Perfluorocarbon Tracers

Introduction

Perfluorocarbons have a number of features that make them uniquely useful as tracers, including very low limit of detectability, very low toxicity, very low background levels and non-flammability. A number of compounds are available; each is uniquely identifiable, allowing a single experiment to track the progress of material from a number of sites. Perfluorocarbon tracers are not radioactive.

Applications

There are broadly four ways that tracers can be used, depending on the phase of the tracer; liquid, aqueous solution, non-aqueous solution and gaseous. Although PFTs are not miscible with oils, they have sufficient solubility that they can be dissolved in small quantities in oil, and furthermore they are unlikely to be extracted from the oil into water. PFTs are volatile, making them ideal also as gaseous tracers. However, they are not suitable as tracers in water, as they have very low solubility in water (ca. 10 ppm). Liquid tracers are specifically detecting the leaking material itself, so are also not applicable to PFTs.

Tracking Air-borne Pollutants

This is an area in which Brookhaven National Laboratories in the US are particularly big, and for example they have released five PFTs around Madison Square Gardens to simulate the effects of a terrorist attack involving toxic gas.[1] Numerous experiments have been performed since the 80's across the world.[2] The two most important issues are that the background concentration of the tracer is very low and the sensitivity very high. The extremely high stability of PFTs means that with each experiment (and indeed every use of the compound) the background concentration will rise ever so slightly, and eventually that particular PFT will no longer be usable as a tracer.

Ventilation systems

This is another major area for Brookhaven, using essentially the same concepts as before. The purpose is to test whether buildings have adequate ventilation, and gases like carbon dioxide and carbon monoxide are not building up (which is becoming more of a problem as people try to reduce heat losses).

Tracers in oil fields

Tracers of one kind or another have been used for a long time to map out oil fields, and PFTs are being used increasingly to replace the traditional radioactive tracers.[3]

Typically, the PFT is introduced at one site in the oil field, and its presence in the extracted oil at other sites allows the oil reservoir to be mapped.

Leak detection

Leak detection in general is a growing market, as companies are facing high costs from government agencies and litigation when leaks occur. It is more and more important that leaks are discovered as fast as possible and located as accurately as possible.

Applications include cables, pipelines, landfill waste, underground storage tanks.[4,5,6,7]

Besides using other chemicals (which are discussed later), leak detection can also be done on an inventory basis (such as noting that the flow at the end of the pipeline is less than that at the start), using the leaking material itself as a tracer, perhaps with conductivity or other probes, depending on the material.

Electrical cables are often laid in liquid filled tubing for cooling (to aid heat transfer) and insulation. If a small amount of PFT is added to the liquid medium, any leak can be quickly found. A portable analyser in a van is driven along the pipeline. When the vicinity of the leak has been found, tiny bore holes are drilled, and the leak location pinpointed to within a few feet. Leaks are found much faster, and without having to dig numerous exploratory holes.

Taggants for Detection

Small quantities of PFTs can be incorporated into various items to allow those items to be detected. The technology involves encapsulating the PFT in a microcapsule which slowly releases the PFT over a long time (up to 30 years, depending on the application). Although the amount of released PFT will be very, very small, nevertheless, PFTs will still be detected as the limit of detection is so very low. The use of these taggants would be in items associated with criminal activity, such as explosives and money, including ransom money (they have been successfully used to track ransom money in Mexico[8,9]). Detectors at strategic points would notice relatively high levels of PFTs as, for example, a terrorist was bring a bomb on to a plane or a criminal carrying a suitcase full of cash. One wonders how effective a sealed container would be in containining the PFT, but workers in the area have considered and tested this to some extent.

Taggants for Identification

Identification taggants could also be used in explosives; a particular ratio of PFTs would be unique to a certain explosive and manufacturer. In the event of an explosion, the PFT residue can be tested, and the source, batch and date of the explosive determined. This seems to have been a big topic around 1980, but appears to have run into problems due to the explosives manufacturers wanting to keep anonymous for fear of being sued.[3] However, the principle is good and could be reality applied to other systems

Sampling

For air-borne tracers, the PFT is typically absorbed on to a substrate (eg Carboxen-569, Ambersorb). This could be active, during which air is pulled over the substrate, or passive, where natural diffusion of the air is relied upon.

Detection

A typical process then involves trapping at low temperature the desorbed sample gases to refocus them. The trap is then heated to 300° in 4 seconds, quickly releasing all the material in one slug. This passes through a pre-column, the short and long retained components are removed by valve switching, while the medium retained samples are mixed with a carrier gas and hydrogen. This is passed over a palladium catalyst which reduces the organics, dried (over Nafion), and passed on to the GC column.[10]

Headspace analysis is also used for soil samples.

GC runs times seem to be just a few minutes, and PLOT columns seem to popular. The PFTs are detected using an ECD or MS (negative chemical ion) detector. Detection is at levels of as low as 1 to 10 parts in 10^{15}.

More Information

Although F2 Chemicals Ltd manufactures PFTs, we have no direct experience in their use, and those interested in learning point might like to look at these web sites:

Atmospheric Chemistry Research Group at Bristol University (UK)
http://www.bris.ac.uk/chemistry/research/acrg/current/trace.html

Tracer Technolgy Center at Brookhaven National Laboratories (US)
http://www.ecd.bnl.gov/TTC.html

Institute for Energy Technology (Norway)
http://www.ife.no/main_subjects_new/petroleum_research/tracer

References

1 – “Anatomy of a Test on Terror”
http://www.ecd.bnl.gov/news/Newsday_03_15_05.pdf
2 – “Use of Project MOHAVE Perfluorocarbon Tracer Data to Evaluate Source and Receptor Models”
http://www.awma.org/journal/ShowAbstract.asp?Year=2000&PaperID=115
3 – “Materials and Methods”
http://www-odp.tamu.edu/publications/tnotes/tn28/c5_2.htm
4 - “Detection Of Interstate Liquids Pipeline Leaks: Feasibility Evaluation”
http://www.ecd.bnl.gov/pubs/BNL65970.pdf
5 – “Monitoring Subsurface Barrier Integrity Using Perfluorocarbon Tracers”

http://www.pubs.asce.org/WWWdisplay.cgi?9802323

6 – "Using Gaseous Perfluorocarbon Tracers To Characterize Leak Pathways In The Below Grade Ducts Of The Brookhaven Graphite Research Reactor"

http://www.wmsym.org/Abstracts/2001/10A/10A-17.pdf

7 – "Leak Detection for Landfill Liners"

Review of different technologies

http://clu-in.org/products/intern/leaklnfl.htm

8 – "Vapor Detection Of Trafficking Of Contraband Money"

http://www.ecd.bnl.gov/pubs/BNL62834.pdf

9 – "Identification and Testing of Available Sensors for the Detection of Perfluorocarbon"

http://www.ncjrs.org/pdffiles1/nij/grants/197719.pdf

10 – "Tracer analysis"

http://rem.jrc.cec.eu.int/etex/24.htm