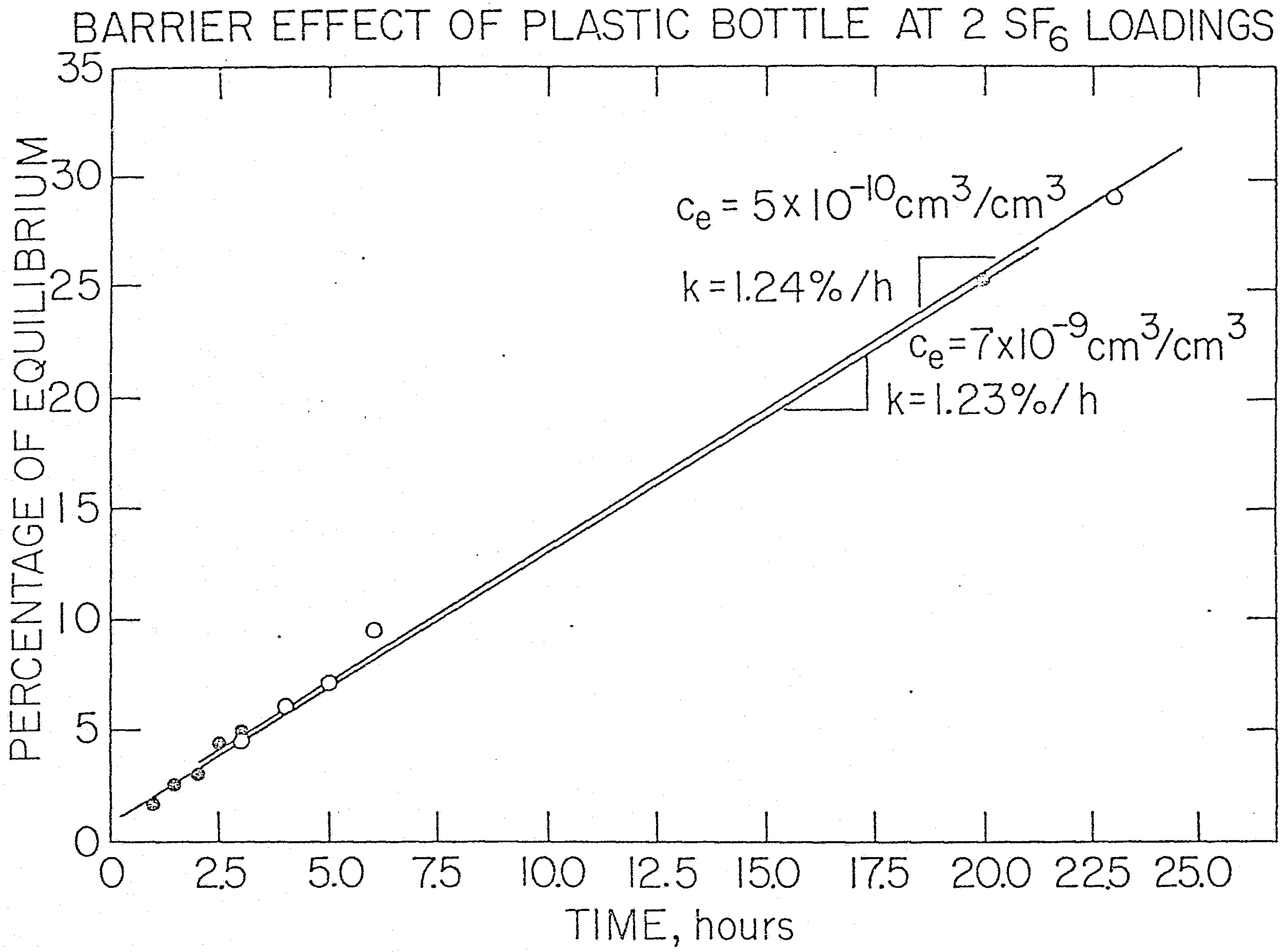

Figure 3-2.

Barrier Effect at Two SF$_6$ Loadings

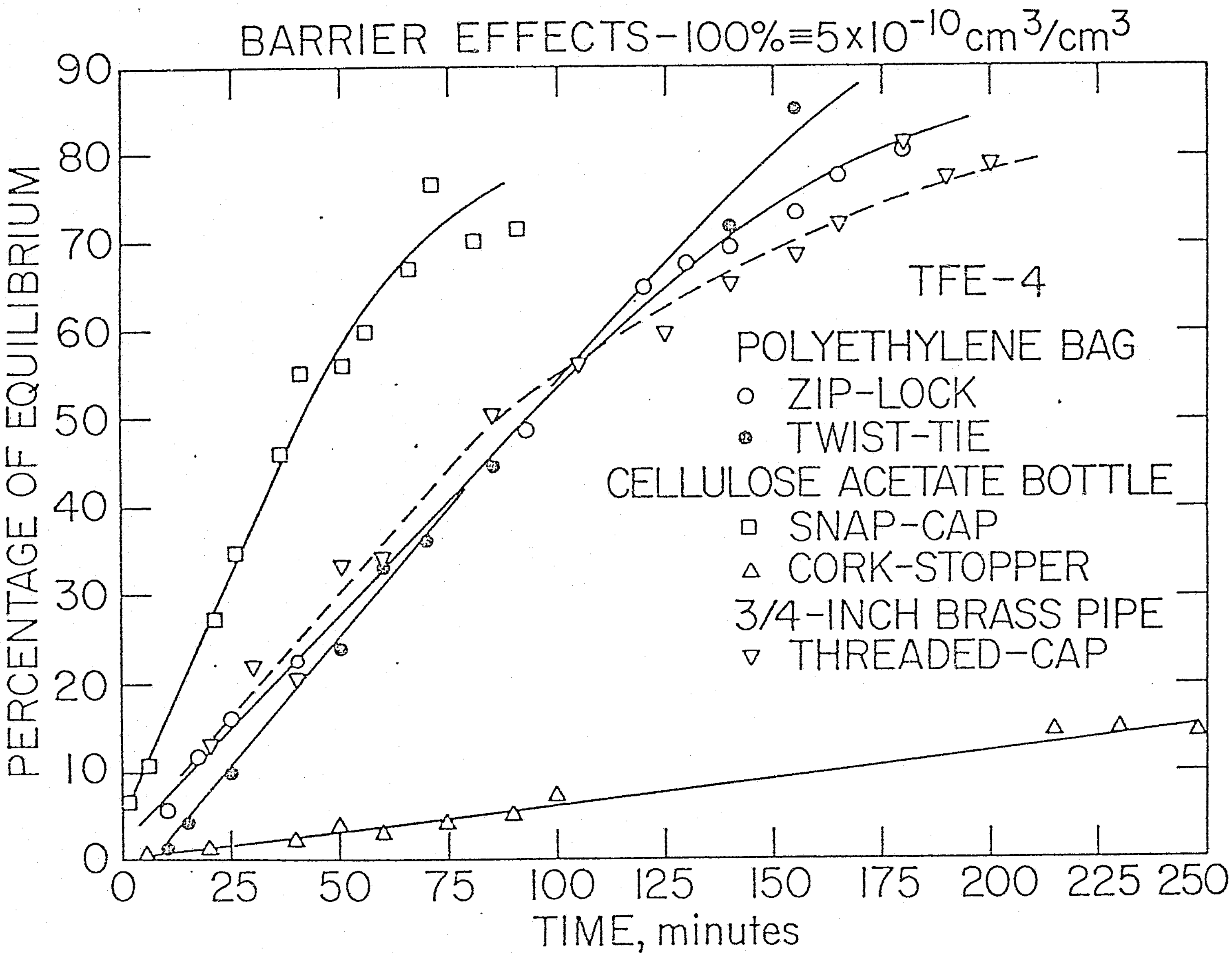

Figure 3-3.

Barrier Effects for Several Materials

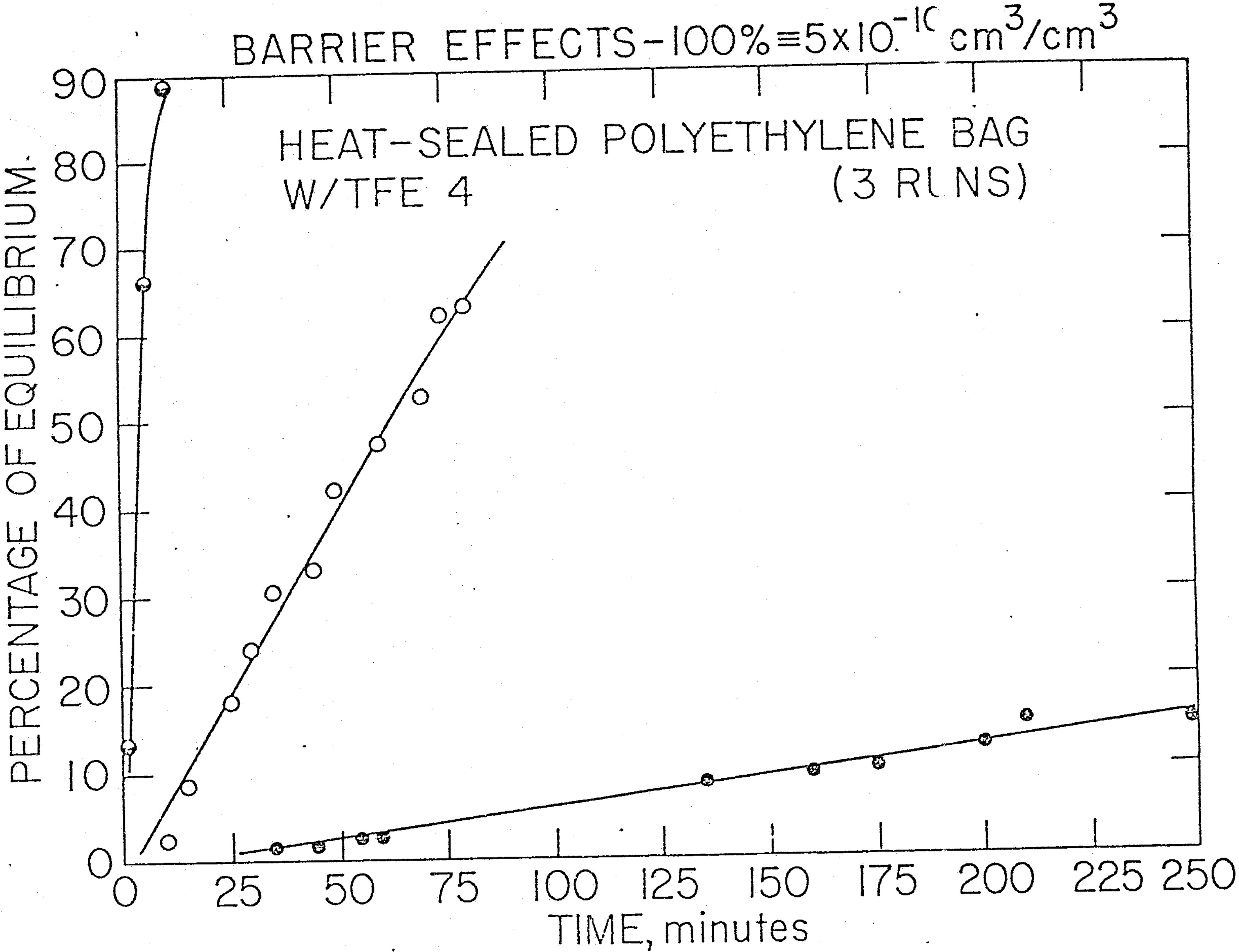

Figure 3-4

Barrier Effect
of Heat-Sealed Polyethylene

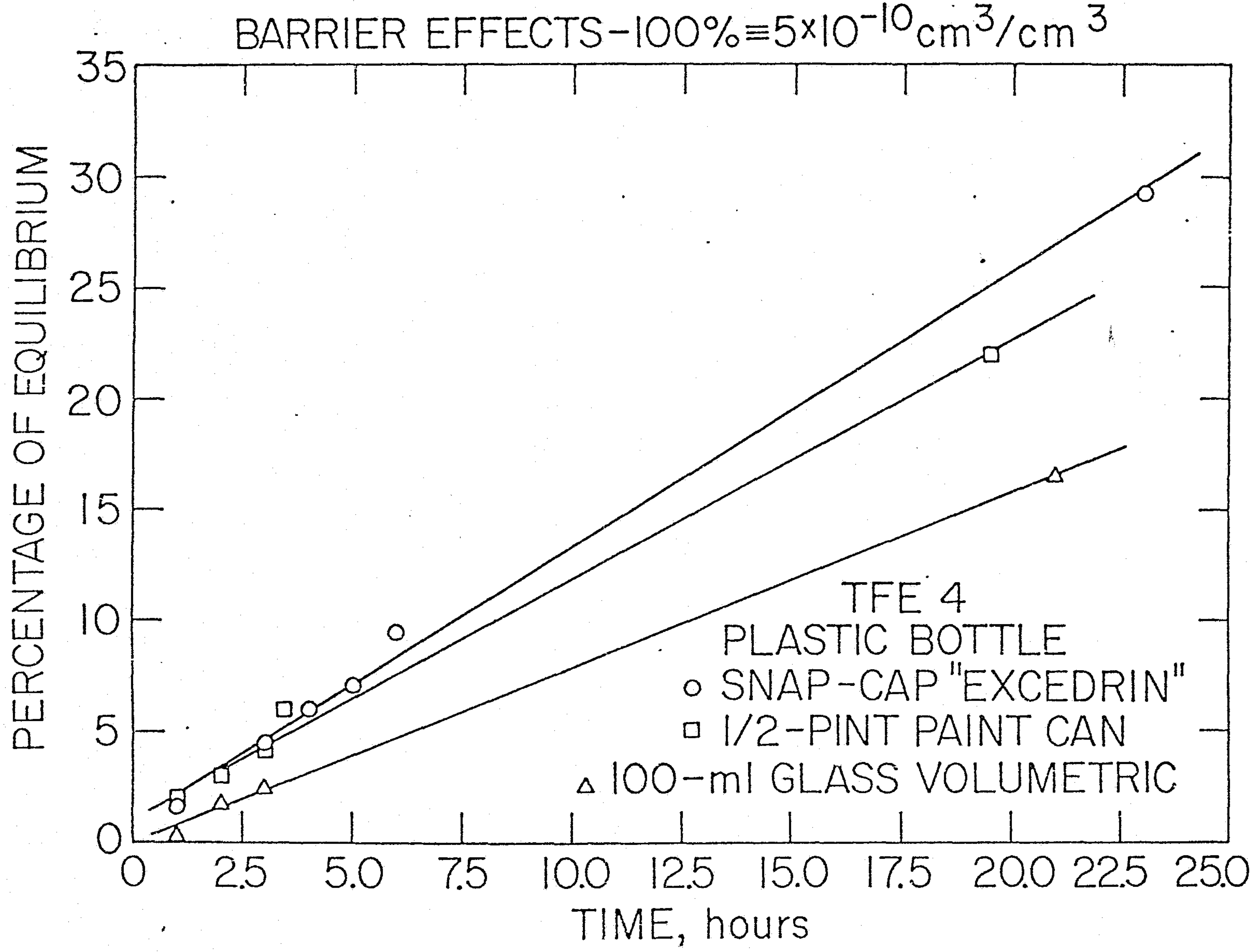

Figure 3-5

Barrier Effects
of Moderately Restricting Materials

Figure 3-6. Barrier Effects of Strongly Restricting Brass Pipe

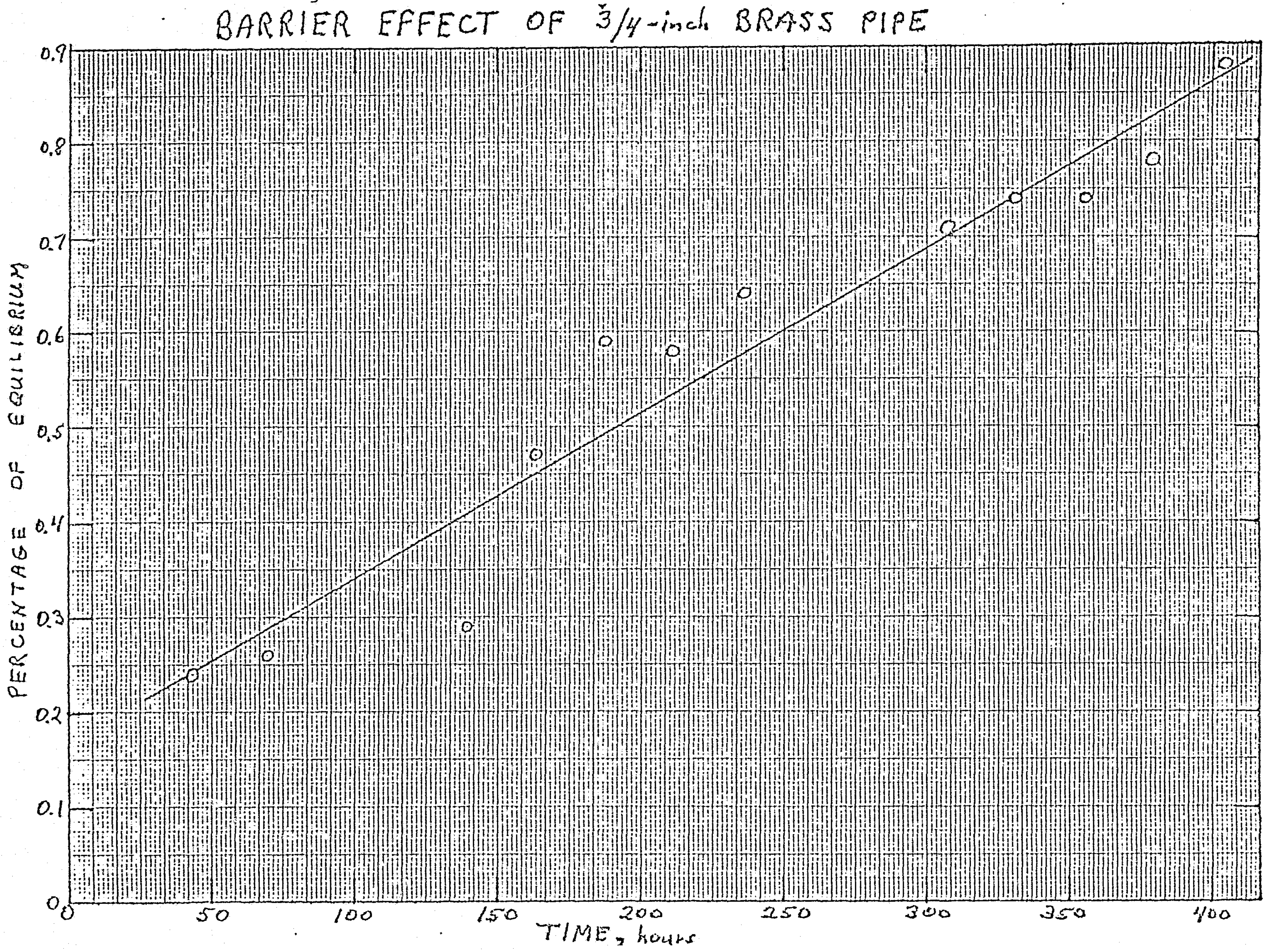

TABLE 3-1

BARRIER EFFECTS EVALUATION

Barrier Material			k		Time to 10%, min	Barrier Capability	
			%/min	%/hr			
Aluminum foil			> 10		< 1	ineffective	(< 10)
Paper bag			"		"	"	
Paper envelope			"		"	"	
Cardboard box			"		"	"	
Plastic wrap			"		"	"	
Polyethylene bag:	twist-tie		0.585		17	negligible	(10-30)
	zip-lock (4 mil)		0.516		19	"	
	heat-sealed:	1	10.56		1	ineffective	
	(2 mil)	2	0.844		12	negligible	
		3	0.0686		146	slight	(30-180)
Cellulose acetate bottle w/snap-cap			1.086		9	negligible	
3/4 inch brass pipe capped w/o tape			0.562		18	"	
Cellulose acetate bottle w/cork stopper			0.0611		164	slight	
Plastic "Excedrin" bottle w/snap-cap				1.236	486	moderate	(180-900)
1/2 pint paint can				1.069	561	"	
100-ml glass volumetric flask				0.794	756	"	
Glass vial w/plastic screw cap				~ 0.4	1500	severe	(> 900)
Polyethylene bottle w/screw cap				~ 0.2	3000	"	
3/4 inch brass pipe capped w/tape				< 0.02	> 30000	"	

TABLE 3-2

BARRIER EFFECTS EVALUATION
SECOND TEST SERIES

Barrier Material		Volume, in.^{3}	k %/hr	Time to 10%, hours	Barrier Capability
Cardboard carton		1	-	<0.01	ineffective
		112	-	0.07	"
Polyethylene bottle	(6 dram)	1.4	0.9	11.1	moderate
	(1 qt.)	58	0.85	11.8	"
Paint can	(1/2-pint)	14.4	4	2.5	slight
	(1-gal.)	231	0.70	14.3	moderate
Glass jar	(1-ounce)	1.8	<0.0004	(>3years)	very severe
	(1-qt.)	58	0.70	14.3	moderate
Polyethylene zip-lock bag		1	31	0.32	negligible
		50	0.52	19	mod. to severe
Brass pipe	(3/4-inch)	1.5	0.0017	5900	very severe
	(2-inch)	23	0.37	27	severe

IV. SF_6 SUBSTRATE DETERMINATION

Based on the present configuration of an electric blasting cap, two methods of incorporating the taggant SF_6 vapors are shown schematically in Figures 4-1 and 4-2 - an externally mounted SF_6-impregnated Teflon disc and an integrally contained impregnated Teflon rod or encapsulated liquified or adsorbed source. An internally retained SF_6 source - that is, one within the area schematically designated as containing the explosive charge (powder) - was eliminated from consideration when it was experimentally verified that SF_6 would not penetrate the rubber sealing arrangement used by the manufacturers. Although not completely eliminated as a possibility, SF_6 impregnation of the elastomeric closure materials in use at that time showed little retention of the gas.

As will be shown in a later section, adequate detection of a tagged blasting cap in a suitcase or box suspected of containing a bomb was achieved by external sniffing provided the SF_6 release rate was about 0.5 to 1.0 ng per minute. Thus, for a ten year supply only 5 mg was needed, assuming a uniform rate of release. At least that much should be contained within no more than 0.5 g of substrate if used in the configuration of Figure 4-1 or no more than 0.1 g of substrate if the method of Figure 4-2 were employed. The range of SF_6 loadings would thus be required to be 10 to 50 mg of SF_6 per g of substrate and the rate of loss should be in the nanogram per minute range. From the preliminary substrate determination experiments described here, those materials meeting the above criteria were investigated in more detail to determine the best possible choice for the substrate.

A. Procedure

The ability of various materials to absorb quantities of SF_6 was surveyed by exposing known masses (ranging from 0.01 to 0.5 g) to SF_6 vapors at 300 psig and at temperatures of room temperature and $100^{\circ}C$. Exposure times usually ranged from 16 to 100 hours. The weight gain following the impregnation with SF_6 was determined either with an analytical balance (Sartorius, Model 2462) with a resolution of 0.1 mg or an electrobalance (Perkin-Elmer, Model AD-2) having a resolution of 0.1 μg. Rate of loss (desorption) of SF_6 was determined by periodically weighing the samples and by measuring the SF_6 concentration in an air stream flowing over the piece using the electron capture gas chromatograph described in the barrier studies effort.

B. Preliminary Survey Experiments

The materials surveyed for retention of SF_6 are shown in Table 4-1. The method of loading SF_6 was essentially the same in all cases (exposure to the vapors at 300 psig and room temperature) except for the activated charcoal when only 100 psig was used. Typical weight of the absorbent material used was either about 1 g or about 0.02 to 0.05 g in order to document total mass effect on rate of absorption of SF_6 and subsequent rate of loss. Both solid pieces and powders were examined to determine particle size effects. The initial mass of SF_6 loaded per unit mass of material was measured and, in the last two columns, the residual SF_6 loading at two different periods of time later gave an indication of how long and how much SF_6 would remain.

For the powdered materials listed, it was apparent that the residual SF_6 loadings very quickly (less than 1 month) were depleted to less than 1 mg/g. Since, as we stated earlier, loadings of 10 to 50 mg/g need to be maintained in order to have sufficient SF_6 for detection, powders that are open to the ambient can not be considered as efficient substrates for retaining the gas. This, of course, does not rule out the possibility of encapsulating the powder within a tube which could then be enclosed in a blasting cap by the manner shown in Figure 4-2. Activated carbon, which was capable of initially retaining very large quantities of SF_6 (~250 mg/g), might possibly be used in an encapsulated source as described later.

Of the solid polymers investigated, those that exceeded the minimum loading requirement were the Teflon materials TFE (40 to 65 mg/g), FEP (50 to 70 mg/g), and PFA (63 mg/g) and polyethylene (11 mg/g). But, of those, only the Teflon materials still retained adequate amounts of SF_6 at the end of one month. Polyethylene very quickly lost the SF_6. The other Teflon materials - CTFE, E-CTFE, and ETFE - did not initially absorb sufficient SF_6. The gray rubber material, which was of the type used by DuPont as end plugs in their blasting caps, experienced significant weight changes during evacuation prior to impregnation with SF_6. Measurement of desorbing SF_6 by electron capture gc showed little to be present. Silicone rubber behaved similarly.

C. Detailed Study of Various Teflon Materials

Since Teflon appeared to be the best absorbent for SF_6, a more detailed study was initiated to determine the most favorable type for maximum loading of SF_6 and longest retention of SF_6. Small pieces (0.01 to 0.05 g) were used so that the loss of SF_6 with time could be more rapidly ascertained.

As shown in Table 4-2, two sets (1-7 and 9-15) of samples were evacuated and impregnated with SF_6 at 100°C. The other 3 sets were loaded at room temperature. The weight of residual SF_6 absorbed(W) was followed with time by electrobalance weight measurements and the SF_6 desorption rate was determined by electron capture gas chromatography. From the initial SF_6 loadings (W at day 0), it was apparent that the CTFE and E-CTFE types did not absorb sufficient SF_6 to meet the minimum requirement of 10 mg/g. Further proof of the deficiency of those two types was indicated by the very low SF_6 desorption rates (R near day 40) compared to those of most of the other types.

Of the remaining samples, the TFE (types 1 and 2), the PFA and the FEP had higher initial loadings when impregnated at room temperature versus 100°C, but the ETFE type had its highest loading when impregnated at 100°C. The FEP Teflon achieved the highest initial loading of all types investigated showing an increasing absorbed weight with loading time at a loading temperature of 25°C - 60.0 mg/g in 18 hours; 71.6 mg/g in 117 hours; and 74.3 mg/g in 166 hours.

Considering, first, the data obtained from samples loaded at 25°C, it was apparent from the residual SF_6 concentration in the Teflon pieces (W) that the FEP type consistently maintained a higher value with time than the other pieces - at least twice that of the next best material, PFA. The TFE types 1 and 2 were about even as the next best and the ETFE material appeared to be significantly inferior.

Examination of the SF_6 desorption rates (R) at different times after initial loading substantiated the trends determined from the weight loss measurements. In order to more quantitatively display the differences between the several Teflon materials, the SF_6 desorption rates were first normalized to uniform piece weights of 0.016 g. Since the size of pieces that eventually would be used in blasting caps might be as much as 0.5 grams in weight and that the surface area of such larger pieces is about an order of magnitude greater than that of the smaller pieces, the normalized rate was then multiplied by a factor of 10. Finally, since a larger piece of Teflon had been shown to lose SF_6 at a slower rate than a smaller piece, an empirically derived factor of time after loading raised to the four-tenths power was used as a final correction to obtain the estimated SF_6 desorption rates shown in Table 4-3. (Regardless of the corrections employed, the relative differences between the different Teflon types remains unaffected. The corrections were made to facilitate comparison in a later section with actual tests of pieces of the larger size).

The estimated SF_6 desorption rates were plotted as a function of time after loading as shown in Figure 4-3 for samples loaded to 100°C and in Figure 4-4 for those loaded at 25°C. Least-mean--square correlation coefficients were used to determine the extrapolated values for the desorption rates at 500 days and 3 years as shown in Table 4-4. The last two columns, in essence, are estimates of the desorption rates one might expect from pieces about one-half gram in size, originally fully impregnated with SF_6. From the results of samples loaded at 25°C, the advantage of FEP type Teflon was more apparent. The desorption rate curve for the FEP type was higher than that for the others and also had less of a decrease with time. Thus, it should be a prime candidate for further evaluation as an absorbent substrate for SF_6.

The data at 100°C followed a similar trend as that at 25° except for the ETFE type. The desorption rate for that material was nearly constant with time so that although its value in the first year was less than that from the other types, in later years it is predicted to have the highest rate. The nearly constant residual SF_6 absorbed weight (W) for ETFE sample no. 13 in Table 4-2 is further evidence for the low, but steady, SF_6 desorption rate.

D. Conclusions and Recommendations

Powdered absorbent material were found to be generally unsatisfactory as absorbents for SF_6 because the gas rapidly desorbed from the fine particles. Possibly in a confined source configuration there may be an application for the highly adsorbent activated charcoal that was evaluated.

Of the polymer materials investigated only Teflon types exhibited sufficient absorptive capacity for SF_6 as well as desorption rates low enough for the SF_6 to last for ten or more years but high enough to be detectable in a bomb sniffing scenario.

FEP type Teflon appeared to be the best of the fluorinated polymer types having had the highest capacity for SF_6 and the most ideal rate of desorption characteristics. There was an indication that ETFE type Teflon might have better desorption rate characteristics - sufficiently better to perhaps even compensate for the material's lower initial absorptive capacity.

Although preliminary results with the polymeric materials used as end plugs by two of the blasting cap manufacturers did not appear promising, new materials may be currently used and should be re-evaluated.

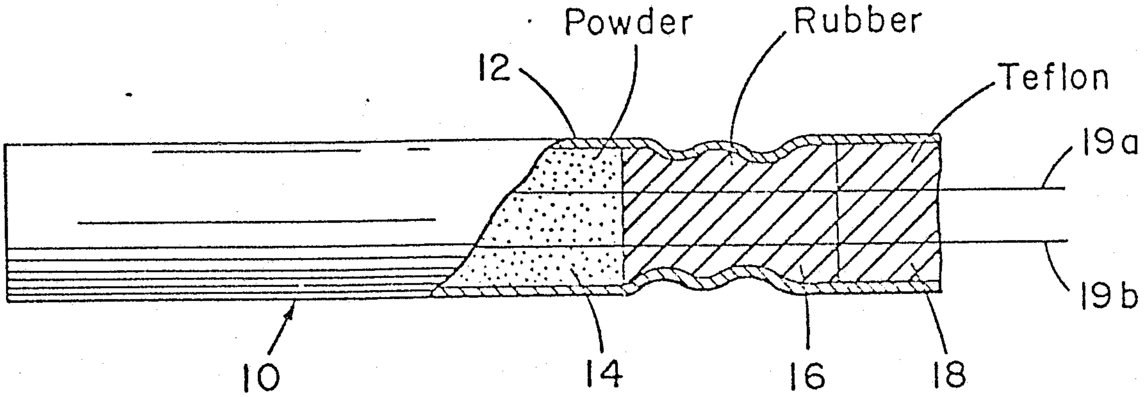

Figure 4-1.

Blasting Cap with SF_6--
Impregnated Teflon Disc Externally Mounted

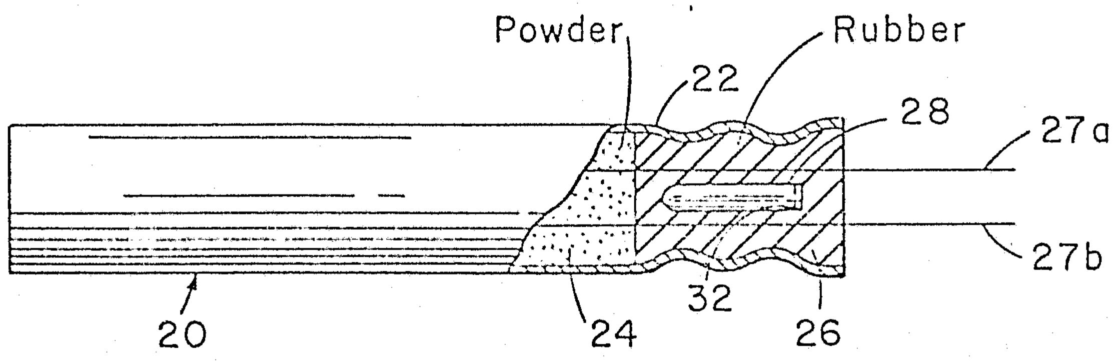

Figure 4-2.

Blasting Cap with SF_6 Encapsulated Source
or Impregnated Teflon Rod Integrally Contained

Figure 4-3.

Normalized SF_6 Desorption Rates for Several Teflon Materials Loaded at 100°C

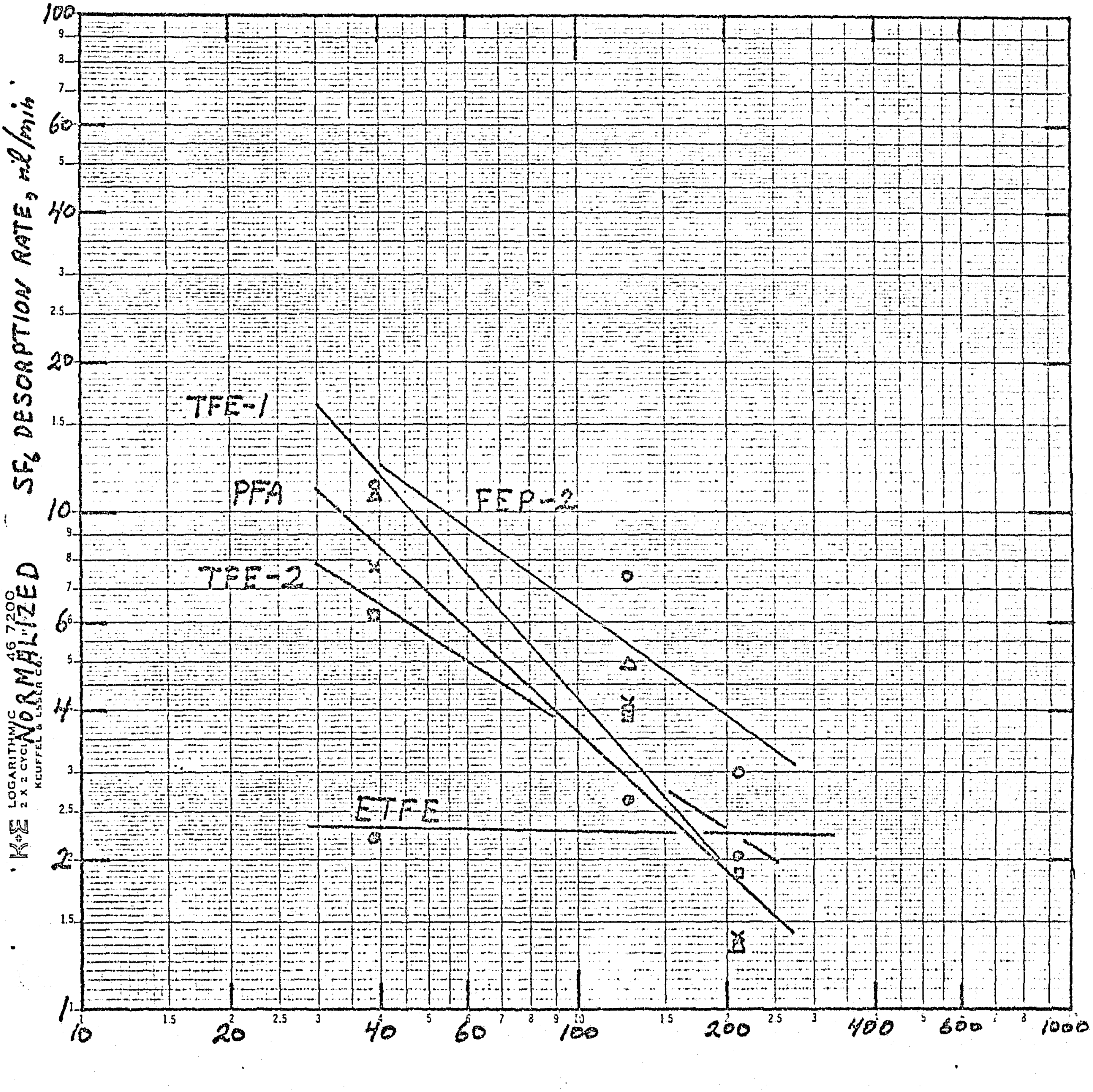

Figure 4-4.

Normalized SF_6 Desorption Rates for Several Teflon Materials Loaded at 25°C

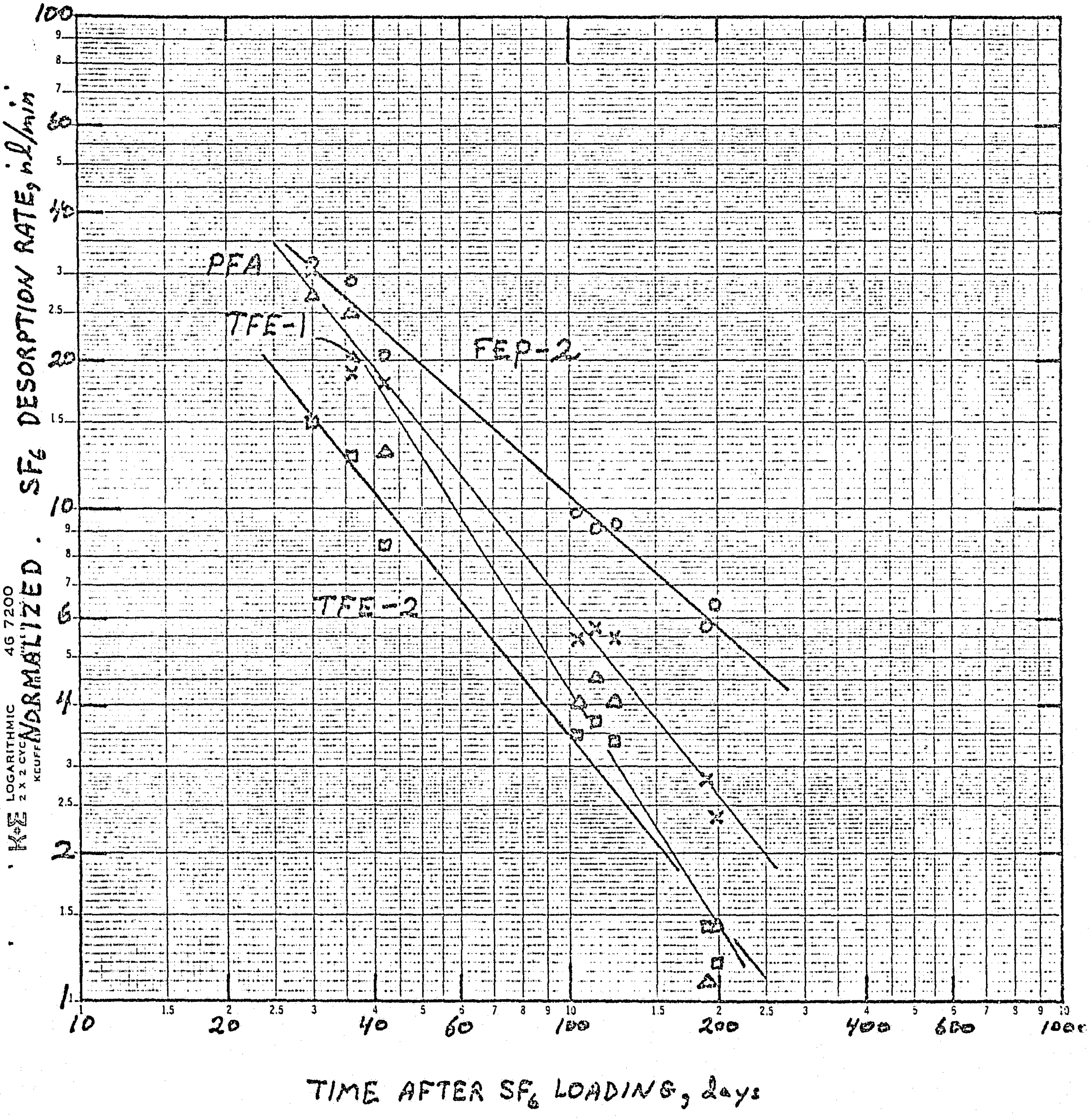

TABLE 4-1

MATERIALS SURVEY FOR ABSORPTION OF SULFUR HEXAFLUORIDE

Exposed to Vapor Phase SF$_6$ at 300 psig and Room Temperature

Material	Type	Wt, g	Load, Time, hrs.	Initial SF$_6$ Loading, mg/g	SF$_6$ Remaining, mg/g, at time (days) after loading	
SOLIDS						
TFE Teflon	1	0.909	65	63.0	37.4(3)	20.8(31)
FEP Teflon	1	0.896	65	48.8	29.0(3)	18.4(31)
polyvinylchloride		0.903	65	5.0	3.3(3)	0.4(31)
nylon		0.783	65	1.5	0.6(3)	<0.1(31)
polyethylene		0.571	65	10.7	0.7(3)	0.2(30)
CTFE Teflon		0.045	117	0.2	<0.1(8)	0.0(43)
E-CTFE Teflon		0.045	117	0.2	<0.1(8)	0.0(43)
PFA Teflon		0.017	117	62.8	17.4(8)	6.6(43)
TFE Teflon	1	0.020	117	64.3	16.2(8)	5.5(43)
ETFE Teflon		0.007	117	4.7	1.5(8)	<0.1(43)
TFE Teflon	2	0.016	117	38.1	10.1(8)	3.9(43)
FEP Teflon	2	0.014	117	71.6	25.9(8)	12.5(43)
gray buna rubber[b]		0.040	166	3.6	–	1.7(35)
silicone rubber		0.096	91	6.6	2.6(2)	3.0(46)
POWDERS						
polyethylene	1	1.208	73	13.7	2.3(4)	0.4(42)
Teflon 126		1.170	73	3.3	0.0(4)	0.0(42)
polyethylene (PE)	2	0.901	18	20.9	1.8(16)	0.0(23)
PE with 5% Teflon		0.897	18	7.8	0.0(16)	0.0(23)
PE with 15% Teflon		1.036	18	7.2	0.0(16)	0.0(23)
TFE Teflon		1.030	48	3.2	0.2(1)	0.1(4)
BK		0.044	52	58.1	1.8(5)	0.1(13)
activated carbon		0.055	2[a]	248	–	<0.1(30)

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[a] SF$_6$ pressure was 100 psig

[b] Sample of plug material used in DuPont blasting cap

TABLE 4-2

DETAILED SURVEY OF SF_6 ABSORPTION ON SOLID TEFLON PIECES

Loaded at 300 psig SF_6 at temperature
and time indicated below[a]

Sample No.	Teflon Material[e]	Initial Wt., g	W,[b] mg/g	R,[c] nl/min	W, mg/g	R, nl/min	W, mg/g	R, nl/min
		Day[d]:	0	41	61	132	212	216
1	CTFE	0.04409	2.16	0.005	0.07	–	1.00	–
2	E-CTFE	0.04403	1.75	0.007	1.73	–	1.95	–
3	PFA	0.01754	16.76	0.259	3.54	0.058	1.37	0.012
4	TFE-1	0.01887	18.60	0.308	3.44	0.063	1.54	–
5	ETFE	0.01170	10.08	0.032	8.29	0.024	7.44	–
6	TFE-2	0.01612	10.86	0.165	4.28	0.056	2.98	–
7	FEP-2	0.01433	18.35	0.259	6.56	0.095	2.51	–
		Day:	0	39	57	127	207	211
9	CTFE	0.04526	4.64	0.001	4.48	–	4.84	–
10	E-CTFE	0.03973	5.49	0.005	5.41	–	5.71	–
11	PFA	0.01748	12.87	0.196	2.75	0.065	0.80	0.018
12	TFE-1	0.02024	14.72	0.315	3.61	0.090	1.09	0.020
13	ETFE	0.01342	9.61	0.043	8.57	0.032	10.13	0.020
14	TFE-2	0.01596	9.27	0.143	4.39	0.056	2.82	0.022
15	FEP-2	0.01418	14.88	0.233	5.92	0.095	2.26	0.031

TABLE 4-2 (continued)

DETAILED SURVEY OF SF_6 ABSORPTION ON SOLID TEFLON PIECES

Loaded at 300 psig SF_6 at temperature
and time indicated below[a]

Sample No.	Teflon Material[e]	Initial Wt., g	W,[b] mg/g	R,[c] nl/min	W, mg/g	R, nl/min	W, mg/g	R, nl/min
		Day:	0	42	54	124	208	209
18	CTFE	0.04418	0.29	0.001	0	–	0.38	–
19	E-CTFE	0.03923	0.15	0.000	0	–	0.41	–
20	PFA	0.01729	64.95	0.438	5.26	0.086	1.50	0.019
21	TFE-1	0.01727	67.46	0.318	3.65	0.064	1.45	0.010
22	ETFE	0.00844	1.18	0.001	0	–	1.18	–
23	TFE-2	0.01552	33.83	0.185	3.03	0.048	1.55	0.010
24	FEP-2	0.01427	59.99	0.410	9.95	0.121	3.15	0.042
		Day:	0	36	71	113	197	198
27	CTFE	0.04456	0.20	0.010	0.27	–	0.22	–
28	E-CTFE	0.04544	0.22	0.010	0.24	–	0.59	–
29	PFA	0.01743	62.82	0.494	4.59	0.094	1.55	0.031
30	TFE-1	0.02037	64.31	0.760	3.78	0.087	0.98	0.022
31	ETFE	0.00737	4.75	0.028	1.08	–	0	–
32	TFE-2	0.01557	38.15	0.297	2.83	0.054	1.35	0.014
33	FEP-2	0.01435	71.57	0.619	9.34	0.123	3.34	0.069

TABLE 4-2 (continued)

DETAILED SURVEY OF SF_6 ABSORPTION ON SOLID TEFLON PIECES

Loaded at 300 psig SF_6 at temperature
and time indicated below[a]

Sample No.	Teflon[e] Material	Initial Wt., g	W,[b] mg/g	R,[c] nl/min	W, mg/g	R, nl/min	W, mg/g	R, nl/min
		Day:	0	30	62	104	189	190
36	CTFE	0.04846	0.14	0.025	0.14	–	0.08	–
37	E-CTFE	0.03928	0.13	0.009	0.28	–	0.28	–
38	PFA	0.01784	65.86	0.862	5.04	0.095	1.40	0.039
39	TFE-1	0.01683	66.49	0.734	3.33	0.067	1.19	0.014
40	ETFE	0.00571	5.25	0.024	0	–	0	–
41	TFE-2	0.01560	37.31	0.376	3.01	0.053	1.28	0.017
42	FEP-2	0.01430	74.27	0.724	10.21	0.137	3.36	0.063

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[a]

Sample No.	Temp., °C	Time, hours
1-7	100	21
9-15	100	64
18-24	25	18
27-33	25	117
36-42	25	166

[b] W is weight of absorbed SF_6 (mg) per unit weight (g) of Teflon

[c] R is the SF_6 desorption rate (nl/min) measured chromatographically

[d] Time elapsed (days) after SF_6 loading

[e] Teflon Material Symbols

CTFE:	poly (chlorotrifluoroethylene)
E-CTFE:	poly (ethylene-chlorotrifluoroethylene)
PFA:	poly (perfluoroalkoxy)
TFE:	poly (tetrafluoroethylene)
ETFE:	poly (ethylene-tetrafluoroethylene)
FEP:	poly (fluorinated ethylene-propylene)

TABLE 4-3

NORMALIZED[a] SF_6 DESORPTION RATES

Sample No.	Teflon Material	Estimated[b] SF_6 Desorption Rate for 0.5g Pieces, nl/min			Loading Temp. and time
	Day:	41	132	216	
3N	PFA	10.44	3.73	0.94	100°C 21 hours
4N	TFE-1	11.54	3.77	-	
5N	ETFE	1.93	2.31	-	
6N	TFE-2	7.23	3.92	-	
7N	FEP-2	12.77	7.48	-	
	Day:	39	127	211	
11N	PFA	7.77	4.13	1.40	100°C 64 hours
12N	TFE-1	10.78	4.94	1.35	
13N	ETFE	2.22	2.65	2.03	
14N	TFE-2	6.21	3.90	1.88	
15N	FEP-2	11.38	7.44	2.98	
	Day:	42	124	209	
20N	PFA	18.08	5.47	1.49	25°C 18 hours
21N	TFE-1	13.14	4.08	0.78	
22N	ETFE	0.08	-	-	
23N	TFE-2	8.51	3.40	0.87	
24N	FEP-2	20.50	9.33	3.99	
	Day:	36	113	198	
29N	PFA	19.01	5.72	2.36	25°C 117 hours
30N	TFE-1	25.03	4.53	1.43	
31N	ETFE	2.55	-	-	
32N	TFE-2	12.80	3.68	1.19	
33N	FEP-2	28.94	9.09	6.38	

TABLE 4-3(continued)

NORMALIZED[a] SF_6 DESORPTION RATES

Sample No.	Teflon Material	Estimated[b] SF_6 Desorption Rate for 0.5g Pieces, nl/min			Loading Temp. and time
	Day:	30	104	190	
38N	PFA	30.83	5.46	2.85	
39N	TFE-1	27.20	4.08	1 09	25°C
40N	ETFE	2.62	-	-	166 hours
41N	TFE-2	15.03	3.48	1.42	
42N	FEP-2	31.58	9.83	5.75	

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[a] Rate from all pieces normalized to uniform piece weight of 0.016g

[b] Rate from normalized weights multiplied by $10(\text{Days})^{0.4}$ - see text

TABLE 4-4

CORRELATION OF NORMALIZED SF_6 DESORPTION RATES

$$R^* = a\ t^{-b}$$

Teflon Material	Loading Temp. and time	a	b	Extrapolated R, nl/min	
				500 days	3 years
PFA		262	0.930	0.81	0.39
TFE-1	100°C	770	1.130	0.69	0.28
ETFE	64 hours	2.5	0.017	2.25	2.22
TFE-2		73	0.652	1.27	0.76
FEP-2		174	0.717	2.02	1.15
PFA		1900	1.243	0.84	0.32
TFE-1	25°C	6310	1.584	0.33	0.10
ETFE	18 to	-	-	-	-
TFE-2	166 hours	1030	1.236	0.48	0.18
FEP-2		620	0.882	2.58	1.29

V. USEFUL LIFE DETERMINATION STUDIES

Factors determining the length of time an SF_6 tagged polymeric source will be capable of being detected on a tagged blasting cap are, broadly, the detection scenario anticipated and the quality of the SF_6 absorbed source. This section deals primarily with the latter and, in particular, with the correlation of weight loss of SF_6 from three Teflon pieces as well as measurements of the rate of SF_6 desorption by electron capture gas chromatography.

The quality of the SF_6 absorbed source was also affected by such factors as the extent of initial loading as well as conditions of loading (temperature, pressure, time, etc.), and by conditions during the decay period including temperature and encapsulation - the latter which would directly affect surface area available for desorption.

The useful life studies described in this section were initiated nearly a year before the detailed studies of the various Teflon materials (described in Section IV-C). An early start was necessary in order to obtain reliable data for a sufficiently long period of time. Selection of TFE-1 material for these tests were made on the basis of early (less than 50 days) absorptive capacity and desorption rate tests. Obviously, as a result of the detailed survey tests, it is apparent that the least effective material was chosen. Thus, conclusions drawn in this section as to the useful life of SF_6 tagged Teflon sources should be regarded as being representative of the least possible results to be expected. The potential for significant improvement with several of the other Teflon types (especially FEP-2 and ETFE) appears to be almost certain.

A. Procedure

Approximately one-half gram pieces of TFE-1 Teflon were loaded with SF_6 at 300 psig for 81 hours. The pieces were pre-evacuated before loading for 20 hours (standard practice) and following impregnation the weights of the pieces were carefully monitored with time as were the measured rates of desorption by gas chromatography. Correlation between the two methods was performed over a time interval from about 150 days after loading to 550 days. Variation of the absorbed SF_6 loading as a function of time of exposure to SF_6 as well as rates of loss of SF_6 by exposure to temperature following loading was also investigated.

B. SF_6 Loading Dependence on Impregnation Time

The variation of the initial SF_6 loading on TFE-1 type Teflon pieces originally weighing between 0.5 to 0.8 g is shown in Figure 5-1. Even after 146 hours, it appeared that the 1/4-inch OD by 3/8-inch long Teflon pieces were not fully loaded to their ultimate equilibrium amount at the conditions used (300 psig SF_6 and room temperature). In order to verify the suspicion that SF_6 was not penetrating entirely through the Teflon, one piece was impregnated for 24 hours (sample 82R) and two pieces were impregnated for 72 hours (samples 71R and 81R). As shown in Table 5-1, along with each rod sample a wafer sample was also impregnated. From each rod sample, after SF_6 impregnation, a 30-mil (0.030-inch) thick slice was cut from the end and a 1/8-inch diameter piece was punched from the center of the slice (labeled EW - end wafer). A 30-mil slice was also cut from the center of each rod (cutting perpendicular to the axis of the rod sample) and a 1/8-inch diameter wafer also punched out from that slice (labeled CW - center wafer). Measurement of the SF_6 desorption rates by electron capture chromatography for each batch of samples was done at several different days following impregnation. For the samples loaded for 24 hours, the wafer sample cut from the center (87 CW) of the rod piece (82R) had one thousand times less SF_6 than the end wafer (86 EW) which had about two-thirds of the amount of the separately loaded wafer piece (85W). Thus in 24 hours only the outermost thickness of the Teflon rod was penetrated by the SF_6.

The 72 hour samples showed that the center cut wafers (74 CW and 80 CW) had an order of magnitude more SF_6 than the corresponding 24 hour CW sample but still two orders of magnitude less than the end cut wafers. However, the end cut wafers were nearly identically loaded with SF_6 when compared to the separately impregnated wafers. Thus, in 72 hours at least the outer 30 mils of Teflon reached saturation with the SF_6.

A more detailed SF_6 penetration test was performed with a 1/4-inch OD by 1/2-inch long TFE-1 Teflon rod exposed to SF_6 for 146 hours. Following impregnation the rod was cut in half (cut perpendicular to the axis) and a 1/8-inch diameter rod was punched from the center of one of the halves. The resulting section (1/8-inch OD by 1/4-inch long) was sliced into seven pieces having weights as shown in Table 5-2. Piece 91 was originally near the outer end of the rod and the remaining samples were numbered consecutively with approach to the center of the original rod. In order to more easily interpret the data, the measured SF_6 desorption rates were normalized by weighting according to the mass of the individual pieces. Clearly, the center pieces more nearly showed full SF_6 penetration than those from the 72 hour tests (Table 5-1) but still about a factor of three below the loading achieved by the outermost piece.

Thus the data in Figure 5-1 does really show that full penetration of a 1/4-inch OD Teflon piece was not achieved even in 146 hours of exposure to SF_6. More severe loading conditions such as exposure to liquified SF_6 at pneumatically elevated pressures of 2000 psig or more and tailoring of the loading temperature may significantly enhance the approach to full penetration as well as increase the equilibrium SF_6 loading.

C. Long Term SF_6 Desorption Studies

As indicated earlier, this series of tests was conducted with three TFE-1 Teflon pieces loaded with SF_6 by exposure at 300 psig and room temperature for 81 hours. The loss of SF_6 from these pieces was followed by electrobalance measurements. First attempts to correlate the rate of weight loss of SF_6 as a function of the residual absorbed SF_6 (see Figure 5-2) indicated that the best fit was obtained with third order dependence on W - the amount of remaining absorbed SF_6 (mg) per unit weight (g) of Teflon. The period of time covered was from 40 to 260 days following impregnation.

A more detailed evaluation of the data for the period of the 157th to the 548th day is presented in Table 5-3. The measured residual weight (W) of absorbed SF_6 was empirically correlated to the equation:

$$-\frac{dW}{dt} = kW^n.$$

where n was varied from 1 to 4 in increments of 0.5. The best fit was obtained with n equal to 3.5 as shown by the straight lines in Figure 5-3 obtained for the three pieces over a period of 400 days.

By least-mean-square analysis the rate constant for equation 1 in Table 5-3 was determined for each of the pieces. The calculated residual absorbed SF_6, obtained from the integrated form (equation 2), was found to agree very well with the measured values of W with an average relative precision of 0.4 to 0.7 per cent.

Equation 1, which represents the rate of desorption of SF_6 in mg of SF_6 per g of Teflon per day, was converted to equation 3 (in Table 5-3) to compute the SF_6 desorption rate in nl/min. The agreement between the measured rates and the calculated values was generally quite good with the measured SF_6 vapor phase concentration typically 30 to 40 percent higher than would be expected as computed from the weight loss correlation. The reason for the consistently higher measured values was not clear but the magnitude of the discrepancy was not considered to be significant. A second method for computing predicted SF_6 desorption rates was generated by plotting the measured SF_6 desorption rates versus days after loading as shown in Figure 5-4. Lease-mean-square analysis gave the rate equation shown in the figure.

D. Comparison of Predicted Desorption Rates

Using the measured SF_6 desorption rate correlation, values predicted at 500 days and 3 years were, respectively, 0.82 and 0.27 nl/min. Those predicted by the weight loss correlation for the same time periods were 0.54 and 0.17 nl/min. The extrapolated values at the same time periods for the TFE-1 type Teflon derived from the detailed survey experiment (see Table 4-4) were in relatively good agreement with the values predicted here. Having further substantiated the predictive capabilities employed in generating the data shown in Table 4-4, greater confidence can be placed on the predicted results for the ETFE and FEP-2 SF_6 desorption rates which were about an order of magnitude higher than the values for the TFE-1 Teflon.

A discussion of the still better expected performance of these Teflon pieces when encapsulated within the end of blasting caps will be reserved for the section on encapsulated sources. As much as another order of magnitude increase in useful life is anticipated by encapsulation.

E. Effect of Storage Condition on SF_6 Retention

An evaluation of the effects of temperature and pressure on the retention of SF_6 was conducted with FEP-3 type Teflon (previously unused) which had been loaded at room temperature and 300 psig SF_6 for 96 hours. The results with eight test pieces are shown in Table 5-4. Initial loadings ranged from only 22 to 37 mg/g which was less than half that of FEP-2, PFA, and TFE-1 type Teflons. Following impregnation the pieces were immediately stored, in groups of two, at the conditions indicated in the table.

At 40 days after impregnation the pieces were removed from their respective storage conditions, the SF_6 desorption rates were measured, and the pieces were thereafter all stored at room temperature and pressure. The differences between pieces stored under vacuum and those left at ambient pressure showed only a slight effect of vacuum at $75^{\circ}F$ on residual SF_6 desorption rates (compare samples 50 and 51 with samples 56 and 57) and no effect of vacuum at $140^{\circ}F$ (compare samples 52 and 53 with samples 54 and 55).

However, maintaining the samples at 140°F versus 75°F did have a significant effect on residual desorption rate. The decrease by a factor of thirty in just 40 days was equated to an equivalent storage time at room temperature by using the results for FEP-2 Teflon sample no. 42 in Table 4-2. Extrapolating the data for sample 42, an age of 1 1/2 to 2 years at room temperature was found to be equivalent to 40 days at 140°F.

As will be shown in the next section, sufficient SF_6 was present on Teflon pieces to be effective for 5 to 10 years or more, depending on the detection scenario employed. Thus a loss of SF_6 equivalent to 2 years was not considered significant. Also, it would seem to be unlikely that blasting caps would be stored for any considerable period at 140°F. Conversely, of course, storage at refrigerated temperatures would also extend the life of the taggant gas.

Detailed tests of the effects of storage temperature on the other types of Teflon material must be conducted. Based on the detailed survey results described in Section IV-C, it is anticipated that ETFE type Teflon should show much superior storage temperature characteristics. In addition, once encapsulated in the end or blasting caps, the rate of loss of SF_6 at higher temperatures should be significantly reduced.

F. Conclusions and Recommendations

Loading one-half gram pieces of TFE-1 Teflon pieces at room temperature and 300 psig did not accomplish full penetration even after 146 hours. The ultimate initial SF_6 loading would appear to be 80 to 100 mg SF_6 per g of Teflon - i.e., 8 to 10 percent by weight of the polymer. Further tests to increase the rate of loading as well as the ultimate absorbed concentration should be conducted. Variables investigated should include pretreatment modifications and conditions of temperature and pressure during loading.

The long term desorption studies performed with the TFE-1 type Teflon was well correlated both by weight loss measurements and SF_6 desorption rate determinations over a period from about 150 to 550 days. The measured desorption rates agreed well with those predicted from the shorter term survey experiments. Long term tests of a selected few other Teflon types should be initiated.

Loss of SF_6 after loading (from FEP-3 type Telfon) was not accelerated by evacuation but the rate of loss was increased by baking at elevated temperatures. Residual SF_6 response after baking at 140°F for 40 days was equivalent to a 1-1/2 to 2 year old piece maintained at room temperature, i.e., still adequate for detection. More detailed thermal loss response curves should be generated for a number of the Teflon types.

Figure 5-1. Effect of Impregnation Time on Initial SF_6 Loading

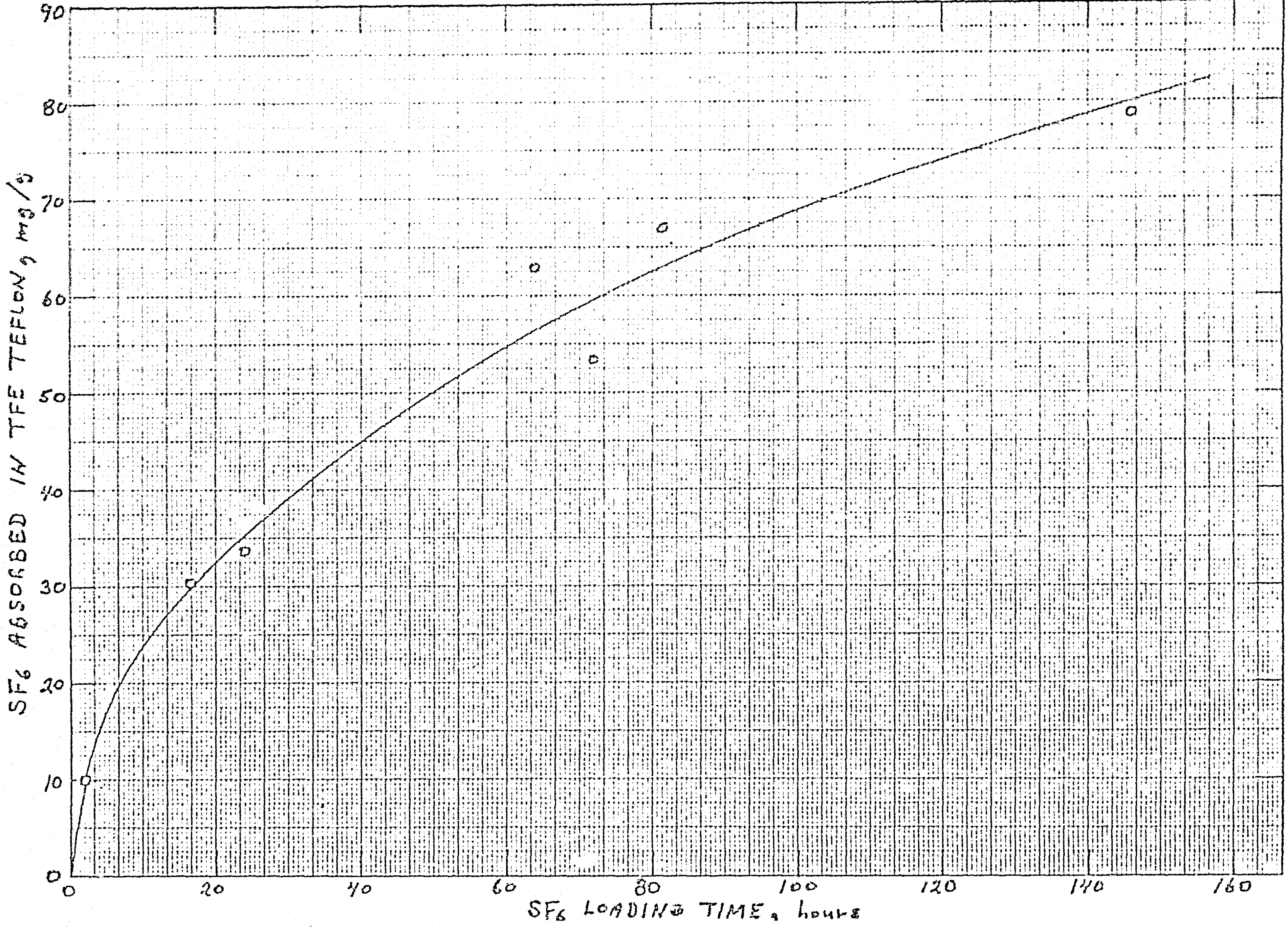


Figure 5-2. Rate Dependence of SF_6 Desorption on Residual SF_6

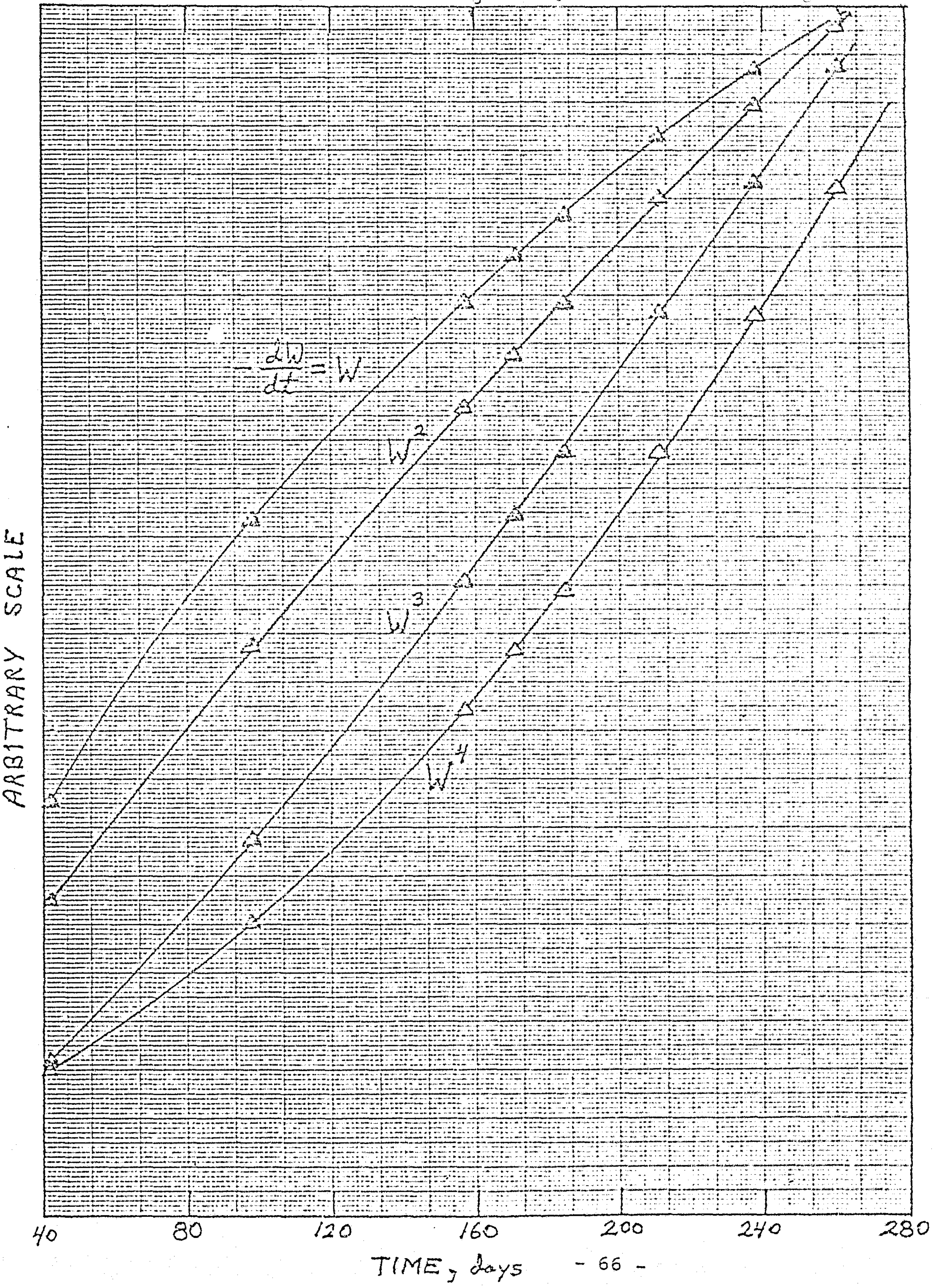
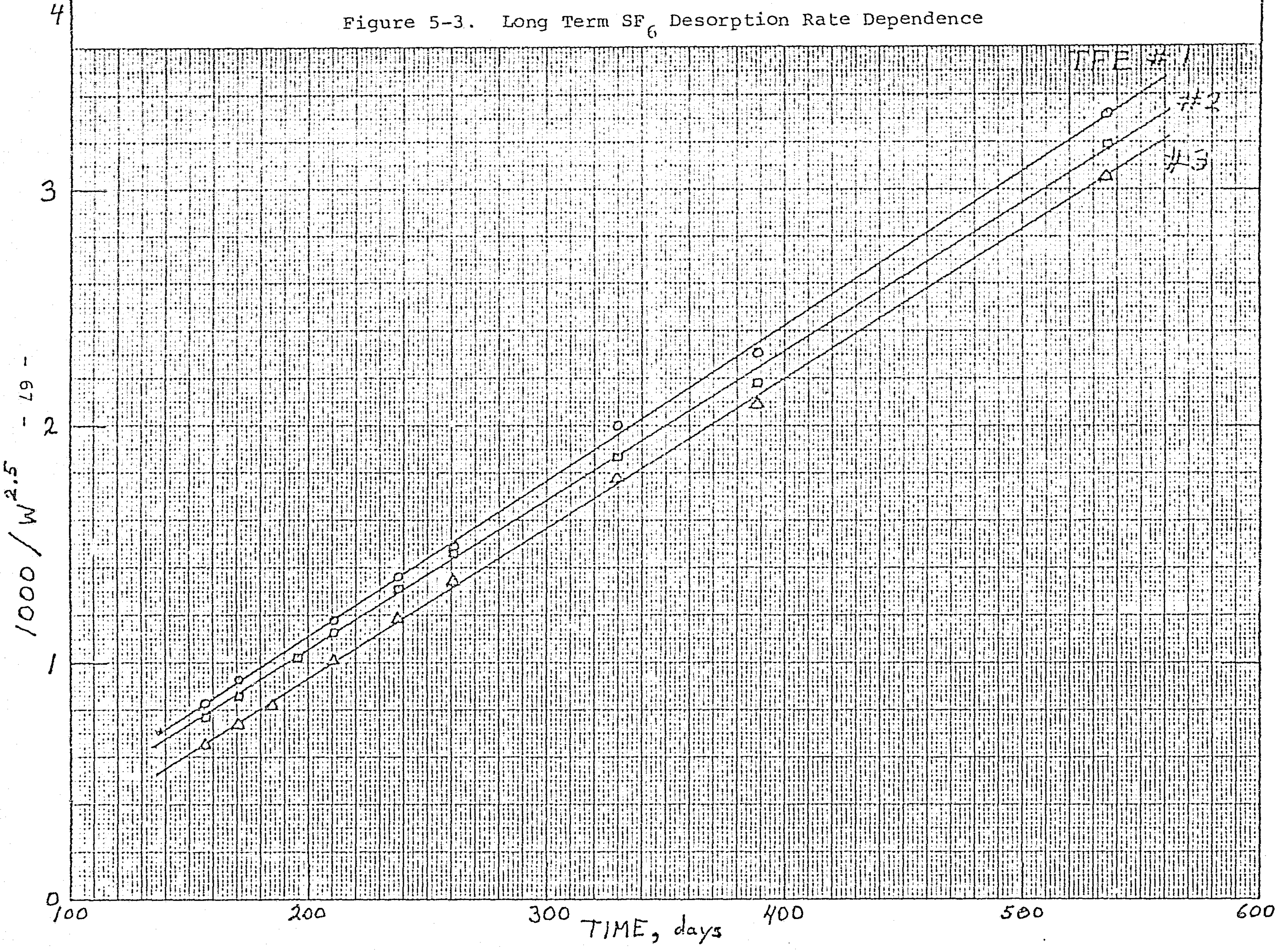


Figure 5-3. Long Term SF_6 Desorption Rate Dependence



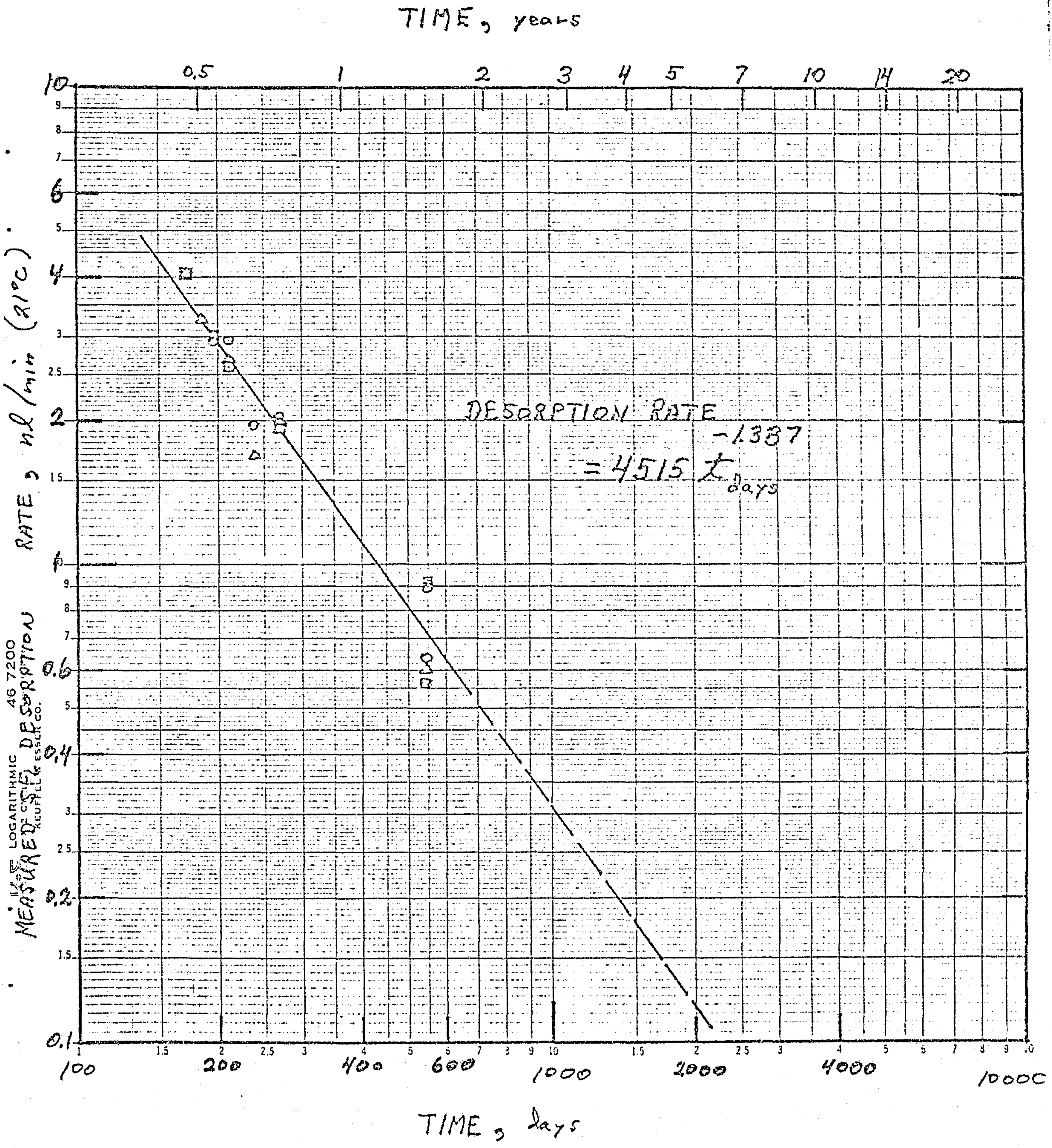


Figure 5-4. Correlation of Measured SF_6 Desorption Rates

TABLE 5-1

SULFUR HEXAFLUORIDE PENETRATION DURING LOADING

TFE-1 Teflon, Rod (1/4-in. OD x 1/2-in.),
Wafer (1/8-in. OD x 0.03 in.)

Loaded at 300 psig and room temperature

Sample No.[a]	Load time, hours	Sample Weight, mg Before SF_6	Sample Weight, mg After SF_6	SF_6 Desorption Rate, nl/min		
			Day:	0	11	
82R	24	567.8	586.9			
85W		23.14	24.86	100.9	1.91	
86EW		-	25.03	65.4	0.55	
87CW		-	19.44	0.045	<0.002	
			Day:	0	1	21
71R	72	794.0	-			
72W		21.22	22.88	68.6	23.1	0.62
73EW		-	17.70	58.4	19.0	0.69
74CW		-	16.90	0.64	0.18	0.066
			Day:	0	1	14
81R	72	598.3	630.3			
78W		22.28	23.79	100.4	31.1	1.42
79EW		-	19.18	99.3	27.4	0.97
80CW		-	20.98	0.28	0.17	<0.002

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[a] R means rod sample, W means wafer sample, and EW and CW mean, respectively, end wafers and center wafers cut from the rod sample of the particular batch.

TABLE 5-2

DETAILED SF_6 PENETRATION TEST

Starting Material: TFE-1 Teflon Rod (1/4-in. OD x 1/2-in. long)
Loaded at room temperature and 300 psig SF_6 for 140 hours
Material Weight Before: 720.5 mg, After: 777.2 mg

Sample[a] No.	Sample[b] Weight, mg	Normalized[c] SF_6 Desorption Rate, nl/min.	
	Day:	0	1
91	9.528	52.1	11.8
92	7.770	47.6	7.1
93	7.642	49.1	6.4
94	4.222	44.2	5.2
95	8.647	44.9	7.4
96	11.351	28.7	6.4
97	11.827	21.9	4.2

---

[a] Slices cut from the solid Teflon rod; sample no. 91 was from the end and sample no. 97 from near the center (see text).

[b] Weights include absorbed SF_6

[c] Normalized on the basis of sample weight

TABLE 5-3

SULFUR HEXAFLUORIDE WEIGHT LOSS CORRELATION

Eq. 1: $\frac{-dW}{dt} = k\ W^{3.5}$; Eq. 2: $\frac{1}{W^{2.5}} = 2.5\ kt + i$; Eq. 3: $R = 116.5\ mkW^{3.5}$

Teflon Piece No.	Time, days	Weight (W) of Absorbed SF_6 mg/g Teflon		SF_6 Desorption Rate (R), nl/min	
		Measured	Calculated[a]	Measured[b]	Calculated[c]
1	157	17.085	17.078		
	171	16.321	16.377	4.057	2.985
$k = 2.62$	196		15.340	2.915	2.374
$\times 10^{-6}$	211	14.846	14.817	2.949	2.103
	238	13.995	14.014	1.951	1.730
$i = -1.987$	261	13.508	13.437		
$\times 10^{-4}$	269		13.255	2.050	1.424
	330	12.003	12.102		
m = 0.5502g	389	11.338	11.262		
	536	9.806	9.817		
	543		9.763	0.636	0.488
	548		9.725	0.891	0.482
		av.S.D. =	±0.056		
2	157	16.732	16.644		
	171	16.120	16.026	4.106	2.563
$k = 2.51$	196	15.118	15.095	2.992	2.078
$\times 10^{-6}$	211	14.585	14.620	2.595	1.858
	238	13.786	13.881	1.924	1.550
$i = -1.004$	261	13.157	13.344		
$\times 10^{-4}$	269		13.174	1.917	1.291
	330	12.087	12.083		
m = 0.5319g	389	11.395	11.279		
	536	9.844	9.875		
	543		9.823	0.564	0.462
	548		9.786	0.907	0.456
		av.S.D. =	±0.092		

TABLE 5-3 (continued)

SULFUR HEXAFLUORIDE WEIGHT LOSS CORRELATION

Eq. 1: $\frac{-dW}{dt} = k\ W^{3.5}$; Eq. 2: $\frac{1}{W^{2.5}} = 2.5\ kt + i$; Eq. 3: $R = 116.5\ mkW^{3.5}$

Teflon Piece No.	Time, days	Weight (W) of Absorbed SF_6 mg/g Teflon		SF_6 Desorption Rate (R), nl/min	
		Measured	Calculated[a]	Measured[b]	Calculated[c]
3	157	16.859	16.796		
	171	16.239	16.154	4.031	2.725
$k = 2.53$	185	15.711	15.590	3.277	2.406
$\times 10^{-6}$	211	14.697	14.703	2.648	1.960
	238	13.905	13.944	1.689	1.628
$i = -1.281$	261	13.300	13.395		
$\times 10^{-4}$	269		13.221	2.035	1.352
	330	12.063	12.111		
$m = 0.5457g$	389	11.367	11.295		
	536	9.883	9.876		
	543		9.823	0.602	0.478
	548		9.786	0.914	0.472
			av.S.D. = ±0.070		

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[a] Calculated from least-mean-square fit of equation 2 above.

[b] Computed from measured SF_6 concentration in air flowing over piece.

[c] Calculated from desorption rate equation 3 above.

TABLE 5-4

EFFECT OF TEMPERATURE AND VACUUM FOLLOWING SF_6 IMPREGNATION

FEP-3 pieces loaded at room temperature and
300 psig SF_6 for 96 hours

Sample No.	Sample Weight, g	Initial SF_6 Loading (W), mg/g	Storage[a] Conditions Temp °F	Storage[a] Conditions Pressure	SF_6 Desorption Rate, nl/min. Day: 40	SF_6 Desorption Rate, nl/min. Day: 70
50	0.13081	31.1	75	1 atm	1.88	1.13
51	0.13387	29.3	75	1 atm	2.16	1.08
52	0.12983	27.9	140	vacuum	0.068	0.032
53	0.13168	37.2	140	vacuum	0.066	0.024
54	0.13029	26.9	140	1 atm	0.053	0.024
55	0.13559	21.7	140	1 atm	0.031	0.021
56	0.13190	26.1	75	vacuum	1.50	0.84
57	0.13020	33.0	75	vacuum	1.38	0.91

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[a] Samples stored at conditions indicated until 40 days following impregnation and thereafter at ambient conditions

VI. ENCAPSULATED SF_6 SOURCE DEVELOPMENT

The absorbed SF_6 - Teflon source pieces described in the previous sections have two limitations - the amount of SF_6 that can be experimentally absorbed (about 80 to 100 mg SF_6 per g Teflon) and the exponentially decreasing desorption rate with time which limits the useful life. Rather than using SF_6 impregnated Teflon sources, a small tube, closed at one end, filled with liquified SF_6, and plugged with the proper polymeric material would release SF_6 at a constant rate over the lifetime of the liquid SF_6 in the tube. With inside dimensions of 1/16-inch ID by 3/8-inch long, about 35 mg of SF_6 could be contained. At a release rate of 1 ng per minute (more than adequate for suitcase sniffing for bombs), such a source would last for more than 60 years. A source of this type was shown schematically contained within the plug material of a blasting cap (see Figure 4-2).

A. Liquid SF_6 Permeation Sources

Stainless steel tubing, 1/16-inch outside diameter, was plugged at one end with a polymeric material and attached at the other end to an SF_6 source for evaluation of rates of permeation using the electron capture gas chromatographic method. Polymeric materials studied included natural rubber, TFE Teflon (type 1), and silicone rubber. The material tested was usually cut from sheet stock by a 1/16-in. diameter punch, inserted into the tubing, and secured by crimping with a hand-tool or by reducing the outside diameter with a wire drawing machine thereby squeezing the rubber closure.

The permeation rates from some of the test pieces are shown in Table 6-1. For the natural rubber and Teflon materials, the permeation rates were about an order of magnitude below the desired level of 0.2 nℓ/min (~ lng/min) and for the silicone rubber, about an order of magnitude too high (the SF_6 would only last about 2 years) with the crimping method. By switching to the drawing method of securing the rubber, the rates could be tailored to the desired level. Decreasing the diameter and increasing the length reduced the permeation rate.

B. Comparison of Potential SF_6 Source Configurations

Considering a Teflon rod 1/8-inch OD by 1/2-inch long (which could be retained in a blasting cap plug), SF_6 could be contained within the overall dimension by absorption to a level of about 90 mg/g Teflon. From the size given, the total volume (0.100 cm^3) is equivalent to a weight of 183 mg (density of TFE Teflon is 1.83 g/cm^3). Thus the total initial weight of dissolved SF_6 would be about 16.5 mg SF_6.

If a portion of the Teflon rod (1/16-inch diameter by 3/8-inch long) were removed from the inside and replaced by liquid sulfur hexafluoride, the volume of Teflon removed (0.019 cm^3) could contain 35.5 mg of liquid SF_6 in its place (density of liquid SF_6 is 1.88 g/cm^3) - about 10 times that which can be contained in an equal volume of Teflon. The pressure inside the Teflon source would be the vapor pressure of the liquid.

Since methods to seal the Teflon tubing source might be difficult and since permeation rates would possibly be too high, consideration was also given to a third method - filling with activated charcoal for adsorption of the SF_6. At 100 psig, for example, the amount of charcoal than can be packed into the tubing (8.6 mg) would retain 3.4 mg of adsorbed SF_6 - about comparable to that which would have been absorbed in the same volume of Teflon. In that pressure range the amount of adsorbed gas would not vary greatly with pressure. Thus the emission rate could be adjusted to the optimum value for sensitivity and lifetime.

C. Encapsulation of SF_6 Impregnated Teflon Rods

The rate of desorption of SF_6 from a piece of Teflon is related to the amount of SF_6 absorbed and the exposed surface area available for desorption. Reducing the surface area should reduce the SF_6 desorption rate.

Since the Teflon pieces that were discussed in Sections IV and V were shown to lose their absorbed SF_6 more rapidly at first

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1 OF 2

and then subsequently at a lower rate, encapsulation of the impregnated Teflon within a non-permeable elastomer would be very beneficial. The initial SF_6 desorption rate, which is normally 3 orders of magnitude greater than desired during the first 2 weeks after impregnation, would be substantially reduced by encapsulation. For example, the 1/8-inch Teflon rod described in Section B above has a total surface area of 1.4 cm^2 including the two ends and the cylindrical surface. Since one end has a surface area of 1/18 of the total, encapsulating the piece with only one end exposed should reduce the desorption rate by nearly the same ratio.

Subsequently, the residual SF_6 loading would remain higher than from a piece which was not encapsulated and the desorption rate would still remain adequate for some time after the rate from the open piece dropped to a value too low for probable detection. This is shown diagrammatically in Figure 6-1. At time T_a, just a few weeks after impregnation with SF_6, the rate of desorption of SF_6 would be much greater than that from the encapsulated piece (respective slopes at vertical line, T_a). Because of the more rapid loss of SF_6 from the open (non-encapsulated) Teflon rod, the residual absorbed SF_6 would quickly decrease to a level much below that of the encapsulated piece. Several years after impregnation, T_b, the desorption rate from the encapsulated source would remain significantly high whereas that from the open piece would become marginally acceptable.

The most probable method of incorporating the SF_6 impregnated Teflon rod into a blasting cap would be by enclosing it within a non-permeable elastomeric material in the end of the cap. All indications are that such a source should have a useful life significantly greater than that projected from previous tests with the open pieces.

D. Conclusions and Recommendations

Selection of the proper polymer material and dimensions for the permeation wafer of an encapsulated liquid SF_6 source would allow blasting caps to be tagged for tons of years with very high probability for detection. However, the cost of manufacturing an encapsulated source for retaining liquid SF_6 would probably be of a magnitude comparable to the cost of a blasting cap because of the difficulty of retaining the high vapor pressure of the SF_6. Should another taggant gas with a lower vapor pressure, for example, cyclic perfluorocarbon compounds, be more favorable than SF_6 (because of lower background concentrations), the encapsulated liquid source method may be more feasible.

For a given volume, much more SF_6 exists in the liquid state than can be absorbed into Teflon. Substantial amounts of

SF_6 can be absorbed on activated charcoal, which, if encapsulated within a permeable device, would provide for tailoring of emission rates to the desired levels.

Encapsulation of SF_6 impregnated Teflon rods in the end of blasting caps appears to be the most promising method of retaining the taggant gas. Detailed desorption rate studies on encapsulated sources should be initiated.

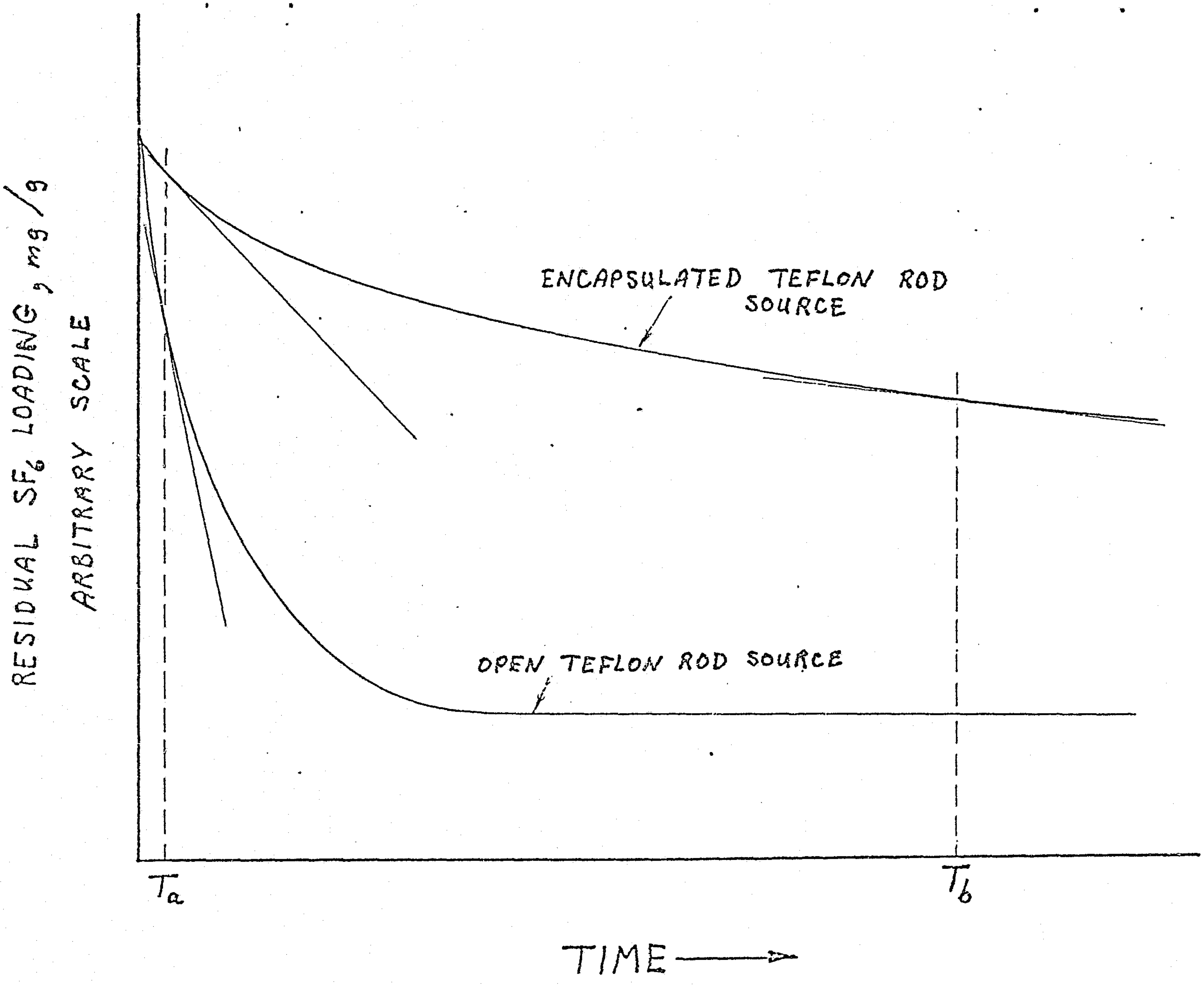

Figure 6-1. Simulation of Encapsulation Effect on SF_6 Desorption from Teflon

TABLE 6-1

PERMEATION SOURCE WAFER MATERIALS

Plugs swaged into 1/16-inch OD tubing

Material	Thickness, inches	Swaging Method[c]	SF_6 Pressure, psig	SF_6 Permeation Rate, $n\ell$/min
Natural Rubber	0.250	crimped	293	0.028
"	0.125	crimped	50	0.019
Teflon (TFE)	0.062	crimped	293	0.089
TFE[a]	0.062	crimped	295	0.037
SR[b] (red)	0.250	crimped	295	5.64
"	0.250	crimped	295	4.49
"	0.250	drawn (0.040-in.)	300	0.98
"	0.250	"	300	0.27
"	0.250	"	280	0.18
"	0.125	drawn (0.035-in.)	300	1.13

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[a] Second TFE piece had been pre-impregnated with SF_6 for 64 hours.

[b] Silicone rubber - different grades gave similar results

[c] Crimping was done with a hand tool; a wire reducing machine was used for drawn specimens.

VII. APPLICATION AND DEMONSTRATION OF DETECTION

Based on the correlations developed in the previous sections, the effectiveness of the use of SF_6 tagged blasting caps can be calculated for various detection scenarios including the sniffing of luggage on a conveyor belt at airport terminals, in baggage containers of the 747/DC-10 type, and in rooms suspected of containing a tagged bomb. The anticipated results indicated in this section would presumably be as much as an order of magnitude better if detailed correlation of the SF_6 desorption rates from encapsulated Teflon rod sources were available.

The type of response to be expected from sniffing at the seam of an attache case containing a tagged blasting cap was demonstrated using the semi-continuous SF_6 instrumentation developed at Brookhaven (discussed in the next section) and SF_6 tagged sources. A description of an approach to the sniffing of suitcases on a conveyor belt at airport terminals is also included in this section.

A. Predicted SF_6 Concentrations in an Attache Case

The concentration of SF_6 in an attache case containing an SF_6 tagged blasting cap is a function of the desorption rate from the SF_6 source, the volume of the case, the length of time the cap has been in the case, the rate of diffusion of SF_6-laden air out of the case, and whether or not an efficient barrier material has been placed around the source material. Since, in fact, most barrier materials were found not to be very effective (see Section III) and since diffusion out of the case might reduce the results by a factor of only two or three, these items will initially be neglected in predicting the SF_6 levels in the case.

A typical attache case has a volume of about 1.3×10^4 cm^3. Assuming that a tagged blasting cap, containing a 1/2-gram SF_6 impregnated Teflon rod, was placed in the case about 2 hours prior to attempts to detect the gas, the results anticipated are shown in Table 7-1. The SF_6 desorption rate, which is a function of the age of the tagged source, and, correspondingly, the concentration in the case, was computed from both the SF_6 weight loss correlation and the measured SF_6 desorption rate correlation.

First, it can be seen that the expected concentrations are nearly the same by either method of calculation. For a blasting cap one year old, the SF_6 concentration in the case would be about 10 ppb - that is, about 20,000 times ambient SF_6 levels (which is the limiting factor for detection of SF_6). As will be shown later, depending on the method of sniffing the case from outside, the extent of dilution would range from a factor of 25 (hand-held sniffing probe) to a factor of 1000 or so (automatic conveyor belt sniffing system). By either method, there is expected to be sufficient SF_6 for detection.

For a blasting cap 10 years old, based on the earlier correlations, an anticipated concentration of about 0.6 ppb (about 1,000 time ambient) would still give sufficient response by the hand-held sniffing approach but might not be enough for detection by the automatic on-line method. However, the SF_6 desorption rates for 10 year old encapsulated SF_6 sources (see Section VI-C) are expected to be significantly (as much as a factor of 10) higher and results from the detailed survey work with other Teflon substrate materials (see Section IV-C) indicated that further improvements using different materials are anticipated.

B. Predicted SF_6 Concentrations in Various Scenarios

In addition to detection of tagged blasting caps in attache cases, other areas where detection would be desirable might include aircraft luggage carriers of the type used on aircraft such as the 747 and DC-10, and special rooms where certain valuable or otherwise important materials were being stored. Table 7-2 shows some of the SF_6 concentrations that might be anticipated in these other configurations.

For the luggage carrier computations, it was assumed that the suitcase containing the bomb had contained the SF_6 tagged source for two hours prior to loading into the carrier and that 2 percent of the air in the case was expelled into the carrier by a pressurization-expansion technique. Compared to the concentration levels in the suitcase itself, those in the luggage carrier are substantially reduced. Since ambient levels of SF_6 range from 5 to 7 x 10^{-13} parts per part of air (see Section II), even a one-half year old tagged blasting cap would be only marginally detected by such a method. Even with the order of magnitude improvements anticipated by encapsulation and use of other substrates, detection of SF_6 tagged caps in this scenario is not expected to be good. Only by switching to another taggant compound (see Section IX) whose present ambient levels are two or more orders of magnitude lower can effective detection be accomplished in luggage carriers in reasonable time (< 5 minutes).

Detection of a tagged blasting cap in a moderate size room (10-ft x 20-ft x 8-ft high) is also limited by the background SF_6 levels. Assuming the suitcase or package containing the bomb had been situated in the room for 1 hour and that there was negligible ventilation of the room during that time, the detection capability would be adequate for a blasting cap as much as a year old. Since most rooms do have some exchange of air, actual results would probably be lower and, therefore, marginal. The same conclusion as in the paragraph above applies - only another taggant compound with lower background levels could be effectively used when cap age exceeds one year. Thus, only the scenario of sniffing luggage (by hand or automatically) holds promise of ready detection for periods of greater than 10 years when using SF_6 as the taggant gas.

C. Detection of SF_6 Tagged Sources in an Attache Case

The sensitivity of the Brookhaven semi-continuous SF_6 detector (which is described in more detail in Section VIII and in Reference 17) was demonstrated by analysis of ambient laboratory air as shown by the recorder scan in Figure 7-1. The approximate one division response of the recorder pen after the start of the SF_6 frontal corresponded to an SF_6 concentration of about 0.5 ppt (5×10^{-13} parts/part).

Two tests were conducted with SF_6 tagged sources in an attache case to determine the relative response to detection by an SF_6 sensor. The first of these sources, an approximately 2 1/2 year old blasting cap containing a Teflon rod, was the demonstration piece originally fabricated for visual indication of the method of incorporation of the impregnated material. At that time no attempt was made to optimize the SF_6 loading and detection tests 950 days later were not anticipated. However, the demonstration blasting cap was placed in an attache case, 2 hours-15 min later the SF_6 instrument was used to measure SF_6 concentration in the air diffusing from the seam of the case, and, as shown in Figure 7-2a, significant response to the taggant gas was indicated. The SF_6 monitor used for these tests had a continuous response capability to SF_6 of 90 seconds. The instrument sniffing probe (see Figure 7-3), which had a sampling rate of 5ℓ/min, was alternately run along the seam of the attache case for 15 seconds and then held several feet away from the case for 15 seconds. Even with the high dilution that probably occurred because of the high probe sampling rate, the right hand chromatogram of Figure 7-2 showed an average concentration of 23 ppt (about 40 times normal ambient) and real-time response of a few seconds during the sample cycling.

Ten minutes later the attache case was partially opened (enough to slip the instrument probe into the case) and an analysis of the air in the case was determined as shown by the left hand seam in Figure 7-2. From the amplitude of the response, a concentration of about 350 ppt was determined. The scan indicated that the probe was left in the case for 40 seconds, removed for 20 seconds, and then returned to the case.

A similar experiment was performed with Teflon piece no. 1 of Table 5-3, a piece whose desorption rate characteristics were better known. The testing, which was similar in procedure with the demo blasting cap, was performed when the Teflon piece had been in the attache case for 150 minutes. As shown in Figure 7-4, the response to sniffing outside the case was very pronounced giving an average concentration of 130 ppt - about 240 times ambient SF_6. In this case the concentration inside the case was measured at 2900 ppt.

The results of both tests are shown in Table 7-3 where a comparison with predicted levels in the attache case is made. For the Teflon no. 1 piece, the correlation of measured SF_6 desorption rates was used to calculate an SF_6 concentration in the attache case of 8810 ppt - about 3 times greater than the measured level of 2900 ppt. Thus, under normal conditions, two-thirds of the SF_6 being emitted from the taggant source would in turn be emitted from the luggage making detection by an automatic conveyor belt luggage sniffer a plausible method. The ratio of measured SF_6 inside the case to that outside indicates about a 20-fold dilution. Comparison of the predicted versus measured SF_6 levels in the attache case using the demo blasting cap was not as reliable because the desorption rate characteristics had not previously been determined.

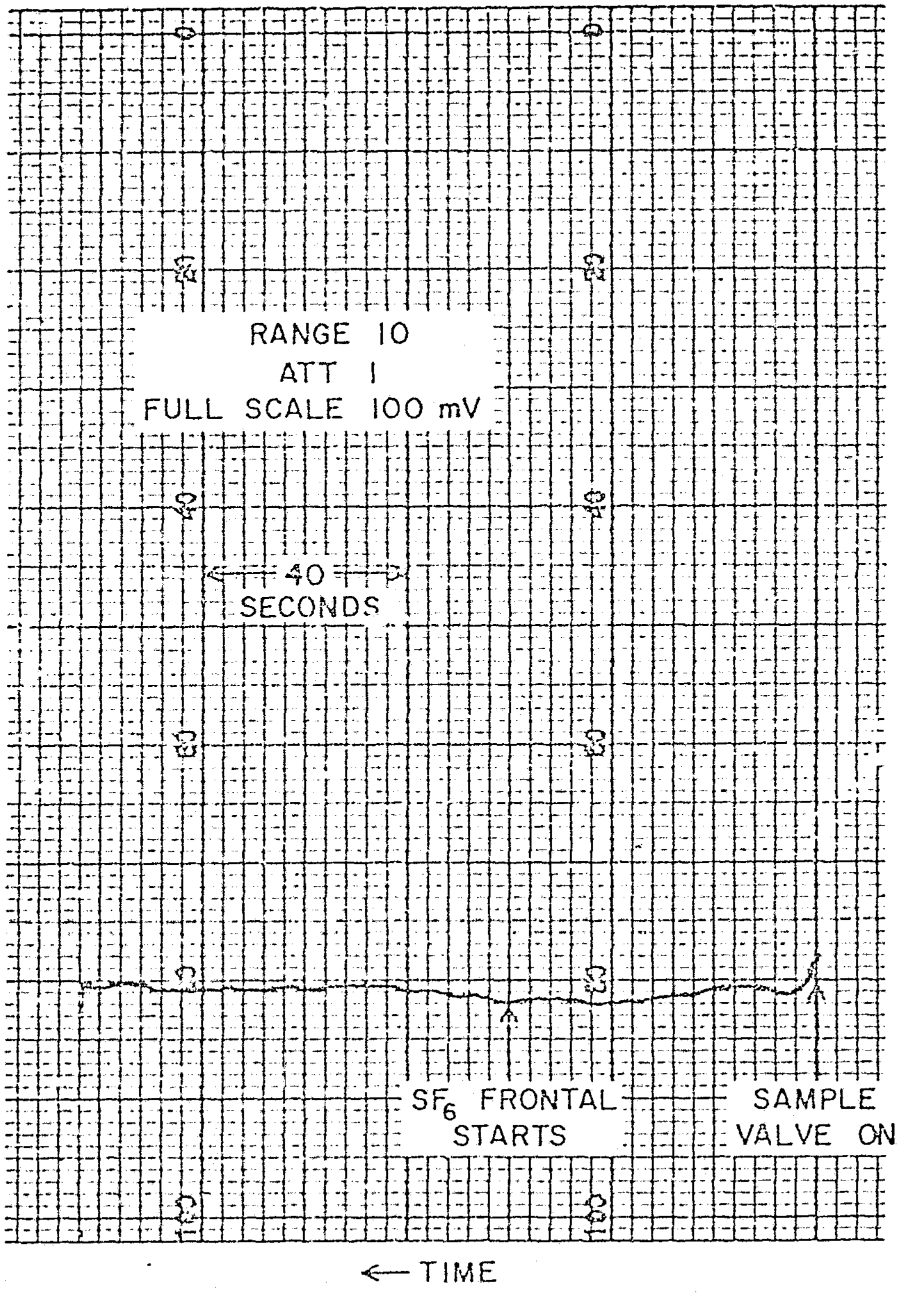
This test clearly showed three important points. First, about one third of the emitted SF_6 from the taggant source did remain in the attache case. Second, sniffing by the hand-held monitor gave only about a 20-fold dilution compared to the concentration in the case. And third, even a far from optimized taggant source with an age of 2 1/2 years could be adequately detected in the attache case by the hand sniffing method. Detailed tests of a similar nature using optimized SF_6 sources and monitoring instruments including effects of various barrier materials should be carried out in the next phase of this program. An effort to design, construct, and evaluate a Luggage Conveyor Belt Sniffer System must be started in order to determine and cope with the problems expected in an actual detection environment. Schematically, a system of the type shown in Figure 7-5 should provide the rapid detection capability (< 2 seconds) while minimizing dilution from ambient air.

D. Conclusions and Recommendations

For ten year old blasting caps (and older with improved SF_6 taggant sources), more than sufficient levels of SF_6 would exist in a suitcase or other package for rapid and significant response using a hand-held detecting instrument. Indications are that automatic on-line conveyor belt systems could be designed to adequately detect SF_6 tagged blasting caps in suitcases and packages. But detailed design and testing needs to be conducted to determine the extent of feasibility.

For other detection scenarios such as in luggage carriers, in rooms, and even in airplanes, the SF_6 taggant approach is at best only marginally satisfactory. In subsequent studies, tests with SF_6 should continue in order to document its predicted performance but, at the same time, effort should be made to evaluate other taggant gases whose background concentrations (which is the current limiting factor with SF_6) are one or two orders of magnitude lower.

Figure 7-1.



Real-Time Determination of Ambient SF_6 Concentration

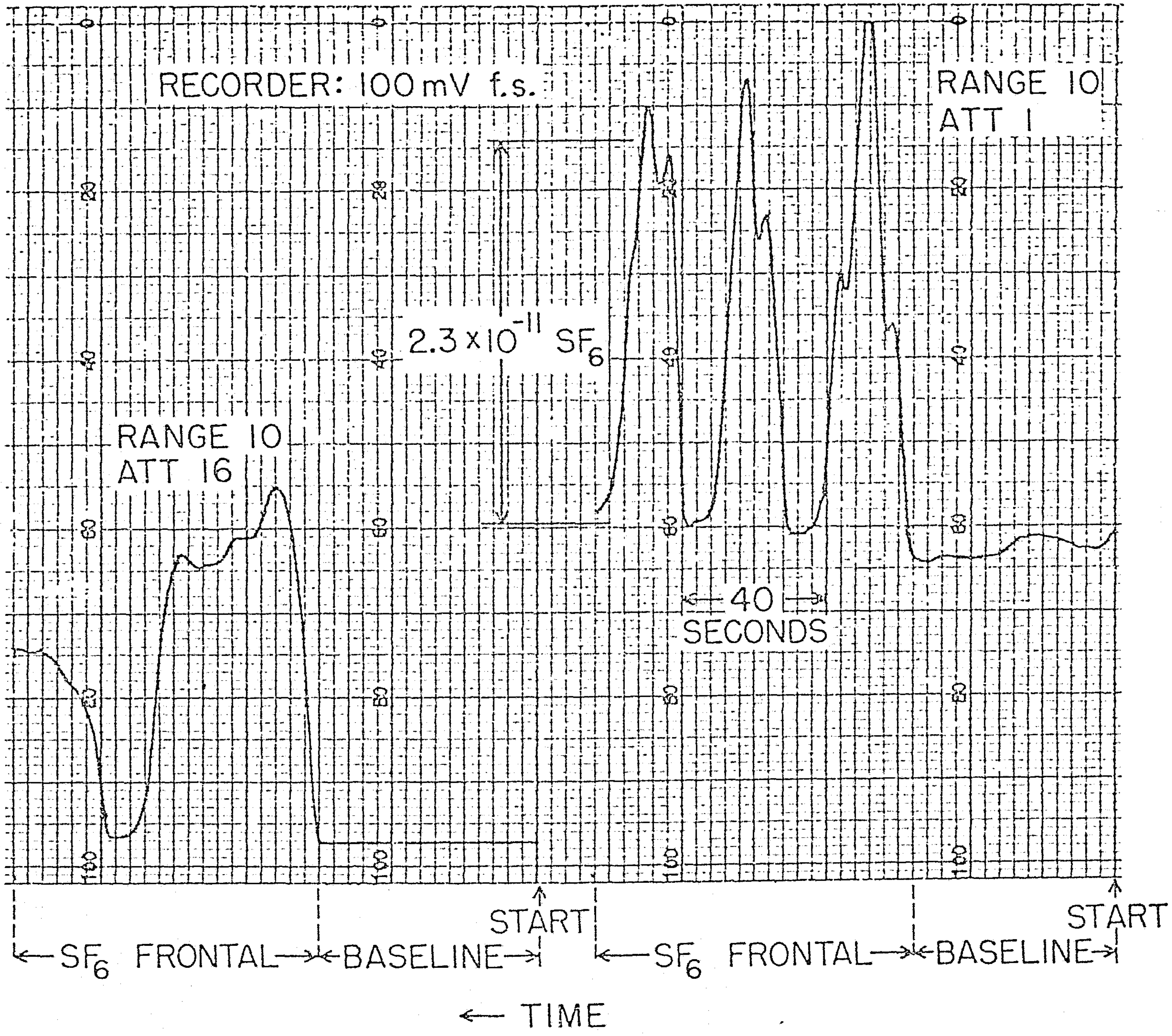
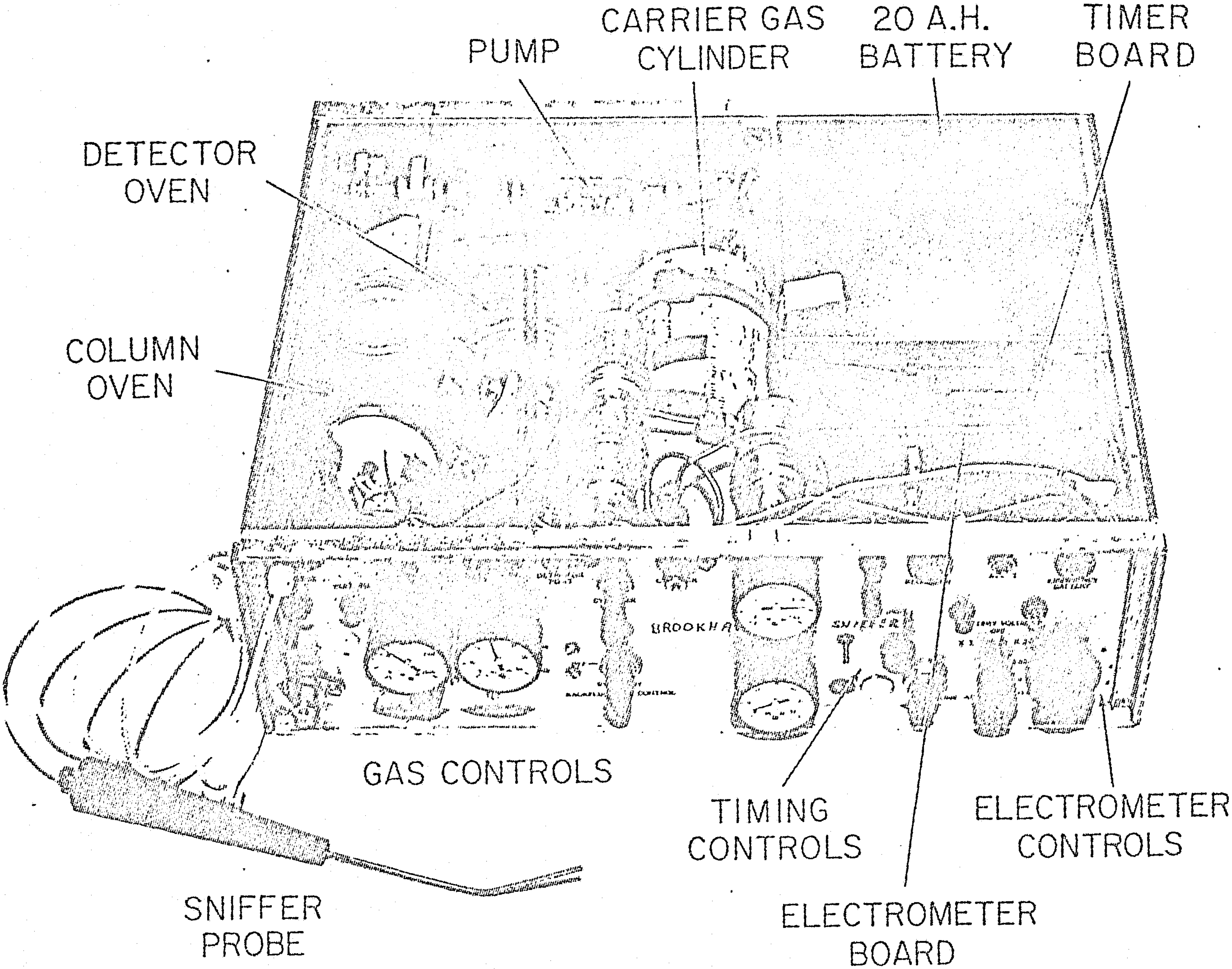


Figure 7-2. Detection of a 2 1/2 Year Old tagged Blasting Cap in an Attache Case

Figure 7-3. Brookhaven Real-Time SF_6 Instrument



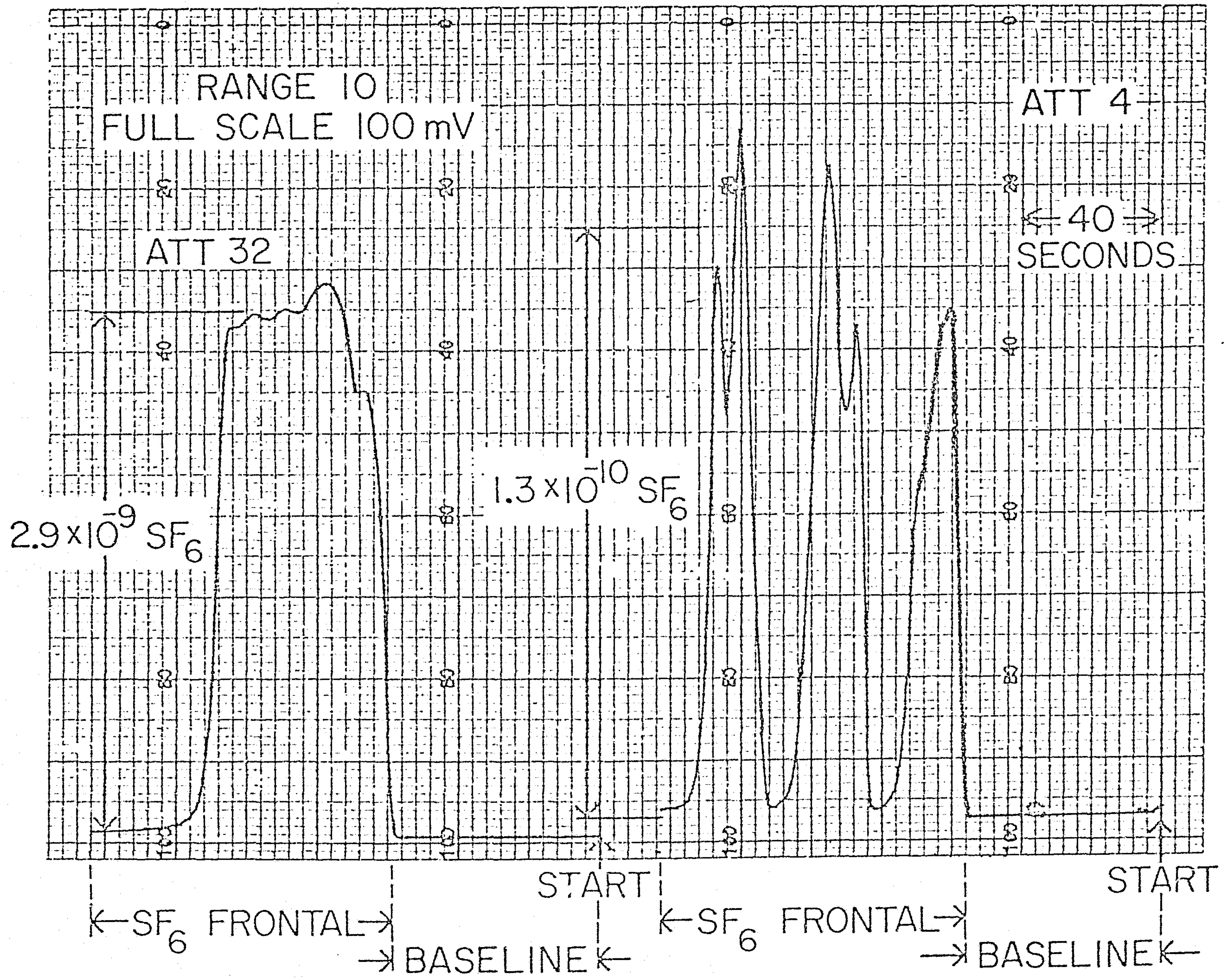


Figure 7-4. Detection of a 1 1/2 Year Old SF_6 Impregnated Teflon Rod in an Attache Case

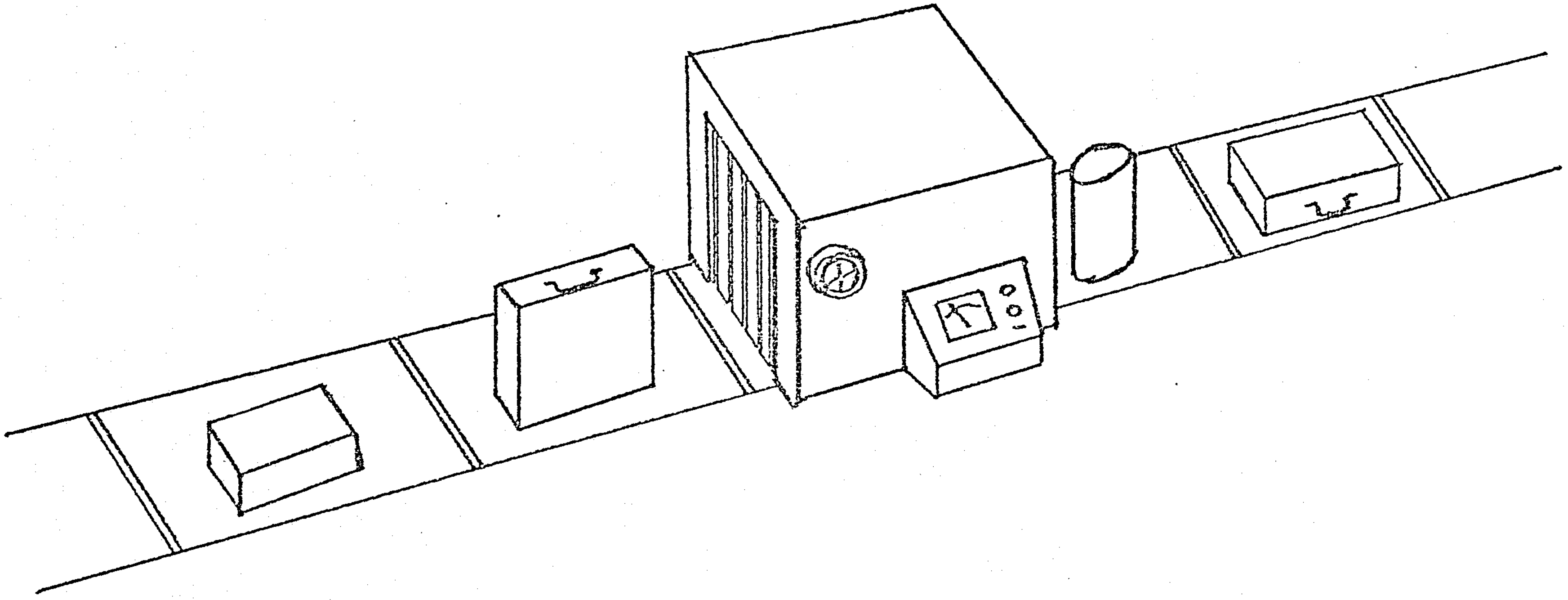


Figure 7-5. Conveyor Belt Suitcase Sniffing

TABLE 7-1

EXPECTED SF_6 CONCENTRATION IN ATTACHE CASE

Volume = 1.3×10^4 cm^3, time = 120 min., m = 0.5g, k = 2.55×10^{-6}

Cap Age years	W, mg/g	SF_6 Concentration, ppb	
		Wt. Correlation[a]	Conc. Correl.[b]
0.5	15.72	21.12	30.45
1	11.59	7.27	11.64
1.5	9.77	4.00	6.63
2	8.68	2.64	4.45
2.5	7.91	1.91	3.27
3	7.35	1.48	2.54
4	6.53	0.98	1.70
5	5.97	0.71	1.25
7	5.21	0.44	0.78
10	4.51	0.267	0.477
14	3.94	0.166	0.299

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[a] C_{SF_6}, ppb $= \dfrac{1.165 \times 10^5\ kW^{3.5}\ t_v\ m}{V}$; t_v(min), m(g), V(cm^3)

[b] C_{SF_6}, ppb $= \dfrac{R_d\ t_v\ 10^3}{V}$; $R_d = 4515\ t^{-1.387}$; t(days)

TABLE 7-2

EXPECTED SF_6 CONCENTRATION IN SEVERAL ENVIRONMENTS FROM TAGGED BLASTING CAPS

1/2 g TFE-1 Teflon Rod, $k = 2.55 \times 10^{-6}$

Cap Age, years	Absorbed SF_6 (W), mg/g	SF_6 Desorption Rate, nℓ/min	SF_6 Concentration, parts per part[a]			
			Attache Case[b]	Luggage Carrier[c]	Room[d]	
					1 hour	1 day
0.5	15.72	3.298	30.45×10^{-9}	12.37×10^{-13}	86.1×10^{-13}	20.6×10^{-11}
1	11.59	1.261	11.64	4.73	32.9	7.9
3	7.35	0.275	2.54	1.03	7.2	1.7
10	4.51	0.052	0.48	0.20	1.3	0.3
30	2.90	0.0112	0.10	0.04	0.29	0.07

---

[a] Based on desorption rates from correlation of Figure 5-4 and assuming tagged blasting cap 2 hours in attache case

[b] Volume of attache case, 1.3×10^{4} cm^3

[c] 5-ft x 5-ft x 9-ft (6.4×10^{6} cm^3) volume and assuming 2 percent of air in attache case enters carrier

[d] 10-ft x 10-ft x 8-ft (2.3×10^{7} cm^3) volume with tagged blasting cap in room for 1 hour and 1 day, respectively

TABLE 7-3

COMPARISON OF MEASURED AND PREDICTED SF_6 CONCENTRATIONS FROM SOURCES IN AN ATTACHE CASE

June 19, 1975

SF_6 Source	Source Age, days	Time in Case, min	SF_6 Concentration, ppt Inside Case Predicted[a]	SF_6 Concentration, ppt Inside Case Measured	SF_6 Concentration, ppt Outside Measured
Teflon	549	150			130
No. 1[b]		160	8810	2900	
Demo[c]	950	135			23
Cap		145	~3730	350	

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[a] Calculated from equations of note b, Table 7-1

[b] Piece no. 1 from Table 5-3

[c] Detailed nature of SF_6 loading uncertain as is predicted concentration inside case

VIII. SF_6 AND OTHER TAGGANT GAS DETECTORS

The critical component in the detection of SF_6 or any other electronegative compound by electron capture systems is the separation or removal of ambient oxygen from the gas to be detected. Since oxygen is also electronegative in character, instruments that do not separate or remove the oxygen are typically limited in sensitivity to SF_6 in the range of 3 to 5 x 10^{-9}. To our knowledge, the Brookhaven semi-continuous instrument is the only method whereby SF_6 can be continuously monitored for periods up to 3 1/2 minutes with a sensitivity of 5 x 10^{-13} - nearly four orders of magnitude improvement over other methods.

A review of some of the commercial instruments available, the monitoring techniques developed at Brookhaven, the concurrent improvements that are in progress, and a discussion of other instrumental approaches are included in this section.

A. Evaluation of Commercial SF_6 Detectors

Using an Aerospace Corporation report as a guide, the companies listed in Table 8-1 were contacted. In general, those detectors on the market which are continuous in operation have a sensitivity no better than 10^{-9} cm^3/cm^3. When operated in chromatographic fashion (i.e., injection of a discrete sample followed by separation from oxygen using a packed column) sensitivities to between 10^{-11} and 10^{-12} have been indicated. However, for successful implementation of the SF_6 taggant approach to the detection of blasting caps, a continuous SF_6 sniffer with a sensitivity of 4×10^{-13} cm^3/cm^3 at 3 times noise is needed. To our knowledge, there is no such instrument available in the market. New detectors and electronics designs have appeared on the market (for example, Analog Technology Corporation Model 140 wide range electron capture detector system) but no commercial gains have been made in continuous SF_6 detectors with high sensitivity.

B. Instrument Developments at Brookhaven

The capabilities and review of SF_6 detection methods developed at Brookhaven are discussed in detail elsewhere.(17)

Basically the Brookhaven semi-continuous SF_6 instrument (shown in Figure 7-3) consists of a 5A molecular sieve packed column through which the air being sampled is continuously pumped on its passage to the detector. The molecular sieve material slows the passage of oxygen and all other constituents in the air sample because of continual adsorption-desorption but does not affect the SF_6 (because its molecular size is too large to be adsorbed) which consequently reaches the detector first. The length of time that SF_6 is monitored continually before oxygen reaches the detector is dependent on factors such as column length, temperature, particle size of the molecular sieve, and flow rate through the column. Practical considerations limit the extent of continuous detection of SF_6 by this method (which achieves a sensitivity of 5×10^{-13} parts per part of air) to less than 5 minutes. Subsequently the instrument must be flushed of oxygen before another analysis mode can be initiated.

For continuous monitoring at, for example, an airport luggage conveyor belt system, in principle, three or four instruments could be operated serially (or perhaps 3 or 4 switching columns) to provide continuous detection capability. But that approach is not without problems and would significantly increase per unit installment costs.

Recent developments at Brookhaven including chemical oxygen removal scrubbers and Teflon membrane concentrators indicate that continuous monitoring of SF_6 with a limit of detection at 5×10^{-14} should be feasible and the analytical instrument would be reasonable in cost when manufactured at large scale production levels (about $3000 to $7000 depending on detection specifications of 5×10^{-13} to 5×10^{-14}, respectively).

C. Detection Methods for other Electonegative Compounds

As indicated earlier, the use of SF_6 as a taggant gas for detection of explosives is limited by the present background levels. Under development elsewhere are detection methods for continuously monitoring cyclic perfluorocarbon compounds whose present background levels are insignificant because of negligible use of the materials. By contrast, as much as seven to nine thousand tons of SF_6 are estimated to have been released to the ambient to date of which most is still in the air.

The techniques for detection of these compounds are currently being developed by J. Lovelock in England. Exact details of the methods are not yet available but basically one method consists of rapid trapping of the gas on a small amount of molecular sieve followed by desorption into an electron capture detector. Sensitivities in the order of a few parts in 10^{15} parts of air should be possible but response time may be too slow - tens of seconds. The other method, a continuous detection technique, is based on catalytic conversion of oxygen in the air being sampled to form water (which is continuously removed) as well as conversion and removal of all other interfering electronegative compounds. Response time of the method is probably quite good (< 2 seconds) but the limit of detection is only a few parts in 10^{13} which does not take advantage of the low background levels anticipated.

For application to the detection of tagged explosives, the method developed by Lovelock must be modified to provide increased sensitivity during continuous monitoring. The Teflon tubing concentrator being developed at Brookhaven may provide one alternative. At the same time methods of incorporating the perfluro-carbon compounds would have to be examined.

D. Conclusions and Recommendations

Commercial detectors for SF_6 using the continuous mode of sampling at present do not have the detection capability necessary for detection of SF_6 tagged explosives.

Developments ongoing at Brookhaven based on continuous determination at very low levels (less than 5×10^{-13} cm^3/cm^3) should be supported with an emphasis on applying the instrument to explosives detection and should be simplified so that non-technical operators would be able to maintain the monitors.

Detection methods for other electronegative compounds that hold promise as more favorable taggants than SF_6 should be improved upon in order to take full advantage of the low level background concentration anticipated for the alternative taggant.

TABLE 8-1

COMMERCIAL SF_6 DETECTORS

		SF_6 Sensitivity, cm^3/cm^3	
Instrument	Manufacturer	Continuous	Finite Sample
-	Xonics	na	not stated
Panatek	Panametrics[a]	10^{-8}	10^{-11} (10^{-12})[b]
112C	Analog Technology	3×10^{-9}	10^{-11}
Bantam	Varian	5×10^{-9}	na
SF_6-B	Ion Track	similar to Panatek	
58	"	not stated	na
62	"	not stated	

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[a] No longer manufactured

[b] Modified by Brookhaven with the addition of a digital integrator, a heated (100°C) detector, and a molecular sieve 5A column.

IX. OTHER ELECTRONEGATIVE COMPOUNDS

A survey of the literature on sensitivity of various alternate compounds to detection by an electron capture detector has yielded the information in Table 9-1. The most promising candidates based solely on sensitivity considerations were: 1,2-diiodotetrafluoroethane, hexafluorobenzene, carbon tetrachloride and difluorodichloromethane. The latter has the additional advantages of volatility (boiling point near room temperature). Other commercially available materials of potentially very high ECD sensitivity include n-C_3F_7I, SF_5Cl and SF_5CF_3 but no experimental data on their ECD sensitivity has been published. Similarly, the sensitivity of various perfluorocarbon compounds although not as yet published should be available soon.

A. Important Properties

Other important considerations in addition to the sensitivity of the material are: cost, vapor pressure, chemical reactivity, long term stability, specificity, and, perhaps most importantly, physiological inertness. The cost of sulfur hexafluoride (about $2.50 per pound) if used at the rate of 25 mg per blasting cap would increase the cost of the blasting by $0.00014 (i.e., less than 2/100th of a cent). Since the substitute taggant would be one which is currently not used extensively or possibly not even manufactured commercially as yet, the unit cost is expected to be higher. However, a fifty-fold increase in the per unit cost would still provide an adequate amount of taggant gas at less than 1 cent per blasting cap.

The vapor pressure of the material would determine the way in which the gas could be added to the blasting caps. If the vapor pressure was less than 0.1 atmosphere, the ability to achieve an adequate release rate for detection might be impeded by physical size limitations. Between 0.1 and 1 atmospheres, encapsulated permeation sources could be more readily manufactured and tailored to desired permeation rates than is possible for SF_6. That would probably be the most desirable vapor pressure range. Above 4 atmospheres and up to 20 atmospheres (the approximate room temperature vapor pressure of SF_6) the methods of impregnation into a substrate material would have to be employed since permeation source fabrication would definitely be more expensive at these vapor pressures. Materials with vapor pressures above 20 to 25 atmospheres could not be used by any practical means.

If the material being emitted from a tagged blasting cap or explosive was chemically reactive, there would be an increased likelihood that common items used to conceal the 'bomb' would adsorb and/or chemically remove the vapors as they were emitted. Increased effectiveness of barrier materials beyond their present levels (by physical means alone) would not be desirable. Similarly, the chemical stability must be such that it does not change significantly in ten or more years and should not be affected by moderate temperatures nor usually encountered environmental conditions. For example, SF_6 is stable at temperatures up to 400 to 500°C, has the lowest known solubility in water of any gas (about 1/5 the solubility of oxygen in water), and is chemically and photochemically inert.

The method used to detect the taggant gas must be very specific in order to minimize false alarms. There are many electronegative trace substances in the atmosphere that would be present at concentrations of from 10 to one million times the concentration of the taggant gas. Thus, great care would be required to assure that none of those gases would be detected by the method employed.

Probably the most important criteria for the taggant gas would be physiological inertness. A number of studies, including one of rats breathing a mixture of 20 percent oxygen and 80 percent sulfur hexafluoride, have shown that SF_6 is extremely inert in this sense. Details of its physiological inertness have recently been reviewed.(18) Many other electronegative gases are toxic or of unknown toxicity. Before a choice of a different gas could be made, extensive toxicological and physiological studies would have to show that during manufacture of the taggant source configuration, during incorporation into the blasting cap, and subsequently during storage and use of the caps that no harm to the environment or individuals would occur. For example, many compounds of choice contain halogen atoms (chlorine and bromine) potentially hazardous to the ozone layer although consumption of the gas would be less than 10 tons/year compared to 10^5 tons/year or more of refrigerants. Those compounds containing fluorine halogen atoms only would not be potentially hazardous to the ozone layer since fluorine does not participate in the same type of chemical chain decomposition with ozone as does chlorine and bromine.

Another potentially desirable property of the ideal taggant gas would be a relatively short lifetime (e.g., a half-life of a few months) once the gas was released to the environment. This would tend to keep the background concentration of the taggant at low levels in the environment. If 100 million blasting caps were manufactured per year containing 25 mg each of the taggant gas, the amount of gas needed per year would be about 3 tons. Of that amount, most might escape to the atmosphere during detonation of the caps. (The amount released versus the amount decomposed during detonation is unknown but would have to be determined). Thus, a release of three tons per year into the total troposphere, which weighs about 4×10^{21} grams, would annually increase the background concentration by about 1 part by volume in 10^{16} parts of air. In ten years, without a natural sink mechanism for removal of the gas, background concentrations would exceed 1×10^{-15} and detection capabilities might eventually be impaired. A gas with a reasonably short lifetime would eliminate this problem.

Finally, once a new taggant compound with a specific detection capability is selected, the use of that material should be controlled in order to prevent more rapid increases in background concentrations and its availability limited to prevent incidences of false detection.

B. Conclusions and Recommendations

Finding another potential taggant gas to replace SF_6 will be restricted by the requirements listed above. Sensitivity, detection specificity, physiological inertness, and cost - among the more important restraints - will severly limit the list. An important candidate material are the cyclic perfluorocarbon compounds for which sensitive and specific analytical methods are currently being developed. These, and other compounds, should be examined in considerable detail. Only with the use of a taggant gas other than SF_6 can detection in large volume scenarios be made practical. For close proximity detection, sulfur hexafluoride would be adequate for a taggant gas.

TABLE 9-1

PROPERTIES OF ELECTRON CAPTURE SENSITIVE COMPOUNDS

Compound	Phase at 20°C	BP, °C	Density	Relative Sensitivity[a]	Experimental Capture Rate Constant[b]
IF_2C-CF_2I	liquid	112-113	2.63	1800	-
Hexafluorobenzene	liquid	82	1.61	1250	-
CCl_4	liquid	76.54	1.594	900	2.81
SF_6	gas	-63.8	6.60 g/ℓ (gas) 1.88 (liq. - 50.5°)	750	2.20
$Cl-(CF_2)-SF_5$	?	-	-	600	
CF_2Br_2	liquid	24.5	-	450	2.61
$CFCl_3$	liquid	23.8	-	250	1.14
CH_2Br_2	liquid	97	2.497	225	-
$n-C_3F_7I$	liquid	40	1.75	140	-

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[a] Data taken from C. A. Clemens and A. P. Altshuller, Anal. Chem., 38, 133 (1966).

[b] This is a measure of the absolute sensitivity of the compound for electron capture; cf. J. J. Sullivan, J. Chromatog., 87, 9 (1973). The units are (ml/molecule-sec) x 10^7.

X. MANUFACTURING COMPATIBILITY AND COSTS

The two methods of incorporating a sulfur hexafluoride source into blasting caps were discussed in detail earlier (see Section IV) and are shown schematically in Figures 4-1 and 4-2. Either method would appear to have the least impact on manufacturers from the standpoint of having to retest blasting cap performance. The modifications, essentially an external change, should not significantly in any way affect the operating characteristics of the caps. This is a desirable approach since any change within the blasting cap would require an extensive 1 to 2 year testing program to assess such a change.

A. Compatibility

Experiments discussed earlier showed that SF_6 does not penetrate the end plug of blasting caps when the source is enclosed completely within the internal portion of the blasting caps. The conventional crimping method used by the manufacturers is sufficient to prevent any diffusion of gases.

Incorporating a taggant gas source by the method shown in Figures 4-1 and 4-2 would essentially require only an increase in the length of the shell of the cap (about 1/2-inch), a slightly longer and modified shape of the plug material, and a change in the crimping tool head to handle the increased length.

Methods to prevent the removal of the taggant source would have to be developed in conjunction with the manufacturers. Fabrication by the technique shown in Figure 4-2 should be a significant deterent to the ready removal of the source. Perhaps a method could be developed whereby the moderate amount of effort required to remove the taggant source would result in the disarming of the blasting cap.

B. Cost

Blasting caps typically sell in the range of $0.40 to $1.25 per cap. Thus it would be desirable to keep the cost of adding the taggant source below 5 cents per device. An estimate of the increased cost by adding a 1/8-inch OD by 1/2-inch long SF_6 impregnated Teflon rod was made by including the cost of the increased length of the shell, the plug material, the Teflon rod, and the taggant gas (in this case, SF_6).

Many blasting caps are made with aluminum shells. Based on the current value of aluminum tubing about 1/4-inch OD by 0.016-inch wall thickness, the increased 1/2-inch length of the cap shell would add about 0.12 cents to the cost of the cap.

The present plug material used in Atlas blasting caps is 5/16-inch OD by 5/16-inch long and weighs about 0.60 g. Changing the shape so that the 1/2-inch long Teflon rod could be incorporated into the end plug would probably increase the weight of the plug material by 0.75 g. Assuming a cost for the rubber plug material of $1.50 per pound, increased cost due to the change would be about 0.25 cents.

Teflon rod material of the TFE type costs about 4 cents per inch for 1/4-inch OD stock. FEP type Teflon is about 2/3 the cost of TFE type. Based on a compromise unit cost, a 1/8-inch OD by 1/2-inch long Teflon rod would cost about 0.40 cents.

Sulfur hexafluoride in bulk quantities costs about $2.50 per pound. Assuming that 20 mg of SF_6 would be consumed while loading about 16 mg into the Teflon rod, the value of the gas per device would be 0.01 cents. Thus the cost of the taggant gas would be the least expense in tagging the blasting caps. If another taggant gas were eventually substituted, a per pound price of 50 times that of SF_6 (i.e., $125 per pound) would still be economical.

The exact cost of manufacturing the SF_6 impregnated Teflon rods should also include the operating and equipment depreciation costs. Assuming that 100 million blasting caps are manufactured per year and that annual operating and depreciation costs would run about $100,000 (including one skilled operator), the cost per impregnated Teflon rod would be about 0.10 cents.

Thus the total cost of including the taggant gas during the manufacture of the caps would be about 0.88 cents or about

1% of the cost of a typical blasting cap. Even if some of the computations above were not completely accurate and if there would be some other costs involved that were not considered, the total expense should be less than 2% of the selling price of blasting caps.

For liquified permeation sources of the type described in Section VI-A, the steps involved in loading the SF_6 would be more complicated and extensive than those required for the impregnated sources, and, consequently, the manufacturing equipment, time, and labor would be more substantial. It is difficult to accurately assess the costs related to the fabrication of liquified permeation sources because a simple and reliable large scale manufacturing procedure has not yet been conceived. The cost of such sources, however, could very well be comparable to the cost of manufacturing a blasting cap which might make liquified sources too expensive from the viewpoint of the cap manufacturers.

C. Conclusions and Recommendations

Placing the taggant source in the plug material is essentially an external modification of the blasting cap and should minimize the time and expense in a re-evaluation program to determine effects on the performance of the caps. Details of the sealing requirements of the manufacturers and the performance specifications of the SF_6 impregnated Teflon sources should be combined to produce an operational taggant source/sealant plug material. Demonstration pieces should be fabricated and tested.

Total cost to the manufacturers of blasting caps to incorporate an SF_6 impregnated Teflon rod source was expected to be less than one to two percent of the selling price of blasting caps. Use of a different taggant gas would not significantly affect the cost of tagging.

XI. PROGRAM TASKS FOR SECOND PHASE

A number of the task elements that were followed in the first period of the explosives tagging program should be concluded during the second phase. Others may be expanded, continued, or redirected. In addition to the former task elements, new areas of effort will also be described in this section.

A. Background Measurement

A significant number of rural and near-urban measurements of SF_6 in the environment indicated that the average value to be expected was in the range of 0.5 to 1.0 parts per trillion. The only additional measurements that possibly should be made are determinations near and directly downwind of electrical generating power plants where SF_6 might be higher than normal. However, operating a detection instrument in the dual detector mode described earlier would eliminate concern for background levels giving false indications of tagged sources.

When other taggant gas substances for replacement of SF_6 are identified, measurements of their background levels will be made. In addition to interference of detection due to the presence of taggant gas in the environment, the as yet unknown analytical method may be susceptible to interferences from other trace gases. When potentially interfering constituents have been identified, their ambient levels would have to be determined.

B. Barrier Effects

The results of the earlier studies showed that the effectiveness of a barrier to the diffusion and transport of the taggant gas to the detector system was primarily (or nearly entirely) dependent on the closure or seal involved rather than the nature of the material. Thus, items such as paint cans, polyethylene zip-lock bags, and completely closed (with thread sealant) pipes were found to be effective barriers.

Barrier effectiveness of several of the materials previously studied will be conducted during detection feasibility tests based on manual (hand-held sniffer) and automatic (luggage conveyor belt) operational scenarios.

C. Absorption Substrate Determination

Selection of Teflon type materials as the prime candidates for absorbing and retaining the taggant gas was based on studies performed with sulfur hexafluoride as the taggant gas. As other gases are evaluated as replacements for SF_6, the need will arise to determine those substrates that have the best absorptive and desorptive properties for the particular gas. Possibly, the Teflon materials will prove to be universally applicable.

The materials currently used in the sealant plugs of the three United States commercial blasting cap manufacturers will be studied in more detail. If new materials are being used, they may have better characteristics then previously tested plug materials. Perhaps slight modifications of the formula of the plug compounds would improve their application as a taggant absorbent substrate. Similarly, blending Teflon or highly adsorbing activated carbon into the material mix before fabrication of the plugs might improve the characteristics.

D. Useful Life Determination Studies

The normal impregnation conditions of the vapor pressure (300 psig) of SF_6 applied to Teflon pieces at room temperature was demonstrated to not completely penetrate the materials. Variations of the pretreatment and loading conditions of temperature and pressure will be performed to determine optimum values for the rate of loading and the ultimate absorbed concentrations both for SF_6 and any other potential taggant gas. Materials will be selected from the results of the substrate determination tests.

Long term weight loss and desorption rate determinations will be performed with the best combinations of taggant gas and absorption substrate. Effects of storage conditions - mainly temperature - will be determined for open as well as encapsulated sources.

E. Encapsulated Source Development

Since the liquid and solid states of a taggant gas have significantly higher densities than the highest that can be achieved by absorption and since permeation of the vapors from the liquid or solid state through a polymeric membrane material gives a constant emission rate, a permeation source is preferred to an impregnated source. Methods for the simple fabrication of such sources for SF_6 as well as other taggant gases will be evaluated.

Rates of emission from SF_6 and other taggant gas impregnated sources will also be measured.

F. Other Electronegative Taggant Compounds

A substitute for SF_6 was shown to be needed in order to detect tagged blasting caps in large volume environments because the present background concentration is a limiting factor. Prospective taggant candidates will be screened for ability to meet the specified conditions of electron capture sensitivity, cost, vapor pressure, chemical reactivity, long term stability, analytical specificity, physiological inertness, and lifetime in the atmosphere, In particular, certain cyclic perfluorocarbon compounds, for which analytical methods are presently being developed, will be evaluated as substitutes for the sulfur hexafluoride.

G. Detection Methods for Taggant Gases

Depending on the detection scenario being considered, different variations of the electron capture sensing methods will be further developed. This applies to SF_6 as well as other taggant gases. For monitoring luggage on a conveyor belt, for example, real-time response of from 1 to 2 seconds with a concentration sensitivity of about $5x10^{-13}$ parts per part of air will be required. Methods that appear promising for oxygen removal followed by subsequent detection of the taggant gas (chemical oxygen removal, catalytic removal, membrane separation) will be studied.

For large volume detection such as in rooms, luggage carriers, and on board planes, the sample and analysis time can be extended to allow levels in the air to be concentrated prior to detection. Those methods which hold promise of sample concentration during a 1 to 2 minute period followed by analysis with a limit of detection of $5x10^{-15}$ or less will be explored further. In this area, consulting and supportive research efforts by several specialists in the field of electron capture chromatography would be invaluable.

H. Manufacturing Compatibility Evaluation

Methods developed for incorporation of SF_6 tagged sources will be implemented in an evaluation program to determine the best method or methods for adding the taggant to blasting caps. The evaluation will include effects on the performance of the blasting caps as well as on the costs of manufacturing, safety, and product contamination.

I. Demonstration and Comparative Detection Tests

The end product of this program, a detection capability to locate bombs containing tagged blasting caps or explosives before they detonate, will be evaluated in at least two scenarios - sniffing for tagged sources in suitcases or packages on an airport conveyor belt and detection and location in a large volume environment. The primary testing scenario, manual and automatic detection on a conveyor belt, should be conducted with simultaneous detection methods by any other means at the same stage of development. Sulfur hexafluoride will be used in the evaluation tests of both scenarios. For the latter, sources with emission rates at least 100-fold greater than eventually to be incorporated will be used unless another taggant gas and the corresponding detection equipment have been satisfactorily developed.

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