



Quantitative passive (diffusive) sampling of trace VOCs in air







Passive sampling

Passive (diffusive) sampling is an easy-to-use, low-cost option for reliable time-weightedaverage (TWA) monitoring of a wide range of target organic volatiles in air.

With a choice of three formats, Markes' passive samplers are ideal for routine work, for large-scale studies, and for monitoring human exposure.



Why use Markes passive samplers?

Markes' new extended range of passive samplers combine with analysis by thermal desorption (TD) and GC(–MS), to offer quantitative, high-sensitivity monitoring of organic vapours in air at sub-ppb to high ppm levels, in full compliance with international standard methods.

Using Markes' passive samplers with TD-GC(-MS) is:

- **Quantitative:** You avoid the uncertainty in results arising from the variability of pumped sampling.
- **Method-compliant:** Multiple national and international standard methods now cite passive sampling and thermal desorption.
- **Affordable:** You can cost-effectively collect large sample sets for truly representative data.
- **Convenient:** The samplers are easy to deploy, lightweight and unobtrusive for personal exposure assessment, and avoid the need for pump calibration.
- Eco-friendly: The samplers are re-usable, and don't need toxic solvent.
- **Easily automated:** Analysis by TD-GC(-MS) eliminates sample preparation and delivers high sample throughput with 1000× better sensitivity than solvent extraction. Sample security is also enhanced by quantitative repeat analysis capability.



Covering every passive sampling application: Passive samplers from Markes are available in axial tube format (left), traditional radiello[®]-samplers (middle), and a new POD Sampler format (right).

Expertise in passive sampling <u>and</u> analysis

With 25 years of expertise as the world leader for TD, Markes is at the forefront of both passive sampling and analytical instrumentation. And with the widest range of passive samplers and other sampling technologies, we'll help you to make the right choice of sampling equipment to perfect your application.

Sampling

Three types of passive samplers are available from Markes: axial-format sorbent tubes, and two styles of radial-format samplers – radiello[®] and the new low-contamination POD Sampler.

	Sorbent tube	radiello	POD Sampler
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Geometry	Axial	Radial	Radial
Sampling time	Hours to weeks	Minutes to days	Minutes to days
Analyte compatibility	VOCs	VOCs (SD and TD) Anesthetics, aldehydes, phenols, NH ₃ , HCl, HF, O ₃ , H ₂ S, NO ₂ and SO ₂	VOCs
Carrier tube	Not needed	Industry-standard tubes	Industry-standard tubes Gerstel TDU tubes or TD Mini-tubes DAAMS tubes and TDS tubes
TD system compatibility	All 31/2" tube systems	All 3½″ and 4½″ tube systems	All $3\frac{1}{2}$ " and $4\frac{1}{2}$ " tube systems Gerstel TDU
Ideal for	Ambient/indoor air monitoring (1–6 weeks) Whole-shift personal monitoring (8 h) for occupational hygiene	Ambient/indoor air monitoring (1–3 days) Options also available for solvent extraction and some key inorganic gases	Ambient/indoor air monitoring (8 h to 14 days) Whole-shift personal monitoring (8 h) for occupational hygiene

Analysis

Passive samples can be analysed using Markes' high-throughput, automated TD100-xr[™] and UNITY–ULTRA-xr Pro[™] systems, which both offer:

- **Easy integration:** Compatible with all major GC(–MS) brands.
- Sample security: Markes' DiffLok[™] caps seal samples both before and after desorption, maintaining sample integrity during a long sequence. Systems also provide quantitative sample re-collection for repeat analysis.
- **High throughput:** Overlap mode allows desorption of the next sample to begin while analysis of the previous sample is ongoing.
- Multi-Gas compatibility: Certification for hydrogen, helium and nitrogen carrier gas delivers even faster and more cost-effective sample processing.
- **Flexibility:** Fully modular TD systems from Markes accommodate both pumped and passive samplers, helping maximise ROI.





Markes' TD100-xr provides capacity for 100 tubes.

Markes' UNITY-ULTRA-xr Pro provides capacity for 199 tubes.

A GLOBAL NETWORK

With a network of technical centres around the world and global partnerships with major GC(-MS) manufacturers, our specialists are uniquely well-equipped to provide you with unbiased technical advice.

Passive sampling: Quantitative and high sensitivity

Whatever the sampler type chosen, passive sampling provides quantitative data on airborne analytes with the high sensitivities needed for trace-level monitoring.

Uptake rates and back-diffusion

As long as the concentration of an analyte at a sorbent surface stays at zero, the rate of diffusion of the analyte into the sorbent will be proportional to the ambient air concentration. The proportionality constant is called an *uptake rate*, and is quoted either in mL/min or ng/ppm/min (equal to pg/ppb/min).

However, if a sampler is used for too long, analytes can back-diffuse from the surface of the sorbent and into the air near the surface, reducing the diffusion gradient and therefore the uptake rate. Thanks to extensive research and careful design, Markes' axial and radial passive samplers delay the onset of back-diffusion, and so **extend the period over which uptake rates are stable**.



In a passive sampler, the concentration of an analyte within the diffusion path length (the gap between the atmosphere and the sorbent surface) falls linearly with distance. This is known as Fick's first law.

How diffusion works in axial and radial samplers

The nature of the diffusion barrier is different in the two main types of passive samplers – in axial sorbent-tube samplers (left), it is the air gap at one end of the tube, whereas in radiello[®] samplers (middle) and POD Samplers (right), it is the porous body.



In **sorbent-tube samplers**, diffusion only occurs at the sorbent surface at the sampling end of the tube, and is controlled by the 15 mm air gap. Uptake rates are low (typically ~0.5 mL/min or ~2 ng/ppm/ min), making them suitable for 1–8 hour workplace monitoring or 1–4 week monitoring in ambient/indoor air. In **radiello samplers**, diffusion takes place through a porous polymeric body that houses a sorbent cartridge. The sampling surface is much greater than in axial samplers, so sampling is faster (typically ~30 mL/min). This makes them ideal for short-term monitoring – but it also means exposure periods are limited for TD sorbents. The **POD Sampler** works on a similar principle to radiello samplers, but diffusion takes place through a sintered metal body. This controls the sampling rate (typically ~5 mL/min), resulting in uptake rates that are stable over a similar time-frame to sorbent-tube samplers.

Thermal desorption: A better, greener option than solvent extraction

Passive sampling first became popular for environmental monitoring in the 1970s, when the tubes were single-use and required solvent extraction. But with the widespread adoption of solvent-free thermal desorption, passive sampling has become not only operationally easier, but greener and more versatile

Benefits of thermal desorption

Monitoring methods for VOCs in air, particularly workplace air, traditionally relied on extracting a charcoal-based sorbent with carbon disulfide (CS_2). An obvious benefit of TD is that eliminates this toxic and odorous solvent, but there are many other more significant advantages:

- Application flexibility: Sensitivity is enhanced by up to three orders of magnitude using TD, with no dilution required, which allows concentrations from high ppm to sub-ppb to be monitored.
- **Ease of automation:** Using TD, passive samplers are analysed and re-conditioned in one fully automated process with minimal sample preparation.
- Eco-friendliness: Samplers are reusable multiple times and the cost of solvent disposal is eliminated, making them much more cost-effective and environmentally benign in the long run.
- Accuracy: TD offers >95% extraction efficiency compared with ~75% for solvent extraction. This greatly reduces analytical uncertainty and reporting errors.
- Cleaner chromatography: Eliminating solvent reduces chromatographic interference (artefacts and quenching).





Two examples of workplace air samples collected by axial diffusive sampling and analysed by TD.

TD: A low-risk option with rapid return on investment

The additional investment required for TD earns a rapid return, thanks to the re-usable samplers and greatly increased laboratory productivity. To minimise risk, Markes supplies affordable single-tube instruments with full functionality for both pumped tubes as well as passive samplers. Not only that, but Markes' TD systems can be upgraded with multi-tube, canister and on-line capability, and are compatible with all major brands of GC(–MS).

Quantitative re-collection: Making TD a 'multi-shot' technique

Despite the advantages of TD, $charcoal/CS_2$ methods were for a time preferred for some air monitoring applications because, in the early days, TD was a 'one-shot' technique, meaning samples couldn't be re-analysed.

This is no longer the case. Markes was the first TD company in the world to introduce quantitative re-collection as a standard feature on its TD instruments. This capability allows samples to be split and retained, enabling the same sample to be repeatedly analysed or held for reference. Quantitative re-collection is now available on every Markes TD system, in manual or automated form.

Wide application range

The easy deployment, low cost, and analytical versatility of passive samplers make them an ideal choice for largescale or long-term environmental monitoring campaigns, as well as for personal monitoring.





Environmental contamination is easily mapped using passive samplers. Left: A network of samplers around Rouen, France (black dots) uncovers 'hot spots' for high benzene concentrations (yellow). **Right: Passive sampling** with VOC-Mole soil probes around an industrial site allows low-cost mapping of contaminated ground.



A number of hazardous VOCs are detected in contaminated air around a refinery perimeter, following two-week diffusive sampling with analysis by TD–GC–MS.



MARKES International

Fenceline monitoring using passive sampling, in accordance with US EPA Method 325.

Personal monitoring with a POD Sampler.

The passive sampling workflow

A key benefit of passive samplers is their ease of use. After choosing a sampler, it is first cleaned to ensure it is free from contamination. Following deployment, the sampler ID and sample information is logged, the sampler analysed, and then used again for the next monitoring campaign.



Method compliance

Passive sampling with TD–GC–MS is referenced in a large number of international standard methods, including:

- EN ISO 16017: Air quality Sampling and analysis of volatile organic compounds in ambient air, indoor air and workplace air by sorbent tube/thermal desorption/capillary gas chromatography. Part 2: Diffusive sampling.
- **EN 14412:** Indoor air quality Diffusive samplers for the determination of concentrations of gases and vapours. Guide for selection, use and maintenance.
- EN 14662: Ambient air quality Standard method for the measurement of benzene concentrations. Part 4: Diffusive sampling followed by thermal desorption and gas chromatography.
- ASTM D7758: Standard practice for passive soil gas sampling in the vadose zone for source identification, spatial variability assessment, monitoring, and vapor intrusion evaluations.
- ASTM D4597: Standard practice for sampling workplace atmospheres to collect gases or vapors with solid sorbent diffusive samplers.
- **ASTM D6306** Placement and use of diffusive samplers for gaseous pollutants in indoor air.
- US EPA Method 325A: Volatile organic compounds from fugitive and area sources: Sampler deployment and VOC sample collection.
- **US EPA Method Method 325B:** Volatile organic compounds from fugitive and area sources: Sampler preparation and analysis.
- MDHS 80: Volatile organic compounds in air. Laboratory method using diffusive solid sorbent tubes, thermal desorption and gas chromatography (August 1995).

Markes International

World-leading technologies and unmatched expertise in VOC and SVOC monitoring

For 25 years, Markes International has been helping analysts worldwide enhance the power of GC–MS analysis through thermal desorption and other sample preparation techniques.

We manufacture a comprehensive range of instrumentation, accessories and consumables, providing customers with everything they need for VOC and SVOC analysis. At the same time, our quest for innovation and deep application knowledge mean that we lead the way with new technologies, and are always in touch with emerging industry trends.

We're headquartered in Bridgend, UK, and support our customers in over 60 countries through a network of offices and distribution partners.



Discover more - Deliver more

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