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DETECTION OF PERFLUORINATED TAGGANTS IN ELECTRIC BLASTING CAPS BY ELECTRON CAPTURE MONITORS

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Abstract. Three types of monitors or detecting instruments for determining the presence of perfluorinated taggants have been developed and validated in field studies. Each of the three versions--a portable continuous real-time monitor, a portable concentrating chromatograph, and a fixed station high sensitivity chromatograph--have been utilized for detecting these types of compounds in atmospheric tracer studies.

The portable continuous monitor, which has a detection capability of two parts of taggant in one trillion parts of air (2 pp 10^{12}), has been used in three field tracer studies in the past 18 months, operating on-board aircraft. In a scenario such as continuous on-line screening of checked and hand-carried luggage at airport environments, the sensitivity and response time are more than adequate. Confirmation of the method applied to conveyor belt suitcase screening has been demonstrated.

A small concentrating field instrument was developed and field tested more than a year ago. Five minute repetitive sampling rates are estimated to ultimately provide limits of detection for the taggant compounds at about 5 pp 10^{16} and could be extended as much as another 50-fold lower. Applications potentially include detecting vapor tagged explosives in meeting rooms, corridors and passageways, and on-board aircraft.

Introduction

Tagging explosive devices for detection prior to detonation and identification after such clandestine use has the potential for significant impact in terms of human lives saved, reduced property damage, lowering investigative costs, and increasing the chances for tracking down bombers and obtaining convictions.[1]

Although numerous methods have been explored for the pre-detonation detection of explosive materials, one of the most promising approaches appears to be based on the vapor tagging of electric blasting caps.[2-4] Of the bombing incidents resulting in deaths, injuries, and property damage, approximately 70% were perpetrated with cap sensitive explosives.[1] Because many of these materials have little or no vapor pressure, it was concluded that the most feasible approach to detection was to add a volatile, sensitively detectable component to the end closure of electric blasting caps (EBCs). This tagging concept had its genesis as far back as 1972, originally as a spin-off of the Brookhaven atmospheric tracer program.[5] Subsequently the approach was patented with respect to the addition of sulfur hexafluoride (SF_6) and has now been extended to certain perfluorocarbon compounds.[4,6]

Of the criteria specified for the vapor tagging of an EBC, one of the most important is that the additive vapor (coined "taggant") be uniquely determinable by highly sensitive means and have a negligible background concentration in the environment.[4] One family of compounds that has met these needs as well as most of the other criteria for successful implementation is the perfluorinated cyclic alkanes. This paper will describe the instrumentation that has been developed to detect these compounds, as a class hereinafter called perfluorocarbon taggants (PFTs), and describe some test results obtained during the simulated screening of luggage on conventional conveyor belts.[7] The reliability and documented utility of the type of instrumentation available as well as the detection sensitivities attainable and needed for various explosive monitoring scenarios will be presented.

Detection Equipment

For nearly a decade, Brookhaven has been routinely using SF_6 as an intentionally added constituent to power plant flue gases and other emission sources in order to study the atmospheric transport and dispersion of these air masses.[8-10] For collected whole air samples, a 40 mℓ sample was sufficient to determine the background SF_6 concentration using a laboratory chromatograph system.[9] As shown in Table 1, the precision of measuring these low concentrations, averaging 0.51 pp 10^{12}, was about 4 percent.[11] The agreement with earlier measurements in December 1975 at the Savannah River laboratory in South Carolina, resulting in a value of 0.52 ± 0.03 pp 10^{12}, was excellent.[10]

After a number of SF_6 tracer releases, it became apparent that to follow air masses for distances greater than 100 km or so, other compounds with lower background concentrations would have to be used.[5] Instrumental methods for measuring several orders-of-magnitude lower ambient concentrations were conceptually feasible. Studies at Brookhaven and in England resulted in the selection of perfluorinated cyclic alkanes.[12,13]

Similarly, the present ambient SF_6 concentration, and its widespread availability, was found to be a

Table 1. Background SF_6 Levels at Baldwin Lake
(35 miles southeast of St. Louis, Illinois)
November 1976

Sample No.	SF_6 Conc. ± σ,[a] pp 10^{12}
W 3	0.48 ± 0.01
W 4	0.52 ± 0.01
W 5	0.47 ± 0.03
W 6	0.51 ± 0.01
W10	0.52 ± 0.01
W11	0.52 ± 0.02
W16	0.48 ± 0.03
W17	0.49 ± 0.01
W20	0.50 ± 0.01
W22	0.51 ± 0.01

Overall Average = 0.51 ± 0.02

[a] σ is standard deviation of two determinations.

limitation in the usefulness of SF_6 as a vapor taggant in EBCs.[3] Studies were initiated to evaluate suitable alternatives, among them, the PFTs.[4] In this section, the various instruments that have been devised to measure PFTs in air will be described.

Laboratory Chromatograph System

A laboratory chromatograph basically consists of a means for introducing the sample to be analyzed just ahead of, typically, a long tubular column packed with a solid or liquid supported adsorbent phase. The column serves to separate the constituents to be measured, eluting them at discrete times--their retention times--prior to entering the detector, in this case an electron capture detector (ECD).[5] One of the requirements necessary for the successful detection of the PFT, in addition to its high sensitivity to electron capture detectors (typically 1 pp 10^{12}), is the ability to be able to uniquely distinguish the compound from among possibly many other interferences.

The ambient air contains many electronegative compounds, both halocarbons as well as several inorganic gases. More than 20 halocarbon compounds have been identified with concentrations ranging from about 5 pp 10^{12} (Freon 21, CH_3I, C_2Cl_6, $C_2H_4Br_2$) up to about 100 to 700 pp 10^{12} (Freon 12, Freon 11, CCl_4, CH_3CCl_3, CH_3Cl), all of which have varying, but reasonably significant, response to an ECD.[14-16] On the other hand, the expected concentration of taggant, depending on the explosive sampling scenario, may range from 10 pp 10^{12} at the highest to as low as 0.1 pp 10^{15} or less, that is, possibly 7 orders of magnitude below the combined concentration of all atmospheric halocarbons.

Since column separation alone could not possibly hope to resolve such trace quantities of taggant from the much larger mix of ambient halocarbons, an additional separation factor was employed. A small bed (1/8-inch lumen by 1-inch long) of 5% palladium supported on 5A molecular sieve in the presence of a few percent of a reducing gas, CH_4 or H_2, was found to quantitatively catalyze the reduction of the halocarbons--provided most of the oxygen was previously physically separated by on-line sample trapping.[5,12] The catalyst bed temperature could be tuned to a temperature of about 175°C, which, as shown in Figure 1, did not affect the survival of the taggants, but did efficiently and completely remove any trace oxygen and all the halocarbon compounds. All the potentially interfering compounds were catalytically reactive at temperatures corresponding to the freon curve or lower. The products of the destruction, traces of water and halogen acid vapors, were removed by an in-line permeation dryer.[17]

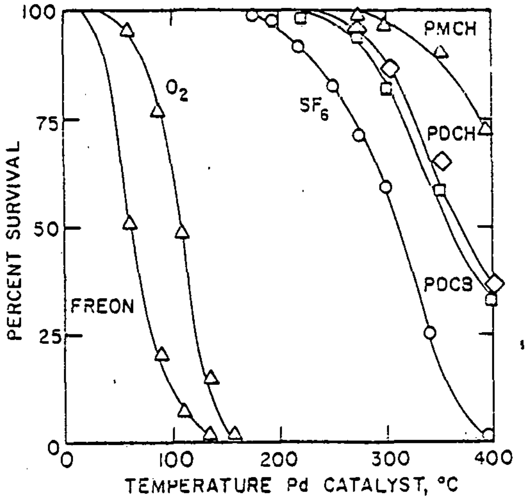

Figure 1. Effect of catalyst bed temperature on destruction of taggants and interferents.

The taggants survived the reducing atmosphere in the catalyst bed because of the inherent chemical stability of fully fluorinated (perfluorinated) organic or inorganic compounds. The most stable taggant shown in Figure 1 was perfluoromonomethylcyclohexane, PMCH, followed by perfluorodimethylcyclohexane, PDCH, and perfluorodimethylcyclobutane, PDCB.

With the combination of catalytic reactor and chromatographic separation, the laboratory instrument has been used to analyze 40 mℓ air samples for the three PFTs and SF_6. A typical chromatogram of a prepared air standard is shown in Figure 2. The limit of detection of the PFTs from that size sample was about 1 pp 10^{14} at a S/N of 2.

Preconcentration Samplers

In order to measure still lower concentrations of PFTs in the atmosphere, several instruments have been and are being developed to concentrate the trace amount of taggant vapor in a large volume of air onto a relatively small amount of solid adsorbent for subsequent thermal recovery and analysis.[18,19] A preliminary indication of the capability of this approach was demonstrated by collecting 41.7 liters of rural (away from any possible local sources) ambient air on just 50 mg of cocoanut charcoal. The chromatogram of the recovered sample, shown in Figure 3, indicated that the clean air background concentration of PDCH

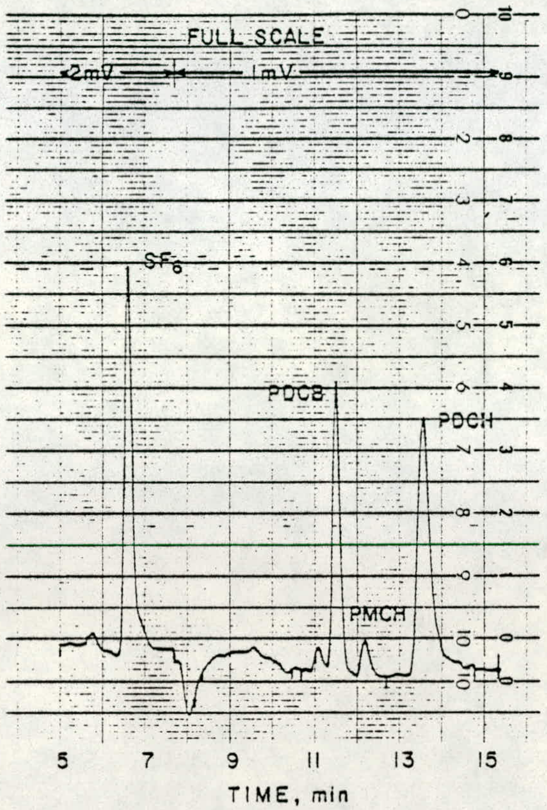

Figure 2. Chromatogram of 40 mℓ air standard containing 1.2 pp 10^{12} of SF_6, PDCB, and PDCH and 0.15 pp 10^{12} of PMCH.

was 1.45 pp 10^{14} (includes about 15% that was recovered from a subsequent heating and analysis) and 1.49 pp 10^{15} for PMCH.

Worldwide production of PDCH indicated that a background concentration of about 1.8 pp 10^{14} PDCH should presently exist.[20] Since PMCH has been an impurity in the production of PDCH, present at about 10%, the agreement between measured and expected levels was quite good. The value for PDCB may have been contaminated with an unknown constituent as well as the PDCB, since its level in the atmosphere, again based on production figures, was expected to be about 1 pp 10^{16}. SF_6 was not measured, in part because it is not efficiently retained by the charcoal and in part because it is reactive with the charcoal during the thermal recovery.

As a result of subsequent studies, the limit of detection of PFTs from a 4 liter concentrated sample has been determined to be about 1 pp 10^{16} at a S/N of 2.

Sequential Concentrating Chromatograph

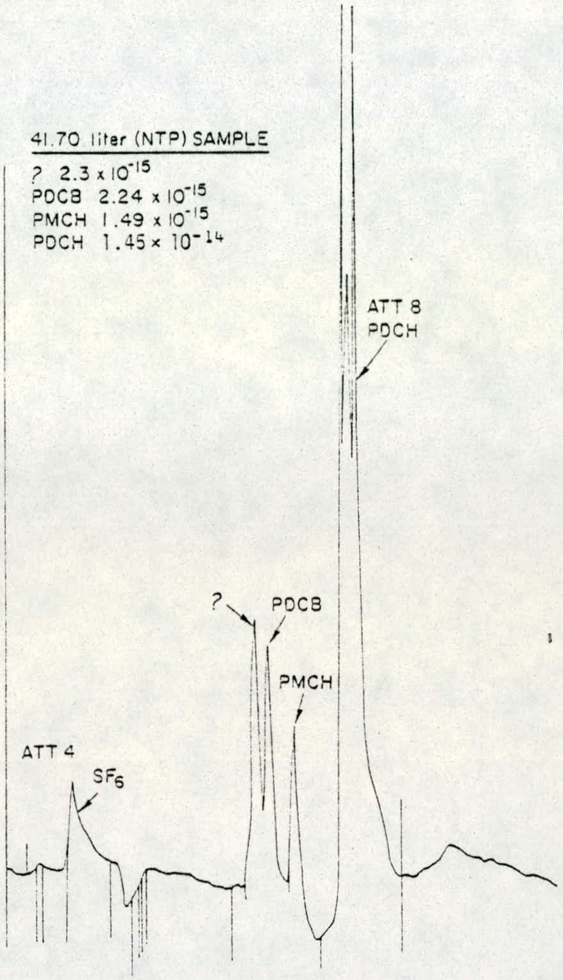

Figure 3. Chromatogram of 41.7 liter ambient air sample.

Based on a combination of adsorption collection followed by on-line desorption and analysis, a two-trap sequential chromatograph was designed and developed in England and evaluated and tested in some field measurements in the U.S.[21,22] For about a 5-minute period, while one adsorption trap was being utilized to remove the PFTs, the other was being analyzed for its contents. Although the limit of detection in these experiments was only 1 pp 10^{13}, the method has the potential for significant improvement.

Continuous Monitor

A portable monitor was developed and field tested in 1972, utilizing a procedure called frontal chromatography to continuously analyze for SF_6 for up to 45 seconds before oxygen eluted from the column and terminated the scan.[23] Since that time numerous improvements were made in the design, increasing the measurement time for up to 3 1/2 minutes of continuous output at a sensitivity of 1 pp 10^{12}, but the method was only specific for SF_6.[5]

To provide a truly continuous monitor and to extend the capability to the PFTs, a new instrument was devised. By utilizing the same type of catalyst bed as described for the laboratory chromatograph system, ambient air was continuously mixed with half as much hydrogen and pumped through the reactive bed. The oxygen in the air was converted to water (steam) and the potentially interfering freon compounds were again converted to their respective acids. Using either a thermoelectrically cooled condenser or a permeation dryer, the water and halogen acids content are reduced to a level sufficiently low to allow the gas stream to pass directly into the detector, where the surviving PFTs and SF_6 in the remaining N_2 are measured.[24,25] A typical scan with the instrument, using a tagged EBC in the inlet tubing at the pump, results in a square wave signal. The PMCH-tagged EBC for the scan in Figure 4 gave an effective concentration of about 1.2 pp 10^9.

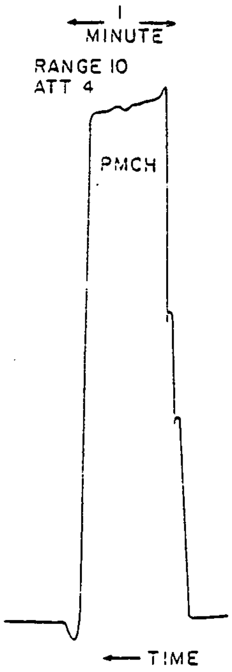

Figure 4. Continuous monitor detection of a PMCH sample at 1.2 pp 10^9 for 1 minute.

Brookhaven has built and field tested two of these continuous monitors, one of which was utilized in the conveyor belt suitcase screening tests to be described in a later section.[7] One instrument was flown successfully in field tracer experiments in Indiana in October 1977 and two were used in recent tracer releases at a coal fired power plant in Tennessee during August 1978, attesting to their field worthiness.[26]

Future Expectations

The instrument capability for detection of PFTs covers a broad concentration range from 2 pp 10^{12} down to as little as 1 pp 10^{16} and is summarized in Table 2. For each of the instruments listed, there are significant improvements that are being implemented or planned.

Table 2. Perfluorinated Taggant ECD Monitors

INSTRUMENT	DETECTION LIMIT PRESENT	DETECTION LIMIT FUTURE
1. CONTINUOUS (portable; any PFT)	2 pp 10^{12}	2 pp 10^{13}
2. CONTINUOUS CONCENTRATING (portable; any PFT)	---	2 pp 10^{15}
3. SEQUENTIAL CONC. GC		
•with packed column (portable; speciates)	1 pp 10^{13}	5 pp 10^{16}
•with capillary column (semi-portable; speciates)	---	1 pp 10^{17}
4. LABORATORY CONC. GC		
•with packed column (non-portable; speciates)	1 pp 10^{16}	5 pp 10^{17}
•with capillary column (non-portable; speciates)	---	1 pp 10^{18}

1. Continuous. By incorporating a form of solute switching and synchronous demodulation, at least one order of magnitude improvement in sensitivity is anticipated.[24,27] The approach is to rapidly alternate the gas flow into the ECD, choosing between one stream as it comes directly from the catalytic bed and another stream that has additionally been treated to destroy the PFT. The repeated cyclic behavior would result in the detector alternately "seeing" and then not "seeing" the PFT. Appropriately synchronized electronics can then be employed to greatly enhance the signal while at the same time substantially reduce noise and baseline drift, the latter of which is a particular problem in almost any long-running continuous monitor. A limit of detection of about 2 pp 10^{13} is expected.

2. Continuous concentrating. Further improvements in the ECD sensitivity or amplifying electronics are not anticipated. Therefore, to extend the detection sensitivity to lower concentration limits, an automatic continuous concentration scheme will be investigated using either packed column tubes or support coated open tubular (SCOT) columns of Ambersorb, a form of synthetic charcoal. The open tube will allow high flow rates with minimum pressure drop and the thin support coating will provide for rapid adsorption and desorption. By adsorbing at 2 ℓ/min and desorbing at 20 mℓ/min, a concentration factor of 100 can be realized. A multi-tube switching valve with 2 or 3 second cycling will provide positions for: 1) adsorption from air; 2) flush with inert gas; 3) heating; 4) recovery of tracer; 5) cool down; and 6) final cool down. This will extend the limit of detection to about 2 pp 10^{15}, while maintaining about 4 second response time but with a delay time of perhaps 12 to 15 seconds.

3. Sequential concentrating GC. An evaluation of Ambersorb (Rohm and Haas) adsorbent has indicated a

capacity for PFTs in humid air of about 100 ℓ per gram of adsorbent. By utilizing just 50 mg, about 1 liter of air could be collected and analyzed for all PFTs with a limit of detection of about 5 pp 10^{16} for a packed column and a cycle time of about 3 to 4 minutes. The unit would remain relatively compact and portable. With a capillary column, the limit of detection could be extended to 1 pp 10^{17} for the same size sample but cycle time would increase to about 6 to 7 minutes and portability would be sacrificed.

4. Laboratory concentrating GC. For sample volumes of about 4 liters, the present limit of detection can only be improved slightly. But by switching to capillary chromatography with on-line sample freezing, the ultimate limit of detection of about 1 pp 10^{18} is anticipated. Since sample collection would be done prior to analysis, the time for determination of the individual PFTs could be as short as 4 minutes.

Expected Scenario Concentrations

Up to this point, the present and future detection capabilities for PFTs have been presented and documented. The probable required detection sensitivities and response times for determining the presence of a bomb in a real-world situation will depend to a large extent on the actual scenario involved. In this section, the expected concentration of taggant in four scenarios, suitcase screening, detection in moderate size meeting rooms, on aircraft, and in buildings will be presented and compared with the sensitivities of the available monitoring instruments.

Suitcase Screening

The first and perhaps most important area of detection of clandestine bombs prior to their detonation is at airport environments. At the present time there is essentially no screening of luggage and packages that are checked for subsequent loading into aircraft. To be able to detect the presence of a tagged EBC in such items as they are either moving on a conveyor belt or, perhaps, as they are individually being ticketed by the agent at the passenger check-in point, a means must be provided to extract a portion of the air within the item. In addition, the concentration within the item must be high enough to counteract any dilution that occurs during the sample extraction.

If suitcase screening could be accomplished on a moving conveyor belt, only one central sampling station would be required but the response time would have to be in the range of 2 to 3 seconds. Screening at passenger check-in stations would allow longer sampling times, up to 15 seconds, but then more instrument systems would be required. Because of the costs, upkeep, and manpower requirements as well as logistics concerned, it is much more desirable to have centrally located on-line conveyor belt screening stations. Thus, for this type of measurement, only the continuous instruments (either item 1 or 2 in Table 2) would be applicable.

A summary of the expected concentration in each scenario, assuming the explosive device with the tagged EBC was placed in the scenario and measurements taken 1 hour later, is shown in Table 3. The emission rate of the tagged EBC was selected from the typical performance of an experimentally measured simulated tagged EBC and extrapolated using a proven diffusion model.[4]

Table 3. Expected Scenario Taggant Concentrations (One hour after placement of tagged blasting cap)

Tagged EBC		Taggant Concentration			
Age, Years	Rate[a]	Attache Case, pp 10^9	Meeting Room,[b] pp 10^{14}	Plane,[c] pp 10^{14}	Building,[d] pp 10^{16}
0.5	1.29	2.44	5.28	2.60	1.20
1	0.919	1.74	3.76	1.85	0.86
2	0.649	1.23	2.65	1.31	0.60
5	0.410	0.78	1.68	0.83	0.38
10	0.291	0.55	1.19	0.59	0.27

[a] Typical rate in 10^{-9} ℓ/min from tagged caps[4]

[b] 40 ft x 50 ft x 10 ft; Air exchange every 57 min

[c] Type 707 or DC-8; 10,000 ft^3 vol.; Air exchange every 10 min; EBC in suitcase for 1 hour but in plane only 10 min

[d] 200 ft x 400 ft x 100 ft; Air exchange every 40 min

For the 15-liter attache case, it was assumed that during the one hour that the tagged EBC was concealed in the closed case, about one-half the taggant emitted from the EBC remained within, a reasonable assumption. At a cap age of 2 years, the concentration was estimated to be 1.23 pp 10^9 within the case. Assuming a 250-fold dilution during the sample extraction procedure, an experimentally confirmed value, the measured concentration would be about 5 pp 10^{12}--about 2 to 3 times the current limit of detection of the continuous instrument.[7] With the further 10-fold improvement in detectability, suitcase screening appears to be quite feasible. Experimental results will be presented in a later section.

Detection in a Meeting Room

To predict the concentration in large volume environments with known ventilation rates, a model was devised to take into account the dilution that occurs when ventilation is included.[4] For the meeting room results shown in Table 3, it was assumed that the air in the room was exchanged completely, once every 57 minutes, with outside air devoid of any taggant.

Over the 10-year lifetime of the tagged EBC, taggant concentrations in the meeting room are expected to be in the range of a few pp 10^{14}. These values are well within the expected capability of the sequential concentrating gas chromatograph (item 3 in Table 2). Thus, important conference areas and meeting places can be continuously monitored on about a 4-minute sequential basis.

Detection on Aircraft

If a suitcase containing a tagged EBC should pass the conveyor belt screening section without being detected, the question arises as to whether or not it could be detected on the aircraft. For an airplane of the 707 or DC-8 type, the total volume is about 10,000 ft^3 and the ventilation rate is about 1000 ft^3/min--that is, about one complete air exchange every 10 minutes.[28]

Assuming the suitcase had a typical slight barrier factor (k = 0.3 ℓ/min) and assuming the suitcase with the clandestine bomb was last opened 1 hour before loading onto the aircraft, the ventilation model with time delay predicted the concentrations shown in Table 3 for the plane.[4] The concentrations would be readily detected with the sequential concentrating type gas chromatograph (item 3 in Table 2). A modified version of that instrument, incorporating more rapid sample collection and measurement (the pilot would hardly care what precise amount was present), would provide for a determination in about 2 minutes.

Detection in Buildings

Again, as shown in Table 3, similar calculations for a large building, indicate that concentrations of taggant slightly less than 1 pp 10^{16} would be expected under the conditions stated. The only reliable way to screen for concentrations less than 1 pp 10^{16} would be to utilize a modified version of the laboratory concentrating gas chromatograph. Such a system would be automated but would require the ready availability of a technical person for maintaining system performance.

Barrier Factors

In the examples cited above, it was assumed that the tagged EBC was contained within an item, such as a suitcase, that presented only a slight to moderate barrier or deterent to the transport of the vapors.[4] If a more severe barrier were employed by the perpetrator, the concentrations indicated in Table 3 could be reduced by 10- to 100-fold. It should be noted, however, that the usual steps in preparing and arming a bomb prior to use, normally would preclude the use of such extremely effective barriers.

Luggage Screening Demonstration

A device for extracting a fraction of the air within suitcases and packages while continuously processing these items on a conveyor belt was developed for the U.S. Customs Service.[29] Measuring about 3 feet high by 3 feet wide and straddling the suitcase conveyor belt for about 8 feet of length, the tunnel-like device contained five weighted fingers which slightly depressed suitcases as they passed through the system, expelling some of the air from the suitcase which was lying on its side. At the same time, two spring-loaded arms containing air sampling tubes ran along the seams of the suitcases, collecting a fraction of the expelled air.

Two of the Brookhaven instruments were used to measure the expelled vapors of taggant, the frontal chromatograph and the continuous instrument. The former could be used only to detect SF_6 tagged EBCs, while the continuous instrument could detect SF_6 and all the PFTs.

Several different tagged EBCs were placed in a variety of suitcases, one per suitcase, and screened with the Customs Service automated baggage examiner.[7] The most definitive test result is shown in Figure 5.

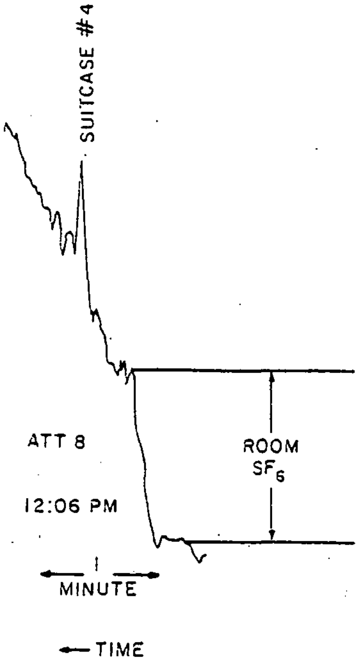

Figure 5. Frontal chromatograph detection of a tagged EBC (1.1 nℓ/min) only 19 minutes after closing the suitcase.

As indicated by the usual frontal step, the room concentration of 14 pp 10^{12} was easily detected. This value was elevated above the normal ambient value of 0.5 pp 10^{12} because of the presence of a large number of SF_6 tagged EBCs in a nearby portion of the room. Assuming an air exchange rate for the room of once every 40 minutes and a total SF_6 emission rate of 100 nℓ/min, an approximate SF_6 concentration of 20 pp 10^{12} can be calculated--in very good agreement with the measured room concentration. This result tends to lend credence to the ventilation model that has been developed.[4]

The small peak that occurred on the rising frontal step, labeled suitcase #4, was due to the detection of the tagged EBC within the suitcase as it traveled under the baggage examiner fingers at a rate of about 2 feet per second. The peak corresponded to about 10 pp 10^{12} of SF_6 and, based on the assumption of negligible diffusion losses from the suitcase during the 19 minute period, corresponded to an extraction efficiency of 1.9%.

Similarly, a PDCB tagged EBC that had been sitting in a suitcase for about 3 hours, was quite readily detected by the Brookhaven continuous instrument as shown in Figure 6. Although there were some baseline disturbances due to a faulty temperature controller, the detection of tagged blasting caps by this means was clearly demonstrated.

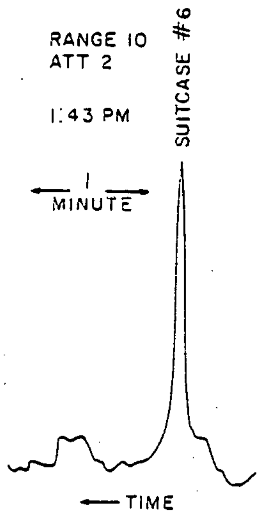

Figure 6. Continuous instrument detection of a PDCB tagged EBC in a suitcase.

Conclusions

Detection instruments with the required sensitivities for determining the presence of perfluorocarbon vapor tagged EBCs have been utilized for some time in atmospheric tracer studies. The vapor concentrations in various scenarios are expected to be in a range for realistic detection success with existing monitors and with those incorporating recent and imminent improvements. As an example, the luggage screening tests clearly demonstrated the practical reality of detecting the presence of a vapor tagged EBC in a suitcase moving on a conveyor belt.

Acknowledgment

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