TDTS 29

VOC air monitoring technology and its application to contaminated land

Summary

In this Application Note we summarise developments that allow sorbent-tube-based sampling technology to be used to monitor volatile organic chemicals in contaminated land.

Introduction

Background to sorbent tube air sampling

Sorbent tube sampling together with thermal desorption (TD)–GC(MS) analytical technology has been optimised and validated over many years for monitoring vapour-phase volatile organic chemicals (VOCs) in air. Both diffusive[1–3] and pumped[4–6] sampling mechanisms have proved their worth for a wide range of common volatile organic pollutants at concentrations ranging from hundreds of parts per million in polluted industrial air to low/sub-part per billion levels in the ambient environment.

While not so well-suited to the most volatile species such as C_2 hydrocarbons, sorbent tubes are perhaps the most versatile of all the available air sampling technologies. Data are reported for C_3 to n-C_{26}[7,8] hydrocarbons, halogenated hydrocarbons[9,10], ketones[9,10], esters[9,10], aldehydes[9,10], glycol esters[9,10], alcohols[9,10], organic nitriles[9,10], aromatic amines[9,10], polyaromatic hydrocarbons (such as anthracene[11]) or some of the more volatile polychlorinated biphenyls, toluene diisocyanate[12] and organic sulfur compounds (see Application Note TDTS 32).

The cost and performance of sorbent tube monitoring methods have also been enhanced by the now-widespread acceptance of TD–GC(MS) analytical technology.

Thermal desorption offers a significant improvement in sensitivity and numerous practical advantages over conventional solvent extraction methods[13]. It eliminates manual sample preparation and allows sorbent tubes to be reused up to 100 times without regeneration or repacking. These factors combine to make sorbent tubes among the most affordable of air sampling techniques.

It is therefore not surprising that a suite of new international standards and protocols specifying sorbent tube sampling and TD–GC(MS) technology for air monitoring have recently become available. Among the most important of these are:

- ISO 16017 Parts 1 and 2
- ASTM D-6196-97
- US EPA Method TO-17
- NIOSH Method 2549
- UK Health & Safety MDHS Methods 72 and 80.

These standards offer well-validated methodologies including clear quality assurance procedures and data acceptance criteria (further details of these standard methods can be found in Application Note TDTS 3).

The stability of properly-sealed sample tubes has been determined over several months[14] and certified reference standard (CRS) tubes are now commercially available from Markes.

Monitoring contaminated land

The quality of such air monitoring methods contrasts sharply with many conventional soil monitoring procedures. Soil is a complex and non-homogeneous matrix, typically of unknown organic/inorganic composition and with its own ecosystem of micro- and macro-organisms. It is difficult, if not impossible, to make absolute analytical measurements given the number of variables involved.

Conventional soil analysis involves a sampling step followed by some form of sample preparation (addition of biocides, buffers, *etc.*), sample screening and then quantitative purge-and-trap–GC(MS) analysis. It is the sampling of the soil itself that presents the most difficult challenge. Even relatively large, kilogram-level samples cannot be considered representative of a wider area, and the very act of soil removal disturbs and modifies contaminant levels. The presence of micro-organisms also means that organic concentrations vary with time. Additional considerations include the expense of manual sample collection and preparation, the limitations of short sample turnaround times, and the cost of both screening and quantitative laboratory work. These all make it difficult to get enough samples to overcome soil non-homogeneity issues and adequately map out the profile of underground pollution. The method is even open to abuse by ploughing/turning-over the land to reduce pollutant levels prior to sample collection.

However, despite the sampling limitations, the issue of contaminated land is currently attracting considerable public attention. There have been several high-profile incidents of leaks from underground storage tanks on

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commercial and retail properties contaminating local drinking water and causing the temporary evacuation of local residents. In some countires there is also political pressure to redevelop derelict industrial land (brownfield sites), rather than build on open greenfield sites in the countryside. Waste tips/landfill sites near residential areas are also causing public concern.

Given this level of attention, the need for cost-effective, rapid and meaningful methods of screening large areas of land for organic and other contaminants has never been greater.

Soil probe technology

Soil probes are a relatively recent innovation that offer a conventional and affordable way of exploiting air monitoring technology for measurements of contaminated land. Soil probes incorporating standard sorbent tubes were originally developed at BP Research Centre in the UK[15] and were subsequently refined by workers at ICI and in Sweden[16].

The original design comprised a hollow, pointed metal probe, 29 or 90 cm long, pushed into the ground. Into this was inserted a brass cap holding a sorbent tube in diffusive sampling mode[1]. The probes were strong enough to be hammered directly into the ground in most areas, though deeper holes in areas of rock or concrete were predrilled. Once the probe itself was in position, the cap containing the sample tube was lowered into the probe and left in place for 24 hours. Such probes were spaced at regular intervals in a grid pattern over a large industrial site or around the perimeter of gasoline retail outlets and landfill areas.

As experience with the soil probes grew, the design was modified to allow pumped as well as diffusive sampling onto the sorbent tubes, and modern commercial probes also offer the option of pumped sampling onto multiple tubes in series or use of direct-reading instruments (Figure 1).

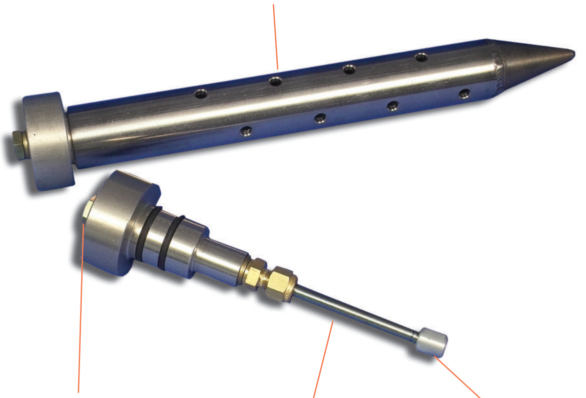

Figure 1: Top: Markes' VOC-Mole™ soil probe, set up for diffusive monitoring. Bottom: The cap assembly that inserts into the body of the VOC-Mole. For pumped sampling, the brass plug is simply removed.

Typically, conditioned sorbent tube/probe cap assemblies are prepared and sealed off-site before being transported to the sampling location. The steel probes themselves may be left *in situ* in the ground for long-term checks on specific point sources, including underground storage tanks, land fill, and fuel retail outlets.

Applications of soil probe technology

The various case studies presented bellow illustrate key soil probe applications:

1. Landfill/domestic waste sites

Approximately 20 soil probes were used to monitor hydrocarbons in and around the Hogbytorp and Bjorkholms waste sites near Stockholm in Sweden. Both contain domestic and light industrial waste. Soil probes incorporating pumped sorbent tubes were used. Some probes were simply hammered into the ground using an impact former, whereas others were lowered into deeper, pre-drilled bore holes.

Vapours from the probes were sampled onto the tubes at a rate of 1200 mL/min for 30 min. Analysis was by TD–GC/MS, and an example total ion chromatogram is shown in Figure 2.

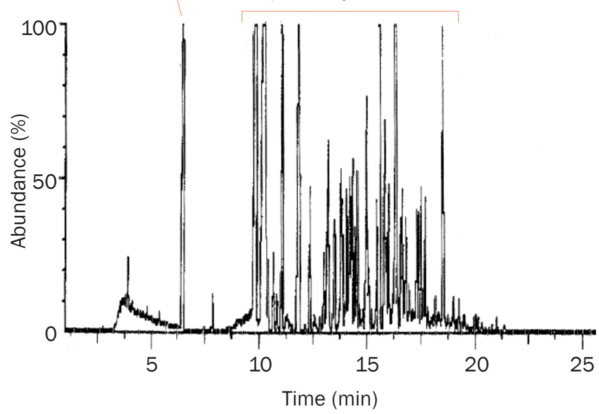

Figure 2: Soil probe sample taken from a waste dump.

Interestingly, data obtained from this study showed that, at one site, benzene concentrations were actually higher on the older parts. This is thought to be related to microbial activity, *i.e.* the digestion of more complex hydrocarbon structures. Less surprisingly, underground migration of volatile organic contaminants from the waste sites was also clearly demonstrated with the identification of a plume of pollution following the direction of the groundwater as it moved away from the site.

Soil probes can also provide a practical option for long-term monitoring around the perimeter of landfill sites. In this case, soil probes were left permanently *in situ*, with sample collection onto sorbent tubes (typically diffusive) bering undertaken at a frequency determined by the nature of the (permitted) waste, the measures taken to control leachate and the geology of the site.

2. Gasoline retail outlets and car service stations

In this example, samples were collected using pumped sampling at six points around a gas station/car wash facility. In addition to the inevitable volatile hydrocarbons, trichloroethane, tetrachloroethane and silicon compounds were detected in significant concentrations. The chlorinated solvents are commonly used degreasing agents and were thought to be derived from the car wash. Silicon compounds are often used in car wax products and may derive from the same source.

3. Productive industrial sites

Productive or derelict industrial sites, particularly those in the chemical/petrochemical sector, present one of the more serious risks of organic contamination of the soil and groundwater. Many sites have been in production for decades, perhaps over a hundred years, and records of accidents, quantities and types of materials produced and even underground storage locations may have been lost in that time. Soil probes provide the ideal technology for cost-effectively surveying the large areas involved.

In practice, most surveys of petrochemical plants have been carried out using a hundred or more short (~29 cm) probes pushed into the surface of the ground. While these do not provide information relating to the depth of contamination, natural migration of non-polar volatile organics upwards through the soil does mean that the technology is able to define accurately the surface coordinates of a contamination source. This done, excavation of that location can identify the actual cause of the contamination and the depth of soil that must be removed or treated. Brief repeat surveys can be used to confirm that remediation is complete. The advantages of short soil probes is that they are unlikely to damage or interfere with any underground structures (pipelines, cables *etc.*). In some cases it is not even necessary to obtain site excavation permits for the monitoring survey, provided probes are shorter than 12 inches (30 cm).

Large-scale monitoring surveys like this are typically carried out using probes containing diffusive tubes. A two-phase approach is often used, with soil probes being inserted into the ground in a grid pattern followed by a more dense arrangement of probes around the contaminated areas identified in the first stage. The steel probes are typically inserted into the ground and sealed for a few hours without exposing the diffusive sampling tubes. This allows the concentration of vapours inside the soil probe to stabilise. Before unsealing the sorbent tube and attaching it to the probe cap to begin the diffusive sampling process, the seal at the top of the probe cap (see Figure 1) can be temporarily removed and air drawn through to a hand-held total hydrocarbon (flame ionization detector) or total aromatic (photo-ionization detector) measuring instrument.

The sorbent tubes are typically exposed inside the soil probes for 24 hours. At the end of this period, they are uncoupled from the probe sampling cap, resealed and stored inside an air-tight container for transport to the laboratory. If required, a second measurement of total hydrocarbon can be made *via* the soil probe as the sorbent tubes are removed. Laboratory analysis of the sorbent tubes by TD–GC(MS) provides information on the mass retained and the identity of each compound.

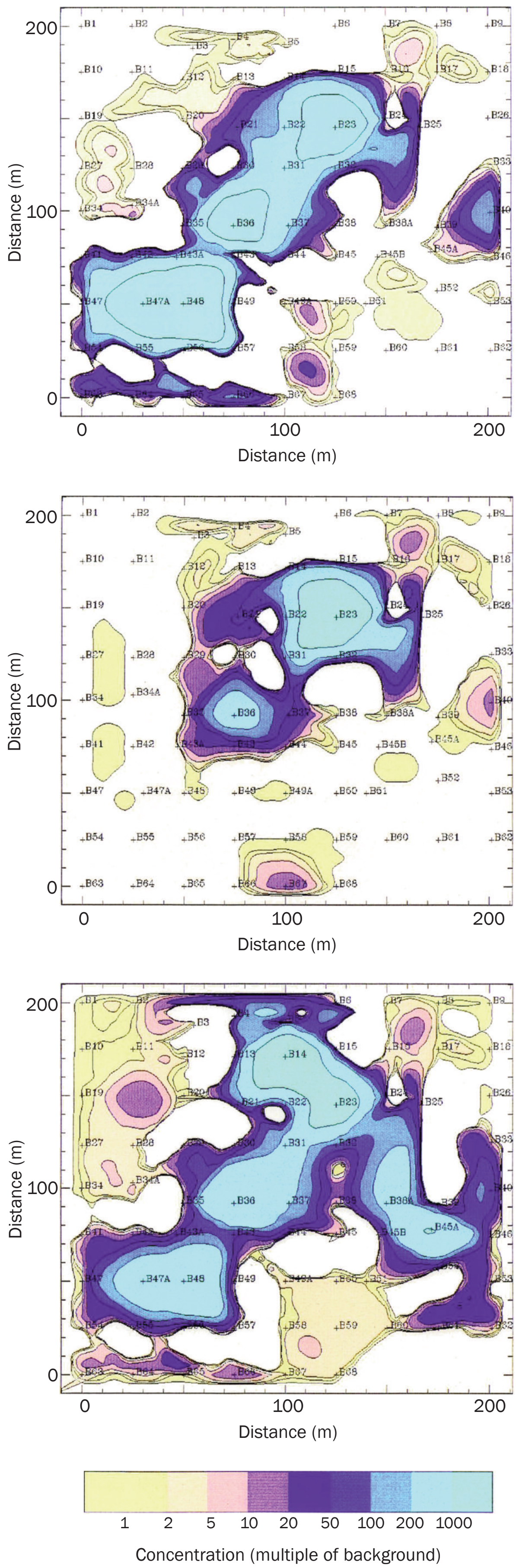

Figure 3: Concentrations of VOCs in soil around a chemical plant. Top: 5-Ethylidene-2-norbornene. Middle: Dicyclopentadiene. Bottom: Total VOCs.

Given the wide range of toxicity of different organic compounds, information of this type is useful for soil surveys and is invaluable whenever the history of a site is unclear or when there is risk of cross-contamination from a neighbouring source. Detailed contour maps of underground pollution can be built up using the soil probe data. Figure 3 shows underground pollution profiles at one European chemical plant for both total and individual organic contaminants.

4. Early leak detection from underground fuel pipelines

Soil probes can provide a cost-effective and long-term solution to detecting leaks from underground fuel pipelines. Probes placed at regular intervals along the length of a pipeline or at critical points – for example, near joints, junctions or areas where the geology changes – can be left permanently in place and used for sorbent tube sampling at whatever frequency is required. A rise in VOC concentrations would give early warning of what could otherwise be a catastrophic pollution (*e.g.* if the leak remained undetected until oil began to bubble to the surface). Special, extended probes have been developed for monitoring in marshy ground.

Soil probes can further assist in pinpointing a leak if multiple pipes run parallel to each other. Once elevated levels of organics have indicated that one of the pipes is leaking, different tracer gases (typically perfluorocarbons) can be introduced to each pipeline for monitored using the same technology. This allows simple identification of which pipe is leaking, allowing the others to remain in operation while the leak in the defective pipe is fixed.

Discussion

While the versatility and simplicity advantages of soil probe sampling have been demonstrated by the above examples, it is important to stress that the soil concentration data obtained are not absolute or quantitative in the true sense. The nature and composition of soil varies dramatically from site to site and across sites. These differences; for example moving from sand to clay or to soil with a high organic content, can significantly affect the partitioning of volatile organics from the soil matrix and into the vapour phase. Humidity, temperature and analyte volatility/polarity are among other important factors affecting vapour-phase concentrations. For these reasons the analyte masses collected from soil probes are always related to their immediate neighbours, so that 'hotspots' or contour maps of underground pollution shown in Figure 3 can be obtained.

Although the lack of absolute quantitative information may appear to be a limitation, underground leaks or surface spills are readily pinpointed using soil probe technology. The masses of target compounds identified on the sorbent tubes typically increase by a factor or 10^3–10^4 relative to average site concentrations in contaminated areas. Analysis of the sample tubes by TD–GC(MS) also provides detailed information on the mix of chemicals present.

Once the spread and composition of the pollution has been determined using soil probes, a site survey may require more expensive 'quantitative' analysis of the affected areas in soil. In these cases, prior site screening using soil probes does at least minimise the number of samples that need to be analysed and the associated expense. In practice, however, use of soil probes for both primary site screening and secondary localised monitoring around 'hotspots' is almost always sufficient to confirm which areas are affected. It is then, typically, most cost-effective to simply remove and treat or replace the contaminated soil.

Conclusions

Soil probes allow well proven, well-documented and versatile VOC air monitoring technologies to be employed for ground contamination tests. Many industrial and service sector laboratories are already equipped with the instrumentation required and are familiar with relevant standards and protocols. The probes themselves are simple and cost-effective to implement in the field, facilitating measurement using direct-reading instruments as well as both pumped and diffusive sorbent tubes. Consequently, soil probe technology has the potential to significantly speed up and reduce the cost of mandatory surveys of contaminated land.

Acknowledgement

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Trademarks

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