BNL--46265-Rev.9/91

DE92 007169

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June 1991

Presented at
the Department of Commerce Environmental Conference,
"Protecting the Environment: New Technologies--New Markets",
Reston, VA
September 5-6, 1991

This research was performed under the auspices of the U.S. Department of Energy under Contract No. DE-AC02-76CH00016.

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ABSTRACT

Tracer technology can be successfully applied in many leak-checking and monitoring evaluations of operating systems (e.g., building HVACs), manufacturing processes and products (e.g., air conditioners), and subsurface components and systems (e.g., underground storage tanks). Perfluorocarbon tracer (PFT) technology is the most sensitive of all tracer technologies because the ambient background levels of the five (5) routinely-used PFTs are in the range of parts per 10^{15} parts of air (i.e., parts per quadrillion-ppq) and this technology's instrumentation can measure down to those levels. The effectiveness of this technology is achieved both in terms of cost (very little PFT need be used) and detectability; for example, very small leaks can be rapidly detected. The PFT compounds, which are environmentally and biologically safe to use, are commercially available as are the sampling and analysis instrumentation. This presentation concerns a) the steps being taken to commercialize this technology, b) new applications of processes currently under study, and c) applications in areas of use that will be particularly beneficial to the environment. A brief video of some applications will be available.

Originally developed as an enhanced tracer technology to better validate atmospheric pollutant transport and dispersion models, one of the first spinoffs was a PFT system for measuring air infiltration and ventilation in homes and commercial buildings. This technology can also be used to certify the performance of heating, ventilating, and air conditioning (HVAC) systems and a version can also be used as a pre-fire detection system.

The PFT technology can be useful in the electric utility industry by providing improved leak testing and other measurements in the various components of operating systems and efforts are currently directed to developing an approach to locate leaks in underground power transmission cables.

Application of the technology in manufacturing processes is just beginning and shows strong potential. A commercial company is planning to market a PFT instrument to validate the leak integrity of manufactured components such as heat exchangers in air conditioners and pressure vessels such as fire extinguishers. Modules for NASA's future Space Station Freedom will be leak certified with PFT technology and the potential exists for rapid screening of the seal integrity of packaging in the food industry.

The most important aspect of this technology may be its enormous potential to improve the environment by its use for detecting and pinpointing leaks in gasoline, fuel oil and other underground storage tasks and natural gas pipelines.

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1. INTRODUCTION

Tracer technology can be successfully applied in many leak-checking and monitoring evaluations of operating systems (e.g., building HVACs), manufacturing processes and products (e.g., air conditioners), and subsurface components and systems (e.g., underground storage tanks). Tracers have also been used in fluid transport and dispersion studies in the atmosphere (e.g., long range transport to distances of 3000 km), in aquifers (e.g., tracking pollutant plumes), and in underground oil and gas reservoirs (e.g., transport over scales of 1000m).

Perfluorocarbon tracer (PFT) technology is the most sensitive of all tracer technologies because the ambient background levels of the five (5) routinely-used PFTs are in the range of parts per 10^{15} parts of air (i.e., parts per quadrillion-ppq) and this technology's instrumentation can measure down to those levels. The effectiveness of this technology is achieved both in terms of cost (very little PFT need be used) and detectability; for example, very small leaks can be rapidly detected. The PFT compounds, which are environmentally and biologically safe to use, have been commercially available as well as some instrumentation, but opportunities exist for commercialization of field-worthy sampling and analysis instrumentation and for providing leak detection services.

This paper will briefly describe the PFT technology and its commercialization and present some of the applications in transport and leak detection currently being studied and new applications being considered in the areas of safety and environmental concern.

2. PFT TECHNOLOGY

For this presentation, tracers are volatile compounds added to various substances for the purpose of tagging and tracking the course of that substance in the environment. The tracer vapors must be detectable at very low levels, part-per-trillion (pp 10^{12}) or less, not have any impact on health nor the environment, and be economically practical in the tagging of substances such as air, gas, liquids, and even solids.

The PFT technology consists of the tracers themselves, tagging techniques, samplers, and analyzers. A complete description of these items appears in ref. 1. A family of up to 5 PFTs have been used simultaneously in many tagging and detection applications in order to distinguish between sources. The PFTs used have essentially all come from the ISC Division of Rhone-Poulenc in England and cost about $150/kg. Another potential source in the U.S. is Air Products in Pennsylvania; costs and quantities available have not been ascertained. Finally, PCR Incorporated in Florida provides gram-quantities only, at about $1000/kg.

Sample collection for determining PFT concentrations in air or gas is by adsorption of the PFTs onto Ambersorb, a commercially-available adsorbent from Rohm and Haas Company and Supelco Incorporated, both in Pennsylvania. Passive samplers, produced by a local company near Brookhaven, and programmable, multitube adsorbent samplers have been produced by three companies in New Jersey--Gilian Instrument Corporation, Computer Control Corporation, and Bios International.

Analysis of the adsorbed sample is by electron capture detection-gas chromatography (GC). Brookhaven has built several Varian-based GC systems for users world-wide. A commercial company, John Booker and Company in Texas, has also supplied several systems following the Brookhaven concepts. Two other PFT analyzers are used routinely. The continuously operating perfluorocarbon sniffer (COPS) - ref. 2, developed to detect PFT-tagged electric blasting caps in clandestine explosives at airport environments (ref.3), is being commercially prototyped by the Vacuum Instrument Corporation on Long Island, New York; the COPS can be used to pinpoint leaking tagged fluids in real-time (less than 10 seconds). The other, the dual trap analyzer (DTA) - ref. 4, available in one commercial version from John Booker and Company, concentrates PFTs from an air sample for subsequent desorption and analysis on its internal GC system.

3. APPLICATIONS

The broad categories of applications include fluid transport and dispersion and leak detection and locating. Other applications such as an early fire detection technique, tagging petroleum products for identification, and a monitor of wear (tribology) in inaccessible spaces are being investigated.

3.1 Fluid transport and dispersion

Originally developed as an enhanced tracer technology to better validate atmospheric pollutant transport and dispersion models (ref.1), one of the first spinoffs was a PFT system for measuring air infiltration and ventilation in homes and commercial buildings (ref. 5). This technology can also be used to certify the performance of heating, ventilating, and air conditioning (HVAC) systems and a version can also be used as pre-fire detection system (ref. 6). Other fluids that are being tagged include water and gas injection into oil and gas reservoirs to improve our understanding of enhanced oil recovery processes (ref.7) and drilling muds for documenting crossflow between wells in subsurface media (ref. 8,9).

(i) Atmospheric tracing. Numerous uses of the PFT technology in atmospheric transport and dispersion studies over large distances, as well as in complex terrain, have been performed for improving predictive and forecast models (ref. 1, 10). The across North America tracer experiment (ANATEX) involved the periodic release of tracer from January through March 1987 with sampling out to distances of 3000 km (ref. 11) at concentrations down to 0.5×10^{-15} L/L of air. The origin of the haze in the Grand Canyon National Park will be investigated in 1992 with several tracers released from the southern California (Los Angeles) region, as well as from the Mohave Power Project in order to attribute the degradation of visibility in the park to specific sources.

(ii) Oil and gas reservoir tracing. Norwegian oil and gas reservoirs were successfully studied in the North Sea injecting just tens of grams of PFTs into millions of cubic meters of gas (ref.7). A new tracer study of several reservoirs in the Elk Hills Naval Petroleum Reserve near Bakersfield, CA, was started this summer. Already, engineers have observed transport to production wells that was unanticipated. By using multiple PFTs in the same injection well, differences in arrival time at the production wells infers estimates of residual pore oil in the transport path.

(iii) Tracers for building ventilation studies. Understanding and measuring air flow within and into and out of buildings and homes is important both for energy conservation and indoor air quality assessments. The PFT technique for inexpensively documenting building ventilation performance (ref. 5) is being used worldwide (ref. 12). In addition to determining air flows, when also measuring indoor pollution levels, the PFT technology can be used to determine pollutant source strengths by zones and thereby aid in locating and pinpointing the unknown pollution source and its magnitude (ref. 13).

3.2 Leak detection and locating

The PFT technology can be useful in the electric utility industry by providing improved leak testing and on-line leak monitoring of equipment in power stations (ref. 14, 15). Efforts are currently directed to developing an approach to locate fluid leaks in underground power transmission cables used in urban environments (ref. 16, 17).

Application of the technology for leak monitoring and certification in manufacturing processes is just beginning and shows strong potential. A commercial company is planning to market a PFT instrument and systems to validate the leak integrity of manufactured components such as heat exchangers in air conditioners and pressure vessels such as fire extinguishers. Modules for NASA's future Space Station Freedom can be leak certified with PFT technology and the potential exists for rapid screening of the seal integrity of packaging in the food industry.

The most important aspect of this technology may be its enormous potential to improve the environment by its use for detecting and pinpointing leaks in gasoline, fuel oil and other underground storage tanks and natural gas pipelines.

(i) Cable fluid leak detection. The entire Consolidated Edison of New York underground high voltage cable system has about 650 miles of piping containing 6 to 7 million gallons of dielectric fluid. In cooperation with Con Ed, the Electric Power Research Institute (EPRI), and the Empire State Electric Energy Research Corporation (ESEERCO), since 1987, Brookhaven has been studying the use of PFTs dissolved within the cable fluid to locate and pinpoint subsurface leaks. In the summer of 1988, a 25-gallon simulated total leak was located to within a one-half block by passive samplers mounted on lamp poles along Union Turnpike in Queens (cf. Fig. 1). Note that the highest concentrations of the PFT (ocPDCH) in the air (about 50×10^{-15} L/L) occurred near the subsurface leak (the X). Boreholing and sniffing with the COPS (ref. 2) pinpointed the leak location to within a few feet.

In the summer of 1990, a second test was conducted. Con Ed crews released just 5 gallons of tagged fluid as a simulated leak at about 0.3 gallons/h; Brookhaven was challenged to find the "unknown" leak site along a 2-mile stretch of Union Turnpike. With the van-mounted DTA collecting air over 6-min intervals, each analysis covered about a 10-block region. As shown in Table 1, the first analysis of ocPDCH was 0.33 fL/L (parts per 10^{15}), essentially ambient background for this PFT. The second 10-block region showed almost a 100-fold increase, indicating the leak site had been passed. Subsequent traverses with the van narrowed the location to within one-third of a block in about 4 hours, while the COPS was sniffing for "hot spots" along the pavement. Boreholing over the next hour narrowed the leak location to within 1 foot of the actual site. Obviously, this same concept and approach could be applied to gas leak patrols and surveys.

(ii) Condenser air inleakage. Excess air inleakage into power station systems can degrade low pressure turbine performance and lead to excess dissolved boiler-water oxygen with subsequent long-term tube corrosion. The Long Island Lighting Company is sponsoring a demonstration of the use of

POLE CATS 8/3 - 8/11/88 (fL/L of ocPDCH)

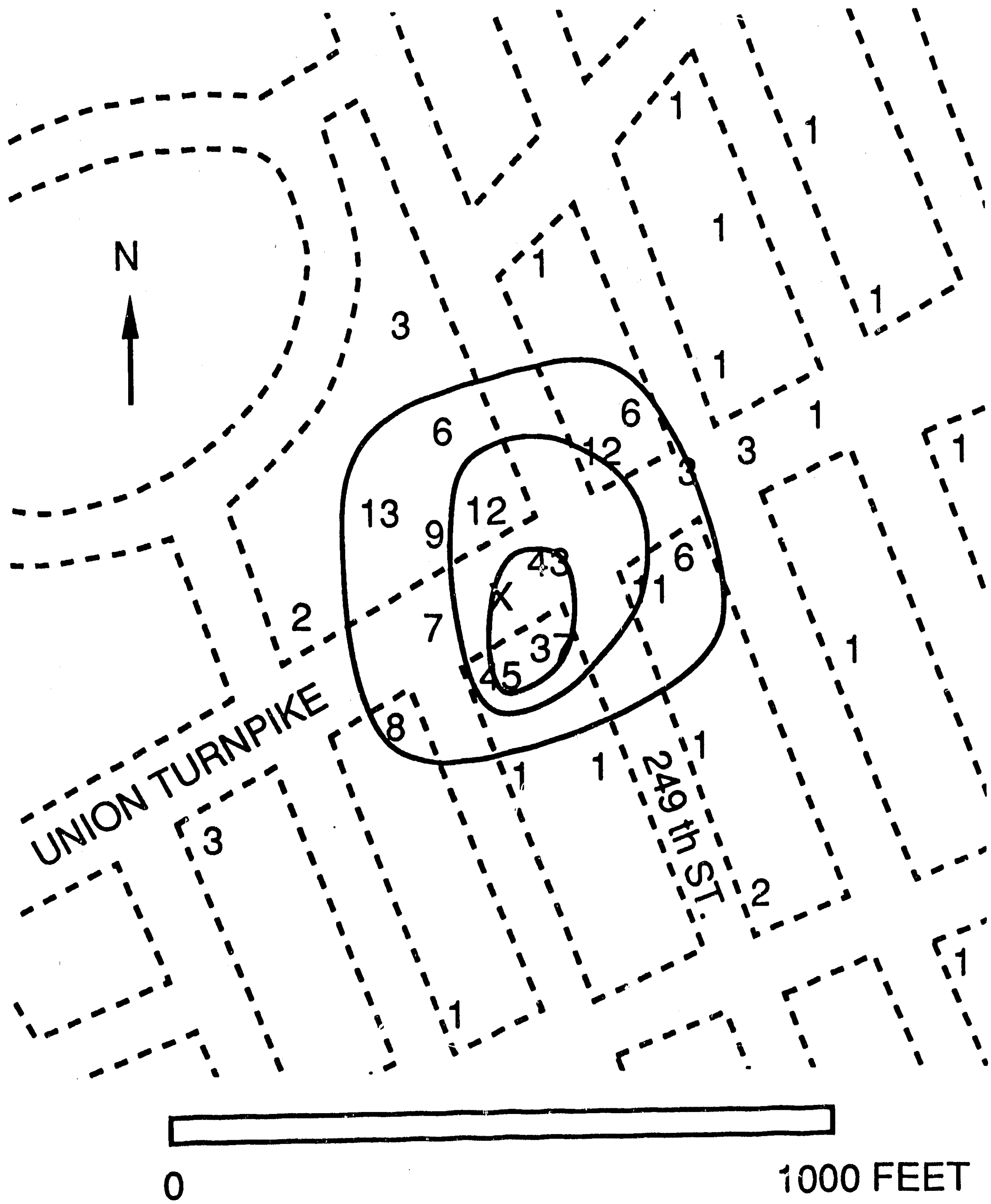


Figure 1

Table 1

	ocPDCH fL/L	PMCH fL/L	Action
U.P.@KILDARE>180	0.33	4.29	
180>189	17.62	5.10	Traversing
189>199	0.52	4.29	East Bound
199>CLEARVIEW	0.43	4.14	
CLEARVIEW>196	0.38	4.14	
196>185	2.14	4.10	Traversing
185>U.P.&80RD	57.14	6.19	West Bound
U.P.>KILDARE	0.43	3.86	
187>186	6.57	5.38	
185>184	302.90	14.05	Locating 1
184>183	36.57	5.57	Block by Block
183>182	2.29	4.10	West bound
182>181	0.38	4.05	
181>180	0.48	4.00	
182>183	0.33	4.24	
183>184	0.43	3.95	Locating 1
184>185	5.67	4.29	Block by Block
185>186	3.33	3.95	East bound
186>187	5.14	4.24	
187>188	7.43	4.38	
184>183	21.57	4.86	Locating 2
183>182	0.71	4.14	Narrow range
182>181	0.48	3.90	West bound
GO TO 186	5.29	4.29	
186	23.48	4.81	
186>185	50.00	5.86	Locating 2
185W	153.19	9.43	Narrow range
185<>184	41.95	5.29	West bound
184	17.10	4.33	
184<>183	5.48	4.24	
183 TO EXXON @178	0.33	3.67	
EXXON TO 185	4.43	4.19	
TO 185	141.86	8.95	
@185	239.71	11.90	
184.67	164.95	9.48	Localizing
184.67	295.43	14.24	within block
184.33	113.48	7.86	
184.33	123.81	8.38	
184	4.24	4.05	
184	0.86	4.00	

the PFT technology to provide on-line quantification of total air inleakage as well as the ability to determine the magnitude of the leaks in up to three or four levels within the plant. Fig. 2 shows how load (squares) at the 365 MW Northport Station Unit 4 varied over the 4-day test period and how total air inleakage (crosses) varied inversely with load. Total air inleakage, which ranged from 30 to 41 cubic feet per minute, was much higher than the EPRI guideline of 1CFM per 100 MW. The highest average air inleakage by floor occurred in the mezzanine section (24 ± 8 CFM), then the turbine deck (9 ± 3 CFM), and least on the ground floor (5 ± 2 CFM).

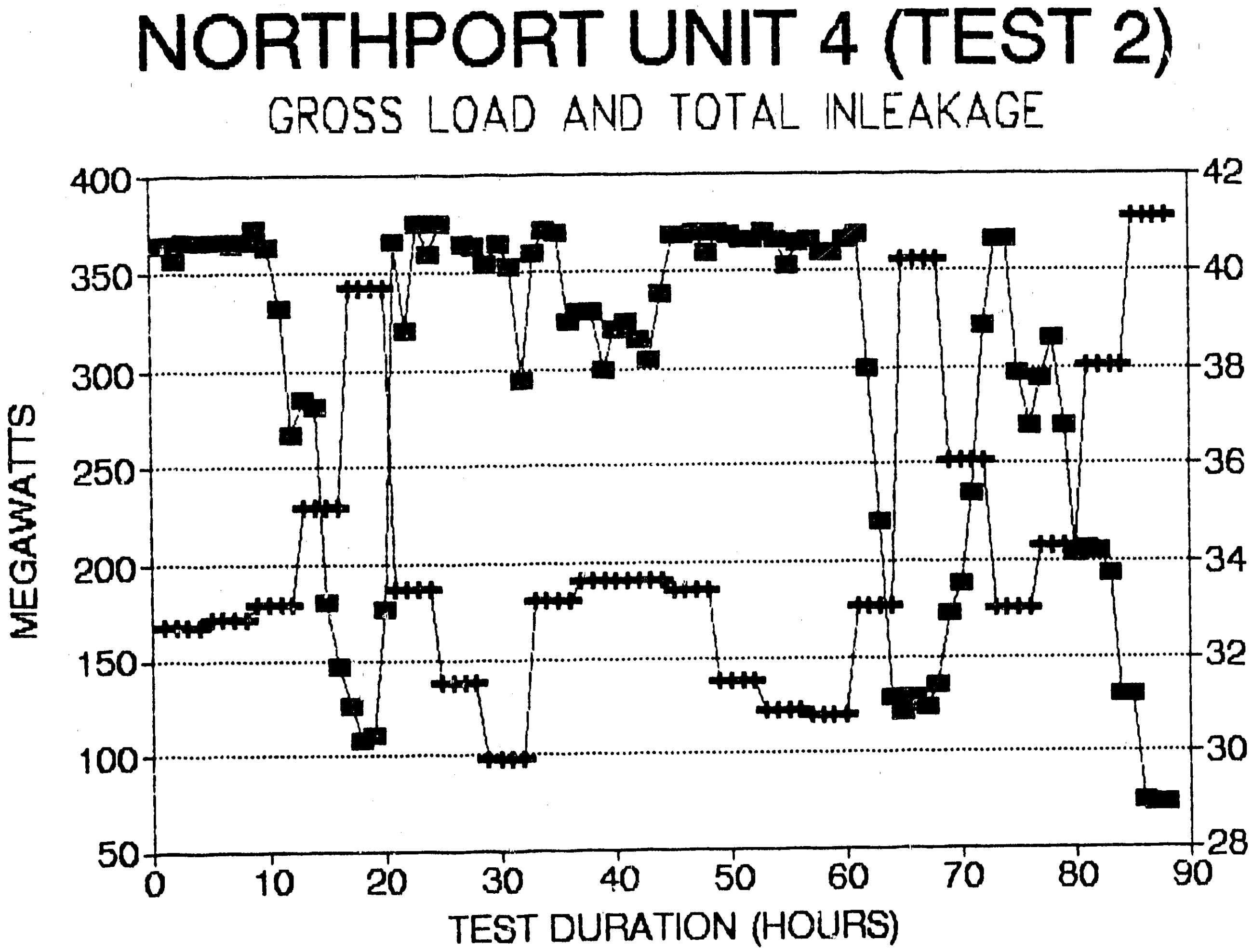
(iii) Stator bar cooling water leaks. Leakage of cooling water from the copper strands of stator bars has been shown to build up under the insulation on the bars when a generator is taken out of service for repairs or routine maintenance; such water ingress will cause failure of the bar to meet electrical tests or could cause failure during operation. Brookhaven has been working with Con Ed on locating and pinpointing stator bar leaks in bars that have failed and were removed from service (ref. 18,19). Testing with the insulation in place and then removed to the bare metal has shown that there is a good probability that any bar in service that has a leak in the copper strand will manifest itself in a signal even with insulation in place. This was confirmed by the in situ testing performed at the Labadie Station of Union Electric in St. Louis (ref. 15).

(iv) Underground storage tank testing. UST testing is performed both hydraulically and with tracer. The Tracer Research Corporation (TRC) in Arizona has developed commercial procedures to determine the integrity of tanks. A PFT was added at about 1 part to 100 parts of the TRC tracer for tagging tanks in 7 cities in Massachusetts. Table 2 compares the number of soil probes around each site found to have the TRC tracer versus the PFT and the approximate maximum signal for each. Whereas the TRC tracer indicated only two of the 7 sites had definite leaks (8 of 8 probes and 6 of 7 probes at Revere and Lexington, respectively), the PFT technology implied that there was some degree of leaks in all 7 locations.

Fuel oil pipelines also are subject to federal, state, and local agency regulations. Many electrical peaking units on Long Island are oil-fired gas turbine systems with the No. 2 fuel oil lines underground; since there is currently no acceptable standard for certifying their integrity, LILCO is faced with the mandate to replace all such piping with properly contained systems. Brookhaven will be performing a demonstration for LILCO using the PFT technology to certify the leak tightness and to develop an acceptable test protocol.

(v) Hermiticity testing of electrical components. Using the real-time (5-second) analyzer (COPS) which can detect PFT concentrations as low as 1×10^{-11} mL/mL and the concentrating analyzer (DTA) which can measure down

Figure 2



NORTHPORT UNIT 4 (TEST 2)
GROSS LOAD AND TOTAL INLEAKAGE
MEGAWATTS
CU.FT./MIN.
TEST DURATION (HOURS)
400
350
300
250
200
150
100
50
42
40
38
36
34
32
30
28
0
10
20
30
40
50
60
70
80
90

TABLE 2

UST Tracer Results
(Comparison of TRC with PFT Technology)

Site	Total No. of Probes	No. of Probes with Tracer		Maximum Found (multiple above LOD)	
		TRC	PFT	TRC	PFT
Milton	3	0	2	---	20,000
Revere	8	8	8	1,000	4,000
Freetown	7	0	6	---	600
Hanover	5	1	3	100	4,000
Concord	8	0	8	---	2,000
Lexington	7	6	7	20	4,000
Peabody	6	1	6	4	300

to 1×10^{-12} mL of PFT--separately quantifying up to 4 PFTs in a 6-min cycle time or less, experimental leak-rate design concepts were proposed for determining the effectiveness (hermeticity) of the seal of semiconductor devices with internal cavities from 0.01 to 1 mL (ref. 20). The concept is based on pressurizing with PFT-containing air for 60 seconds, purging with PFT-free air for 60 seconds, pressure pulsing with air or He to extract the PFT leaked into the internal volume and finally detecting the PFT vapor concentration with one of the two instruments. The COPS analyzer can quantify gross leaks from 1×10^{-7} to 1×10^{-3} mL/s in just 3 minutes for the complete test. The more-sensitive concentrating analyzer (DTA) can quantify fine leaks from 0.2×10^{-8} to 1×10^{-3} mL/s in just 12 minutes for the complete test; the latter procedure includes two determinations per test.

(vi) Module leak certification for Space Station Freedom. In January 1991, a demonstration of the PFT technology to rapidly and quantitatively determine the leak tightness of future NASA space station modules was performed at the Marshall Space Flight Center in Huntsville, Alabama (ref.21). The technique may replace the currently proposed pressure decay approach which was limited to a leak specification of about 2 mL of air per second. With the PFT technology, a leak rate of 0.002 mL/s would require less than 1 hour to quantify versus decades by pressure decay; the PFT approach can ensure leak tightness down to less than 1×10^{-4} mL/s in less than 1 day.

3.3 Future applications

Potentially large markets exist for the use of the PFT technology in other applications including:

- Early warning pre-fire detection
- Gas transmission and distribution line leaks
- Gas leaks in homes and buildings
- Integrity of food packaging
- Petroleum product manufacturer identification.

(i) Pre-fire detection. Sensitive electrical equipment and computer facilities, nuclear reactor buildings, NASA space stations, and other items may benefit from an early warning system to detect the precursor to fire, namely, heat from electrical component failure. Brookhaven has demonstrated that a PFT dissolved into an electrical insulating paint deposited on electrical components emitted no PFT vapors at room temperature. Subsequent warming caused the PFT emission rate to increase rapidly with temperature and the process was reversible (ref. 6)

(ii) Natural gas leak detection. In the same way that PFTs have been used to tag dielectric fluids in buried cables, a PFT can be added to natural gas at a concentration of about 0.1 ppm. Only $30/month of PFT would be needed to tag one 10,000 CFH distribution line, but the enhancement in leak detection over that of looking for the methane itself in the natural gas is 1,000-fold or more. Using the passive sampler developed for ventilation determinations, the integrity of gas systems within the home could be readily surveyed. An on-line home monitor to detect the PFT added to gas, similar to a smoke detector unit, may be feasible.

(iii) Food packaging integrity. Refrigeration of food retards spoiling from microorganisms and oxidation processes as a result of leaks in the packaging. If packaging containment can be improved, costly refrigeration and concern for the environmental impact of refrigerants could be reduced. PFTs can be prepared as emulsions in water (ref. 9) or dissolved in ethanol. Less than 1 microliter of the carrier fluid would need to be added to the food prior to packaging in order to scan the packaging for seal integrity and/or penetrations.

(iv) Petroleum product identification. The high affinity of PFTs to dissolve in petroleum fluids makes them suitable for tagging and subsequent product identification. Loss of a tagged product due to a shipping or transport accident would more readily allow the product to be followed and later cleansed from the environmental media. Liability as to product identification could be established. The use (authorized or unauthorized) of petroleum products within other products could be ascertained.

CONCLUSION

The PFT technology has been developed over the last 15 years at Brookhaven. The tracers have been used to tag various media for transport and dispersion studies in the environment and for certifying and pinpointing fluid leaks in many environmental and processing situations.

Although some instrumentation has been commercialized, the need exists for several instruments to be commercially prototyped and manufactured according to specific end-user requirements. The opportunity also exists for establishing commercial services based on the technology.

The potential for new applications and markets is significant in the areas of leak certification and monitoring and in special applications such as early fire detection.

ACKNOWLEDGMENT

Many have contributed to the development of the PFT technology and are as well responsible for the success of the numerous applications being explored within the Tracer Technology Center at Brookhaven.

Appreciation is expressed to all my colleagues in the Center and to those in other government and private offices and laboratories who have played a key role in inspiring our work.

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