

TDTS 46

Monitoring organic vapours in air – A comparison of thermal desorption and carbon disulfide (CS₂) extraction

Summary

This Application Note describes the benefits of thermal desorption (TD) analysis of sorbent tubes compared to solvent extraction for the detection of volatile organic compounds in air.

Introduction

Use of pumped sampling onto glass tubes packed with charcoal, followed by carbon disulfide (CS₂) extraction and gas chromatography (GC) analysis, was developed as an air monitoring method for vapour-phase organic compounds (VOCs) in the 1970s. The approach is still used today for some personal exposure assessment (occupational hygiene) applications and stack emission testing, but its detection limits are fundamentally limited.

Thermal desorption (TD) is an appealing alternative to solvent extraction, whereby sorbent tubes (Figure 1) are heated in a flow of carrier gas. Trapped vapours desorb from the sample tubes into the gas stream and are transferred, *via* a refocusing device, into the GC(MS) analyser.



Figure 1: A selection of Markes' thermal desorption sampling tubes.

TD offers much better sensitivity than solvent extraction (see below) and has now almost universally superseded charcoal/CS₂ for environmental (ambient and indoor) air monitoring. Steady reductions in exposure limit levels¹ and restrictions on chemicals such as CS₂, in Europe and elsewhere, have also led to increased use of thermal desorption for occupational hygiene, *i.e.* for exposure assessment in the workplace. The most recent international standard methods for thermal desorption include workplace air monitoring in their scope^{2,3}.

The trend towards thermal desorption for all air monitoring applications (workplace, indoor and ambient air) has been further encouraged by recent TD technical developments. The latest commercial thermal desorbers now allow quantitative re-collection of split flow (both tube and trap desorption split flow) for repeat analysis.

This overcomes the one-shot limitation of traditional TD methods and simplifies method/data validation.

In this Application Note, we summarise the key advantages of thermal desorption *versus* solvent extraction for monitoring organic vapours in air, and explain why TD is preferable in most cases:

Sensitivity

Solvent extraction of charcoal tubes requires at least 1 or 2 mL of CS₂ followed by injection of only 1–2 µL of extract into the GC(MS). This results in a 1000-fold dilution of the sample right at the start of the process. Other factors limiting sensitivity include solvent artefacts, interference from the solvent itself (masking volatile target analytes) and low desorption efficiency (see below). In contrast, thermal desorption allows complete transfer of all target analytes to the analytical system, with no dilution or solvent interference. Detection limits offered by thermal desorption methods are typically at least 1000 times lower than equivalent solvent extraction methods, facilitating ambient monitoring at ppt/ppb levels as well as higher ppm (and %-level) concentrations.

In comparison, charcoal/CS₂ methods are invariably limited to concentrations above 0.1–1 ppm.

Desorption efficiency

The efficiency of thermal desorption is always greater than 95%. Such efficiencies are independent of ambient conditions (and the nature of the target analytes), and are both easy to achieve and readily validated.

In contrast, the desorption efficiency of charcoal/CS₂ extraction methods is only about 80%, even under best-case conditions, *i.e.* with volatile, non-polar target compounds collected from dry atmospheres. In addition, charcoal is hydrophilic and adsorbs a significant amount of water from humid air. The presence of water can reduce desorption efficiency (e.g. to 20–30%), especially for polar compounds. The user may not even be aware that this problem has occurred, yet it can cause atmospheric concentrations to be under-reported by as much as a factor of four. Solvent extraction efficiencies for semi-volatile compounds are also low, often below 50%.

Reproducibility

As described above, the desorption efficiency of solvent extraction is significantly lower than that of TD, and can vary from 20 to 80% depending on analyte volatility and atmospheric humidity. This significantly compromises reproducibility. Other factors contributing to analytical uncertainty/error include the evaporation of CS₂ during sample preparation and its absorption into the rubber septa of GC autosampler vial caps.

Variability of solvent extraction data can also be caused by compounds co-eluting with the solvent. CS₂ is almost 'invisible' by FID detection. However, the FID response to compounds that co-elute with CS₂ will be quenched by the relatively large concentration of solvent. Quenching effects of this sort are notoriously variable, and result in poor precision for the compounds affected.

Solvent interference can have an even more dramatic effect on GC methods using mass spectrometer (MS) detection – see below.

Cost saving

Thermal desorption offers enhanced automation and greatly reduced running costs. Tubes are re-usable at least 100 times (typically >200 times). TD also eliminates solvent purchase and disposal concerns.

While automated thermal desorption systems typically have a higher initial cost than liquid autosamplers, the thermal desorber also replaces the need for a conventional GC injector. In addition, every GC system used for the analysis of CS₂ extracts requires installation of sophisticated ventilation equipment to minimise the health risks to laboratory personnel (see below). These costs vary, but can bring the total capital cost of automated TD–GC into the same range as automated liquid injection–GC.

Manual thermal desorption systems offer affordable entry-level TD but without compromising performance or capability. For example, Markes' UNITY™ thermal desorber offers method-compliant, cryogen-free TD–GC(MS) analysis of sorbent tubes together with quantitative re-collection of split flow for repeat analysis, and is roughly half the cost of a fully automated system.

Perhaps the major cost eliminated by thermal desorption is that of manual sample preparation, as TD tubes arrive at the laboratory ready for analysis. In contrast, charcoal tubes require a relatively lengthy sample preparation procedure. First they have to be broken in order to tip the two separate beds of charcoal into individual vials. One or two millilitres of CS₂, containing suitable internal standard(s), is then added to each vial and the vials are subsequently capped. These samples are typically agitated for at least 30 minutes before the supernatant liquid is decanted into a second set of vials, which again require capping before being placed on the autosampler. All of these procedures are manual, time-consuming, very difficult to automate and a potential source of sample loss and error.

Passive sampling option

While thermal desorption tubes are used extensively for pumped air sampling, they are also compatible with low-cost passive (diffusive) sampling (Figure 2). Extensive data is now available for quantitative passive sampling using standard TD tubes^{2,4,5}, and this can mean major cost savings for applicable studies. Passive samplers eliminate the requirement for personal monitoring pumps, making them much less heavy and intrusive. Instead of a pump, each tube is simply fitted with a diffusion cap at the sampling end.



Figure 2: A thermal desorption sampling tube being used in diffusive (passive) mode, with the sampling end uppermost.

Monitoring workers using lightweight passive samplers minimises the risk of individuals modifying their behaviour and facilitates more representative measurement. The combination of low sampling costs and automated TD–GC(MS) analysis also make passive sampling the method of choice for large-scale ambient air monitoring campaigns, e.g. across an entire city⁶.

N.B. Thermal desorption tubes may be used for either pumped or passive sampling without modification.

Solvent interference

Originally, charcoal/CS₂ methods were intended for use with packed column GC technology and FID detection. In this case, the limitations of CS₂ were minimised by its very low response on FID. However, even under these conditions, impurities in the solvent, solvent-related baseline disturbances and the large dilution factor (see above) all contributed to limit method sensitivity, typically to ppm-level atmospheric concentrations. Solvent effects also increased analytical uncertainty/error.

In addition, CS₂ brings additional limitations to GCs configured with MS detectors. It generates a large response on the MS, often requiring deactivation of the detector ionisers until after the solvent has completely passed through the system. This makes it impossible to analyse target compounds co-eluting with the solvent.

Environmental health & safety

CS₂ is one of the most toxic common solvents. It is banned completely by some countries/companies, and international occupational exposure limit values¹ are now 5 ppm, which effectively means average workplace concentrations should not exceed 0.5 ppm to minimise exposure risk. As described above, solvent extraction of charcoal requires multiple manual operations, leading to significant risk of personal exposure to CS₂ vapour. In many cases, laboratory staff carrying out CS₂ extraction procedures may be at higher risk of hazardous chemical exposure than those workers whose samples they are trying to analyse. Personal monitoring of these laboratory staff for CS₂ is therefore recommended.

In addition to this, CS₂ has an extremely unpleasant odour, leading to increased discomfort in the working environment. Moreover, new environmental legislation means that solvent disposal is an increasingly costly and administration-intensive process.

By eliminating the need for the solvent, TD completely overcomes all these issues.

Repeat analysis

Historically, the only real limitation of thermal desorption relative to charcoal/CS₂ methods was that it was one-shot. With early TD equipment, once the sample tube was desorbed (*i.e.* heated in a stream of carrier gas), it was gone. Therefore, if anything went wrong with the subsequent analysis there was no chance to repeat the run. However, since the introduction of SecureTD-Q™ technology (quantitative re-collection of split flow during both tube and trap desorption) by Markes, this is no longer the case.

TD-GC(MS) methods for routine workplace, indoor and ambient air monitoring invariably employ a single or double split. Markes' innovation was to make possible quantitative re-collection of all TD split flow (see Application Note TDTS 24). This allows samples to be archived indefinitely (most compounds are stable on sorbent tubes for several months), used for third-party validation or re-analysed immediately to confirm results. In other words, SecureTD-Q allows repeat TD-GC(MS) analysis of all but the lowest-concentration (ppt-level) samples, *i.e.* those which are analysed splitless.

Since its introduction, the value of quantitative sample re-collection for repeat TD-GC(MS) analysis has been recognised in standard methods³ as an aid to TD method/data validation.

N.B. Repeat analysis was always a slightly dubious claim for charcoal/CS₂ solvent extraction methods. CS₂ is an extremely volatile solvent, which is rapidly lost by evaporation and by absorption into the rubber septa of the vial caps. If the first sample of a sequence is re-analysed at the end, different results are obtained. Even refrigeration may not guarantee sample stability because of the absorptive losses of CS₂.

Method compliance

Another historical advantage for solvent extraction was the number of applicable standard methods. Though equivalent thermal desorption methods were initially slow to be advertised, this situation has now completely changed. Well-validated thermal desorption methods, describing both pumped and diffusive sampling and applicable to workplace monitoring, ambient air, indoor air and materials emissions testing, are now available from all the major international standards agencies. Key examples include EN ISO 16017, ISO 16000-6, ASTM D-6196, US EPA Method TO-17, NIOSH 2549, MDHS 72, 80, *etc.*, and EN 14662.

References

1. 3rd Indicative Occupational Exposure Limit Value (IOELV) Directive Update, European Commission, 2007.
2. 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 1: Pumped sampling.
3. ASTM D6196-03: Standard practice for selection of sorbents, sampling and thermal desorption analysis procedures for volatile organic compounds in air.
4. EN ISO 16017-2: 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.
5. EN 14662-4: Ambient air quality – Standard method for the measurement of benzene concentrations. Part 4: Diffusive sampling followed by thermal desorption and gas chromatography.
6. N. Gonzalez-Flesca, M. Bates, V Delmas and V. Cocheo, Benzene exposure assessment at indoor, outdoor and personal levels. The French contribution to the Life MACBETH program, *Environmental Monitoring and Assessment*, 2000, 65: 59–67.

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