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Analyzer to Detect Perfluorocarbon Tracers for the Tag,
Track and Location Program**

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Introduction

The Tag, Track and Location System (TTL) Program is investigating methods of tracking an asset using perfluorocarbon tracers (PFT). The success of any TTL method requires sound detection/location instrumentation. Tracer Detection Technologies Corp (TDT), through a contract with the Office of Naval Research (ONR), is investigating different detection systems. The detection systems generally fall into two categories; proximity detectors and standoff detectors. Proximity detectors, as the name implies, need to be in close proximity (e.g., meter to 10's of meters) to the PFT source. Standoff detection searches for the PFT from a greater distance away from the source (e.g., 100's of meters to kilometers). Gas Chromatographs (GC) are generally considered a proximity detection systems, but in the case of PFTs should be considered for both proximity and standoff detection with the caveat that in standoff use the GC needs to be somewhere in the PFT plume, i.e., generally downwind of the source. With a properly sized PFT source, the right GC can afford fairly large standoff (distance from the source) distances; 100's of meters to kilometers downwind. Brookhaven National Laboratory (BNL) has such a GC system and offered to demonstrate the CDTA for TTL as a no cost addition to the TDT-TTL project, of which BNL was a participant.

BNL is a leading authority on the sampling, collection, release and detection of PFTs. In addition, the BNL team has extensive background in atmospheric dispersion, the application of PFTs to such studies and the development of applications utilizing PFTs such as building infiltration measurements, control room integrity determination, leak location and environmental investigations. This experience and expertise is essential in developing any PFT application where dispersion, dilution and overcoming environmental conditions and interferences are integral to success. BNL has developed sophisticated gas chromatography methods and instruments that allow detection of up to seven PFTs at part per quadrillion levels (10^{15}) with sample times as short as 60 seconds. The Continuous Dual-Trap Analyzer (CDTA) was developed for leak hunting applications and can continuously sample the air for PFTs without interruption. Sample time can be as short as 60 seconds. The CDTA has been extensively used in the commercial sector to detect PFTs that have been introduced to leaking buried dielectric fluid-filled cables or leaking subsurface gas lines. The PFTs travel through the cable or pipe until they reach the leak site. PFTs then escape into the surrounding soil and permeate/diffuse to the surface where they can be detected with the CDTA. Typically a cable is tagged with ppm levels of PFTs resulting in ppt to ppq concentrations in the air at the leak site.

The CDTA is proven to be rugged, reliable and has a proven track record of successful leak location. The application of the CDTA to PFT detection for TTL is identical to application for leak detection. The CDTA operator has a general idea, with a few miles of

roadway, where the leak is located, but no specific knowledge of the location (it can be any where along the road). The CDTA is mounted in a Chevy Astro Van (see Figures 1 and 2) and is dispatched to the field. In the field the van is driven at nominally 15 mph along the road. The CDTA continuously samples the air outside the van (via a ¼" plastic sample tube stuck out a side window) until a positive detection occurs. The van then covers the road section where the detection occurred at a slightly slower pace to pin-point the area where the leak is and to direct soil probe samples. The soil probe samples take soil gas samples every 10 yards or so and the samples are analyzed on the CDTA. The leak can be located to within a few feet in 95% of the cases. To date the CDTA has been successful in every leak hunt performed by BNL. One interesting case was a leak hunt that resulted in repeated negative detections. The confidence in the CDTA forced the utility to recheck its "plumbing" which lead to the discovery that a valve was turned that shouldn't have been so that gas was being diverted rather than leaking (the pressure drop was due to this diversion of the gas to another line).



Figure 1 The Brookhaven Continuous Dual Trap Analyzer for Perfluorocarbon Tracer Detection

For TTL application, a tagged item or person is known to be in a general area and can be located by detecting the PFT emanating from the tagging source. The CDTA can be deployed in the area and by sampling in a grid fashion (starting on the downwind side of the area of interest) can easily find even very small sources. The CDTA is a perfect match for this application and the leak hunt use basically a simulation of Track and

Locate. No other PFT detection technology has the detection sensitivity, proven track record and ruggedness of the CDTA. For these reasons, BNL offered to demonstrate the CDTA for TTL as a no cost addition to the TTL lidar demonstration project. This report details the demonstration scenario and results.



Figure 2 The BNL Van used to Transport the CDTA for Tracking and Locating a PFT source

Demonstration

For the TTL demonstration at BNL, the CDTA performed in three different PFT detection scenarios. The CDTA was left in its current leak hunt mode which had a sampling interval of 90 seconds. While the CDTA can and has been used with 60 second sample intervals, BNL did not reprogram the CDTA to use the faster times since the van is “on call” for leak hunting and this was a “free” demonstration designed to show the ability of the unit and the principles utilized in PFT location. Two of the demonstration scenarios were performed on the TTL demonstration day, the third was performed on two separate days prior to the TTL demonstration and was not repeated at the TTL demonstration due to time constraints.

The main demonstration involved the CDTA remaining stationary and detecting a tagged vehicle driving by at 30 mph. This simulates a checkpoint or chokepoint detection. Allowing a 30 mph (or greater) drive-by allows the detection system, the CDTA, to

remain clandestine. The speed of the drive-by was set at 30 mph as that is the BNL site speed limit. Faster drive-by speeds are possible. The CDTA was parked on the roadside along an east-west roadway on the BNL site. A van was tagged with an INEL-18 small source (75 uL/min vapor) and was then driven by the CDTA at 30 mph. The tagging was accomplished by opening the source in the van and waiting ~5min before beginning the tests. The van drove by first from the east with the windows closed and vents closed and then from the west, also with windows and vents closed. Following this the van repeated the two 30 mph drive-bys, but with the vents opened and the fan on. Obviously, this case also demonstrates the inverse situation; where the CDTA van drives by a suspect area/vehicle at 30 mph to determine if a tagged asset is present.

The second scenario was a “walk by” where a TDT team member had a patch taggant source adhered to his shirt. The source was an INEL source containing PMCH taggant and released the PFT at a rate of 15 to 30 uL/min vapor. The team member stood by the CDTA with the patch unopened without detection by the CDTA. He then walked across the street approximately 20 to 25 meters from the van and initiated the PFT release by breaking the seal of the patch source. This allowed the PFT to begin emanating from the source. After two CDTA sampling intervals he moved further away from the CDTA until he was ~50 meters from the van and then moved away again to ~75 meters from the van.

The final scenario was a search for a small hidden source and this demonstration was not conducted for the visiting group due to time constraints. This task was performed on two separated days prior to the August 27th TTL demonstration. Two variations were performed; in the first, 2 uL/min vapor sources were placed at three locations along a nominally ¼ mile long section of road located on the BNL site. Each location had a different PFT taggant source and the locations all had different orientation to the winds that day. One was located perpendicular to the wind on the upwind side of the road; a second was located on the upwind side of the road but such that the wind swept across the road at approximately a 45 degree angle and the third source was located on the downwind side of the street perpendicular to the wind. The CDTA van was then dispatched to the area and began a slow survey of the area to find the sources. The second variation was a single 10 uL/min source placed along the same roadway and was oriented parallel to the wind. In both cases, the CDTA team had no knowledge of the source locations other than they were along the road they were sent to.

Results

The results of the drive by tests were all successful and the source strength and low, 30 mph speed combined to give a signal that “railed” (off-scale reading) the gas chromatograph. The chromatograms of the drive-by test are given in Figure 3. There are five large peaks present. The first represents a team member from the walk by coming up to the van while wearing the patch source (see following for walk-by test results). The source was removed and located a distance downwind so that it would no longer interfere with the testing. The next four large peaks (#2-#5) represent the tagged van driving by at 30 mph at 90 second intervals. All of the peaks are near or greater than 1 volt and as can be seen three railed the instrument (see flat tops on peaks). Normally a peak of 30 to 60

mV is considered a good positive detect. The “hits” from the drive by are more than an order of magnitude greater than this. The east bound direction, which bring the van closer to the CDTA (near lane) and the west bound direction (far lane) showed no real differences, both railing the instrument. Having the windows closed and vents closed did not inhibit the detection of the PFTs and the drive by with the vents open and fan on was similar to the drive by with the vents closed, again both railed the instrument. We did not drive the van by with the windows open as this seemed trivial given the signal strength seen with the windows closed. The CDTA clearly could identify when the tagged vehicle went by and had no reading when untagged (regular site traffic) passed by.

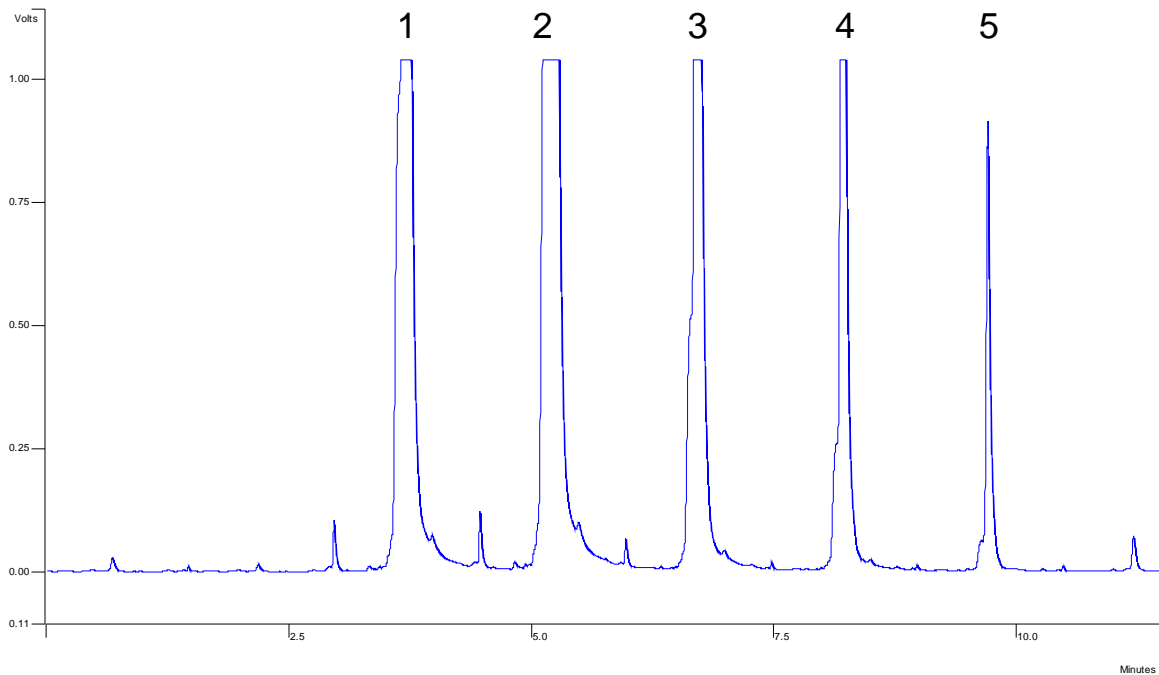


Figure 3 Chromatograms from the BNL CDTA during 30 mph Vehicle Drive By

The chromatograms for the walk by scenario, where PFT was released via a taggant patch placed on a TDT member, are shown on figure 4. The chromatogram peaks (PMCH) of interest are labeled 1 to 5. The PMCH peaks #1 and #2 are normal background (no added PFT) peaks (as are the previous two cycles recorded on the chromatogram, but not labeled). Peak #1 represents the TDT team member standing directly in front of the CDTA air inlet port with the taggant patch unopened (as expected, no response was indicated). Peak #2 represents the sample taken with the TDT member standing ~20 to 25 meters distance from the van and then activating the taggant patch. As one might expect, no PFT detection occurred at that moment and the chromatogram indicates a normal background response. Peak #3; the next CDTA trap cycle (~20-25 meter distance) indicates the first response following the activation of the PMCH patch. Peaks #4 and #5 show increased PMCH responses even though the distances from the van are increasing to ~50 and ~75 meters, respectively. Once the TDT member left the area (downwind), the signal returned to background levels.

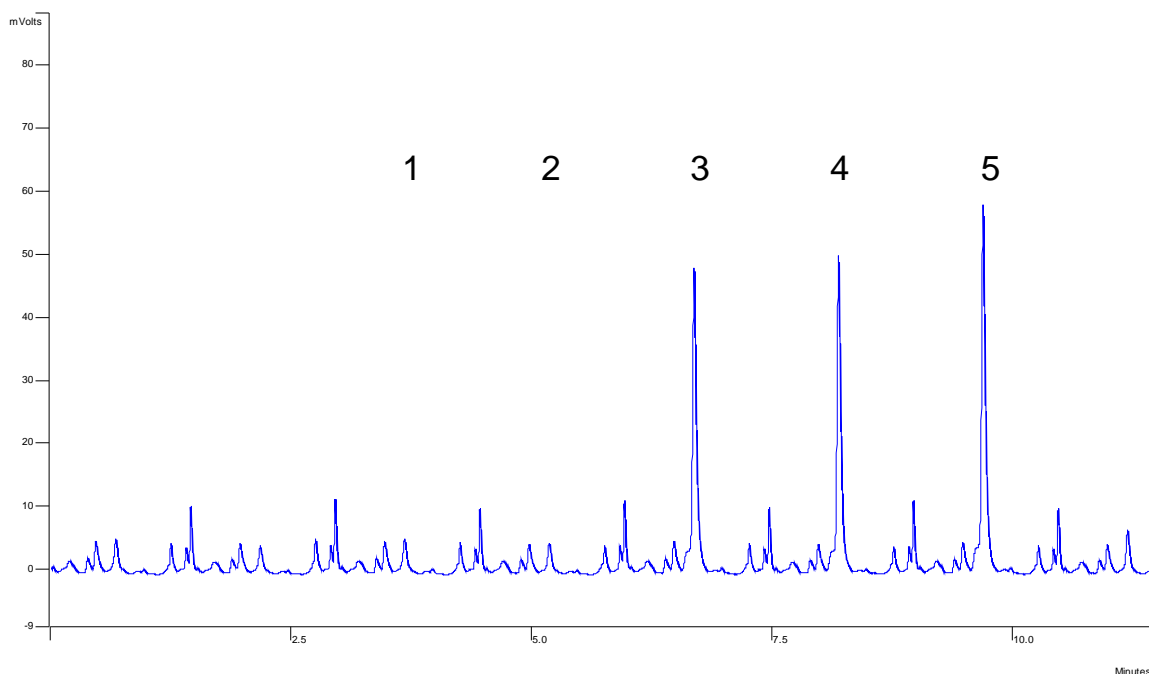


Figure 4 Chromatograms from the BNL CDTA during the Walk By

The source used was deemed small by TTL program use, but was considered fairly large by CDTA/BNL standards. For leak hunts, we often place a 2 uL/min source on a telephone pole along the street and use this known PFT release rate as a calibration to size the leak (estimate how big the leak is from the ratio of the PFT from the cable/pipe to the PFT from the telephone pole source). The source is normally “visible” to the CDTA at 50 meters.

In the final scenario, the search for the hidden small source, the CDTA was able to find all three of the 2uL/min sources, including the downwind source, in about 45 minutes. The time to find the sources was greatly exaggerated by the long sample time (90 seconds) and highlights the need for faster sampling and faster analysis. Finding the three general areas of the sources (the 100 meter stretch of road that the source was on) took about 15 minutes. The slow honing in on the sources (about 1 ½” x ¾” clear bottle) placed on the side of the road took longer as the van had to wait 90 seconds at each halfway point (the 100 meters of road is sampled in two halves then the positive half sampled in two places until the van pinpoints the source). The CDTA gets positive detects along a large part of the road. During a search, the magnitude of the hits as the van approaches the source increases and then decreases again as the van moves away from the source. The PFT peak height on the CDTA output rises and falls and the source is closest to where the largest peak height occurs.

The larger source, a 10 uL min vapor source placed parallel to the wind was found in about 20 minutes. This case was more difficult and required the CDTA team to use their experience in leak detection to interpret the results and expedite the search process. The positive hits for PFT seen by the CDTA occurred slightly downwind of the source. Since the wind was parallel to the road, the PFT emanating from the source plume was blown

slightly down the road before it was “in the road” where the CDTA would pick it up and get a detection. The peak heights seen on the CDTA did not rise and fall as in the case of cross winds or light/calm winds. Instead the peak height remained at background levels and then suddenly the peak height was off scale and remained high a few samples past the source. The signal strength was sufficient to saturate the CDTA when close to the source. The CDTA team realized the wind was strong and parallel to the road. Based on their experience they knew the hit would occur slightly downwind of the source and that the source should be slightly upwind of point that the CDTA peak failed. They found the source about 25 meters upwind of the point where the largest peak was observed.

Conclusions and Discussion

The CDTA performed exceptionally well in all of the test scenarios. The parts per quadrillion (ppq) sensitivity meets the demands of the TTL program both for proximity detection and standoff detection. The drive by at 30 mph was accomplished using a realistically sized source, i.e., one that can be both covert (small, discreet) and long lived (weeks to months). Without the ppq detection limit, a source of this size would not be practical. The walk-by scenario demonstrated that the CDTA could be 50 to 100 meters from a small source and still result in a large detection signal. A source of the size used in the demonstration, is detectable by the CDTA a few hundred meters downwind. Finally, the CDTA demonstrated the ability to use GC location in a search and find mode. This is precisely what the system was designed for, albeit, the “asset” was a leaky pipe/cable.

The sample and analysis time of the CDTA is a problem for TTL applications. The demonstrated 90 second sample time (60 second minimum) and 4 minute delay for results is insufficient for choke point detection and inefficient for search and locate applications. While the CDTA takes samples continuously, unlike the operation of some GC systems that have recovery time between samples, the time delay to receive the output and the long sample collection period limit an excellent instrument from being a superb instrument with wide spread TTL applicability.

Recommendations

The CDTA must be optimized to minimize both sampling and analysis time, and should be made smaller and more portable. BNL has conceptual designs that should allow a GC system with 15 second, continuous sample times and a 30 to 60 second analysis time. At the same time, BNL has been developing PFT systems for other programs and has been asked about designing a rack mounted unit for aircraft deployment. Such a unit will meet the requirements for TTL applications. Its small size would make deployment simpler and a rack-mounted, aircraft approved unit could be flown in a helicopter making tracking and location very efficient.

BNL had worked with several commercial companies over the last few decades developing GC/CDTA units. This relationship would benefit the TTL program by allowing rapid development of prototype units and fast turn around to a commercial unit. A two or three year development program is needed to bring the CDTA to TTL

requirements. Since the unit already fits comfortably in a mini van and function is more important than form, it is recommended that the first part of a development program be used to make the system faster and, if funding allows, the second part to make it smaller.

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