# Thermal Desorption Technical Support

## *Note 77: Using Thermal Desorption for Industrial (Stack) Emission Testing*

**Keywords**

Environmental; Sample Collection; Pumped

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## Introduction

Stack gases are often aggressive matrices comprising both high and low concentration organic vapours with acid gases, high levels of particulates, high humidity and a wide range of inorganic gases. Another challenge is that no two stack samples are alike.

Environmental regulations in Europe[1,2], the US[3] and elsewhere require industry to control and monitor emissions of organic vapours relative to limits specified in their respective site operating permits. Various sampling devices are used for collection of the organic vapours depending on the compounds of interest. These typically fall into two categories:

- containers (glass ‘bombs’, canisters, Tedlar bags, *etc.*)
- sorbent tubes (charcoal (for subsequent solvent extraction) or thermal desorption tubes)

Whichever sampling method is selected, a ‘sampling probe’ and a ‘sampling train’ are invariably required upstream of the organic vapour collection device. Rigid sampling probes may be permanently installed in the stack and are used to position the sample collection point away from the inner walls of the stack. Sampling trains comprise components to remove particles, reduce corrosive gases, lower humidity and lower gas temperatures before the sample reaches the sorbent tubes. They can be very simple or quite complex and will vary from stack to stack. Local expert advice should always be sought with regard to which sample train components should be used in each particular case.

Guidance given in this application note covers selection of the appropriate organic vapour sampler for the analytes of interest and optimisation of the subsequent sampling and TD-GC analytical process. The advantages of thermal desorption versus solvent extraction for stack gas monitoring are also described.

## Use of whole air/gas containers for stack monitoring

Many organics, particularly very volatile or unstable species such as freons and mercaptans respectively, are collected in glass or passivated stainless steel ‘bombs’. The vapour sample is then introduced to the GC via some sort of gas sampling valve (*i.e.* without concentration) or *via* a focusing trap.

In some cases, the concentration enhancement potential of thermal desorption is not required for quantitative GC analysis; for example, if organic vapour levels are in the order of 10 ppm or above (Table 1). In this case, the volume of vapour that can be introduced via the loop of a conventional GC gas sampling valve contains sufficient mass of analyte for quantitative GC analysis without concentration enhancement. However, even if all the target

| Analyte vapour concentration | µg/ml | µg/ 10 ml | µg/ 100 ml | µg/L |
|---|---|---|---|---|
| 1% | 40 | 400 | - | - |
| 1000 ppm | 4 | 40 | 400 | - |
| 100 ppm | 0.4 | 4 | 40 | 400 |
| 10 ppm | 0.04 | 0.4 | 4 | 40 |
| 1 ppm | - | 0.04 | 0.4 | 4 |
| 10 ppb | - | - | 0.04 | 0.4 |

***Table 1: Approximate analyte masses in various air/gas volumes at a range of vapour concentrations.***
***(Calculations for compound with nominal molecular weight 100 and at 25ºC)***

organic compounds are at high concentrations, selective focusing of the analytes on a suitable small sorbent trap followed by subsequent thermal desorption is often the preferred method of transferring/injecting the compounds into the GC system.

The advantage of using a focusing trap before injection/transfer to the GC is that it allows selective elimination of interferences – water, oxygen, other inorganic gases, *etc* - which might otherwise compromise the analysis and reduce the lifetime of the GC system. The process in this case is that the stack gas sample (from the sample container or even, occasionally, online) is introduced directly into the electrically-cooled sorbent focusing trap of a thermal desorber. At the end of sample focusing, the trap is purged briefly with carrier gas, in the sampling direction, to sweep water, inorganic gases and other interfering species to vent. The flow of carrier gas is then reversed and the trap heated rapidly (~100°C/sec) injecting the target analytes into the GC analytical system in a narrow, discreet band of vapour. The sorbents, temperature and gas flows used during sampling and purging are selected to ensure quantitative retention of the compounds of interest while unwanted interferences such as water and inorganic gases are purged to vent.

Modern TD systems for whole air/gas samples, such as the Markes UNITY-Air Server™, are compatible with high concentration samples (> 10 ppm) because they allow accurate metering of low flow rates (*e.g.* 10 ml/min) and low volumes (*e.g.* 10 ml) during the sample focusing process.  They also allow the user to set reproducibly high split ratios (*e.g.* 200:1) during the subsequent trap desorption stage. In this way the mass of analyte reaching the GC, even from 10 ml volume of a sample containing 1% vapour (nominal M.W. 100), can be reduced to 2 µg or less, thus preventing system overload and enabling quantitative analysis.

Pre-concentration of organic analytes using a focusing trap is also sometimes necessary to improve analytical performance (figure 1). Very volatile freons such as $CF_4$ (Bp ~-169ºC) for example, merge into the GC baseline if they are introduced to the system as a gas sample, without any trapping stage. Pre-focusing of the freon compounds sharpens the chromatographic peaks and improves the GC analysis. Data for figure 1 were obtained by introducing 30 ml gas standards to the cryogen-free focusing trap of a Markes UNITY-Air Server system (figure 2) linked to GC/MS (conditions listed oveleaf). A very strong sorbent was used in the focusing trap and quantitative retention of $CF_4$ (bp -169ºC) was demonstrated by introducing different concentration standards.

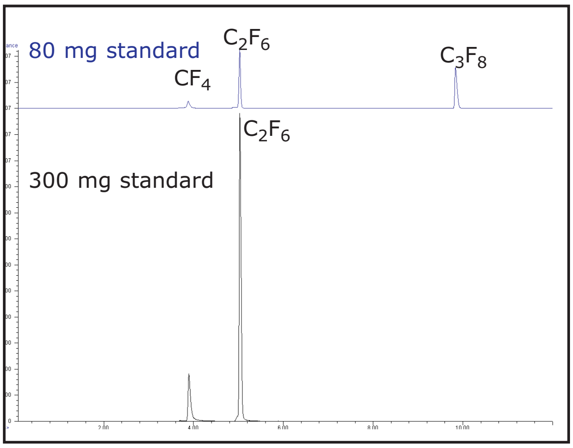

***Figure 1: Cryogen-free analysis of very volatile freons using UNITY-Air Server with GC/MS, showing quantitative retention of $CF_4$***

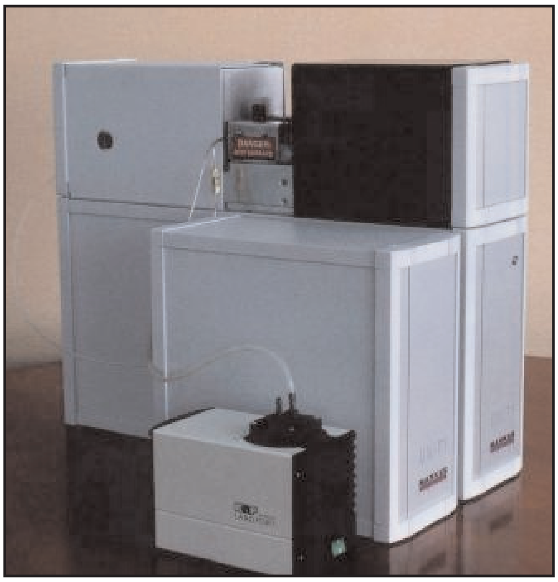

*Figure 2: UNITY-Air Server system*

## UNITY-Air Server Conditions

1 minute prepurge

Standard gas sampled at 10 ml/min for 3 min

1 minute trap purge

Trap desorb: -15°C to 350°C (hold 3 mins)

50ml/min split

Flow path temperature 80°C

UNITY Supply Pressure: 8 psi

Cold Trap: Carboxen 1000/Carbosieve SIII

## GC Conditions

Column: 50 m x 0.32 mm I.D. PLOT ($Na_2SO_4$)

Start temperature : 30°C - held for 3 minutes

Ramp rate: 5°C/min to 55°C - held for 3 min.

## MS Conditions

MS Source temperature : 230°C

MS Quadrupole temperature : 150°C

MSD transfer line temperature : 280°C

Mass Scan Range: 45 to 450 amu

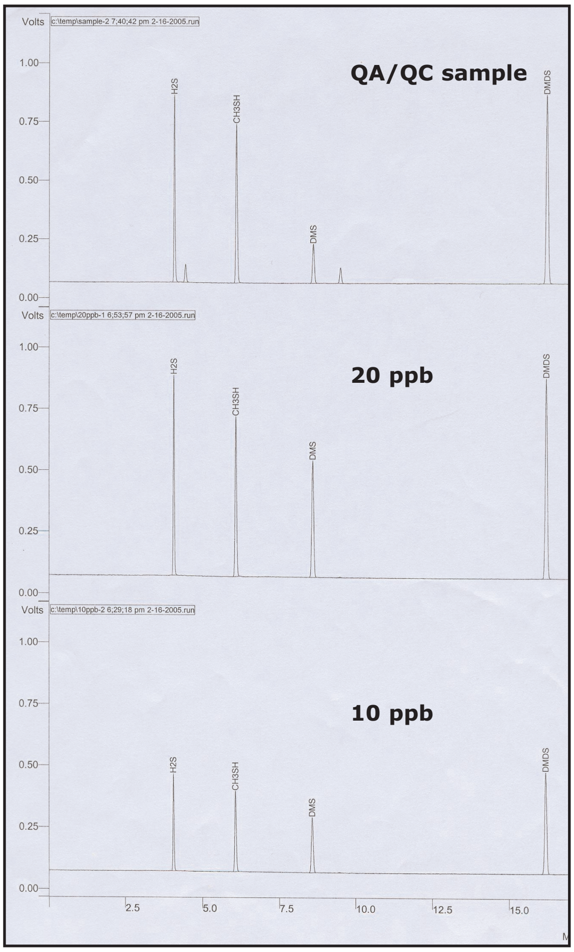

***Figure 3: Analysis of reduced sulphur compounds using UNITY-Air Server with GC-FPD (For analytical conditions and more details see Markes TDTS 32[6])***

*[Chromatogram courtesy of Professor K.-H. Kim of Sejong University, Seoul, S. Korea (khkim@sejong.ac.kr) and ITC21, Sung Nam City, Korea (www.itc2000.co.kr)]*

Sorbent focusing of whole gas samples is also used to improve detection of trace level toxic or odorous vapours, such as reduced sulphur compounds, in industrial emissions (figure 3). In this example, 100-200 ml of gas were transferred from a sample container to the focusing trap of a Markes UNITY-Air Server thermal desorption system linked to a GC with flame photometric detection[4]. The method was developed in response to new Korean regulations for environmental odour[5]. Various focusing trap packings were tested during this project until an optimum combination of sorbents was found that ensured quantitative retention and recovery of the most volatile and reactive species such as $H_2S$.

Sub-ppb detection limits were demonstrated for all the compounds of interest.

The above examples show the suitability of whole gas containers for sampling very volatile and/or very reactive and/or relatively low concentration compounds in stack gas. However, even the best, most inert sample containers (glass bombs or passivated canisters) have serious limitations when it comes to higher boiling species (>$C_6$ hydrocarbons) particularly given the high concentrations and high humidities typical of most stack gas samples.

The main challenges are: incomplete recovery of analytes during analysis, interactions between the canisters/bags and the analyte, and subsequent difficulties in reconditioning the container for re-use. This situation is exacerbated if humidity from the stack gas is allowed to condense on the inner walls of the container causing a multi-phase partition system to develop inside. Quantitative recovery and accurate analysis is impossible if this happens.

Canister sampling methods have previously been drafted for relatively high concentration workplace atmospheres[7] but have shown incomplete recovery of even 'well behaved' species such as toluene plus have specified up to 100 lengthy cleaning cycles (evacuation plus purging) between uses. Needless to say, such methods have never been finalised. The organic concentrations, volatility range and potential interferences present in most stack gases render whole-air/gas containers wholly unsuitable for most stack monitoring applications. [For more information please consult Markes TDTS 27[8]]

## Use of sorbent tubes with thermal desorption for stack monitoring

For these reasons, the preferred approach to stack sampling has been to use sorbent tubes/traps. Sorbent tubes are much more versatile than containers offering compatibility with both low and high concentration organic vapours (ppt to high ppm) ranging in volatility from $C_3$ hydrocarbons to $C_{26}$ and above. They also facilitate selective elimination of interferences such as water.

Historically, the most popular stack monitoring method has been to use charcoal sorbent tubes followed by $CS_2$ extraction and GC analysis of the liquid extract.

This method is usually limited to vapour concentrations above 1 ppm, which, while an issue for many other air monitoring applications, is not normally a concern for high concentration industrial emissions testing. However, charcoal tube/$CS_2$ extraction methods do have several other major drawbacks – notably:

- Variable and incomplete recovery (typically <80%)
- Poor and very variable recovery of polar compounds (Recoveries can be as low as 20-30%, particularly in the presence of high humidity)
- Labour intensive and manual sample preparation/extraction
- Use of toxic solvents – $CS_2$ is highly toxic, requires the installation of laboratory extraction/ventilation equipment and is banned on some industrial sites and in some countries
- Masking of peaks of interest by the solvent during subsequent GC analysis – especially if MS detection is employed

Thermal desorption (TD) overcomes all these limitations and has the major additional advantage that samplers are re-usable. Whereas charcoal tubes are broken during the sampling and solvent analysis procedure, TD tubes remain intact. Furthermore, the process of thermal desorption automatically reconditions/cleans the tubes allowing them to be reused immediately if required. [For more information on the general advantages of thermal desorption versus solvent extraction see Markes TDTS 46[9].]

The recent Markes' innovation of Secure TD-Q™ (quantitative re-collection for repeat analysis[10]) has also meant that TD is also no longer a 'one-shot' procedure. Samples can now be quantitatively re-collected for repeat analysis using either the same or a different method (figures 4 and 5, table 4 and 'AutoSecureTD Analytical Conditions').

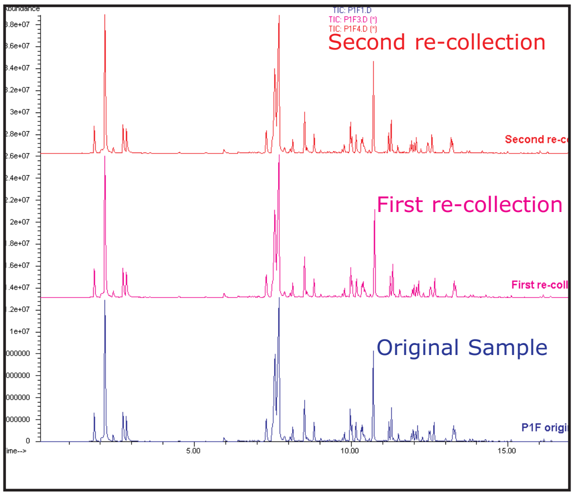

**Figure 4: Repeat analyses of a 1.5 L stack gas sample collected on a sorbent tube & analysed using a Markes ULTRA-UNITY™ TD with GC/MS, a split ratio of 3,000:1 and SecureTD-Q**

**Figure 5: AutoSecure TD™ system for fully automated quantitative re-collection of <u>inlet</u> and outlet split flow**

## AutoSecureTD Analytical Conditions

Sampling: 100-1500 ml pulled through tube using gas syringe/low flow pump

Sorbent tubes: Tenax/Carbon black or 2 beds of carbon black

Tube Desorption: 5 mins at 330°C (280°C if using Tenax)

Trap desorb: 30°C to 300°C (hold 5 mins)

Split: 3000:1 double split with SecureTD-Q

Cold Trap: Tenax/Carbograph 1TD or Carbograph 2TD/Carbograph 1TD

Analysis: GC/MS (SCAN) or GC-FID

| **Compound** | **Mass (µg) determined** | | |
|---|---|---|---|
| | Run 1 | Run 2 | Run 3 |
| MEK | 580 | 583 | 580 |
| Benzene | 0.14 | 0.18 | 0.18 |
| Toluene | 94 | 91 | 93 |
| Ethyl benzene | 30 | 30 | 29 |
| PGMEA | 43 | 43 | 43 |
| *m*/*p*-Xylene | 261 | 262 | 258 |
| *o*-Xylene | 13 | 13 | 13 |
| DMS | 28 | 28 | 28 |
| 1,2,3-Trimethyl benzene | 43 | 44 | 42 |

**Table 4: Data from 3 repeat analyses of the same 1.5 L stack gas sample shown in figure 4. Use of 'SecureTD-Q' overcomes the 'one-shot' limitation of traditional TD, and allowing repeat analyses & validation of emission data**

Early official guidance documents for monitoring stack gases using sorbent tubes with subsequent thermal desorption analysis include US EPA Method 18[11] and the 'Volatile Organic Sampling Train' (VOST) procedure[12,13]. These are important methods because they illustrate the principle of using thermal desorption for stack monitoring. However, sorbent tube and thermal desorption technology have both moved on significantly since these documents were first published. An expanded range of well-characterised sorbents is now available with potential to pack up to three sorbents in series in a single sample tube. This has allowed tubes to be reduced in size and standardised on 3.5-inch (89 mm) long and ¼-inch (6.4 mm) O.D. samplers in stainless steel, Silcosteel™ or glass which are easy to condition and handle. These developments have, in turn, facilitated use of much simpler and lighter sampling equipment on the stack itself.

Similarly, TD technology has evolved to incorporate two distinct stages – primary tube desorption with refocusing on an electrically-cooled focusing trap followed by fast secondary desorption of the focusing trap to inject the compounds of interest into the GC system. Each of these desorption stages can be carried out split or splitless and use of a split both on the way into the focusing trap (*i.e.* inlet splitting during primary (tube) desorption) and on the way out of the trap (*i.e.* outlet splitting during secondary (trap) desorption) allows high (double) splitting of concentrated samples as applied in figure 4. Double splitting allows high performance capillary GC-MS analysis to be carried out even if mg-level masses of analyte were collected on the sorbent tube.

Markes' development of SecureTD-Q – quantitative re-collection of **both inlet and outlet split flow** for repeat analysis and method/data validation – takes sample splitting to a new level of sophistication. In the example shown above (figure 4 and table 3), 2,999 parts out of 3,000 of the stack gas sample were re-collected on a single, clean sorbent tube. A repeat analysis of the sample can therefore be performed as a check on the first result and as confirmation of analyte recovery across the volatility range. In the case of industrial emissions testing, the key benefit of SecureTD-Q is that it allows an analysis to be reliably repeated if something goes wrong in the first run – in other words it overcomes the need to climb back up the stack to collect another sample if the analysis fails first time around!! [For more information on SecureTD-Q please see Markes brochure on TD method validation[10].]

A more recent guidance document for industrial emissions testing - UK EA Guidance Note M2[14] - cites method EN 13649 (charcoal/$CS_2$) but also allows equivalent TD procedures (see note 1 on Table 6.7.2 of M2). Similarly, UK EA docs S4.01[15] and S4.02[16] both specify analytical methodology based on EN 1076[17] (monitoring industrial air with pumped sorbent tubes followed by solvent extraction or thermal desorption.) All of these procedures are based on the small, industry standard sorbent tube sizes given above.

Suitable vapour concentrations for sorbent tube sampling and TD-GC analysis range from low % to ppb. Thermal desorption also facilitates simultaneous quantitative analysis of compounds ranging in concentration over three orders of magnitude (see Table 4).

Sample collection can either take the form of 'grab sampling' – using a large 100-250 ml gas syringe to simply pull a sample of stack gas through the sampling train and onto the sorbent tube over a period of about a minute – or time weighted average (TWA) monitoring. This involves use of a low flow (*e.g.* 10 ml/min) intrinsically safe pump to pull a, typically, 0.5 to 2 L sample through the sorbent tube over a period of perhaps 30 mins to 2 hours. Use of pumps does add slightly to the complexity of stack monitoring relative to the syringe/'grab-sampling approach, but it allows meaningful time weighted average emission concentration data to be obtained which is important for calculating the total mass emitted per unit time (*e.g.* per 8 hours or per 5 hours). It is also useful for monitoring variable manufacturing processes such as polymerisation.

Optimum TD-compatible sorbents for stack monitoring will depend on the analytes of interest and should be selected such that the retention volume of the most volatile compound of interest is not exceeded during the sampling phase. Use of weak or medium strength **hydrophobic** sorbents (for example porous polymers or carbon blacks) is strongly advised in most cases and will still allow quantitative retention of compounds as volatile as $C_{3/4}$ hydrocarbons because stack sample volumes are normally so small. The advantage of hydrophobic sorbents is that most water will be lost through the tube during the sampling process, leaving the collected sample relatively dry with less risk of water interference during the subsequent TD-GC(/MS) analysis. Hydrophobic sorbents also have more stable retention/breakthrough volumes whereas the retention volume of strong sorbents, such as carbonised molecular sieves, can be reduced by as much as a factor of 10 at high (>80%) relative humidity. [For more information on sorbents and sorbent selection please ready Markes TDTS 5[18] and TDTS 20[19].]

Another important issue to be aware of during industrial emissions testing is the temperature differential between the stack gas and the sorbent tube, particularly if the stack gas is wet. It is important to ensure that the stack gas is cooled and/or the sorbent tube is warmed such that the temperature of the sample tube is one or two degrees above that of the stack gas, at least at the sampling end. This reduces the risk of water condensing inside the tube and interfering with analyte retention. If liquid water is allowed to condense inside the tube it can begin to flow through the tube during the sampling process and may even carry more polar and volatile analytes with it in a type of liquid chromatographic effect. Retention volumes will be adversely affected if this occurs. This said, it is also important that the temperature of the tube is not warmed excessively as retention/breakthrough volumes typically halve for every 10ºC rise in temperature. It is also risky to take sorbent tubes much above 40 or 50ºC during sampling particularly if the stack gas has a high oxygen content. Some porous polymer sorbents and organic analytes are prone to oxidation.

With particularly hot (>100ºC) and humid stack gases (for example; emissions from combustion processes and kilns) water will inevitably condense in the sampling lines as the gas is cooled and may remove polar organic analytes from the gas stream as it does so. In this situation, one of the best options is to incorporate a readily-accessible cooled section of line containing an impinger in the sampling train. This allows the condensate to be collected and analysed separately using GC(-MS) to measure the level of organics which were either partially or completely taken out of the gas stream by the condensing water. Total organic emission levels can then be determined by summing these results with those from TD-GC(/MS) analysis of the sorbent tube.

With respect to the sorbent samplers, care must be taken after sampling to adequately seal the sorbent tubes using long term metal screw-type caps with combined PTFE ferrules (Ref.: US EPA Method TO-17, ASTM D 6196, ISO 16017, *etc.*). In the case of high humidity stacks, another useful precaution is to dry purge the sorbent tube, with pure dry gas flowing in the sampling direction, immediately prior to TD-GC(-MS) analysis. With Markes thermal desorption systems, this can either be done on-line (*i.e.* as part of the automated TD process) or offline – for example, using the TC-20™ multi-tube conditioning/dry purge unit.

The temperatures and times selected for subsequent thermal desorption will be dictated by the choice of sorbents (porous polymers have relatively low maximum temperatures) and the volatility range of the analytes of interest. Parameters are usually chosen such that sorbent tubes are left completely clean and ready for immediate re-use. High split ratios, both during primary (tube) desorption and secondary (trap) desorption are normally required, as described above, in order to prevent high concentration samples from overloading the analytical system. This facilitates optimum application of SecureTD-Q for quantitative repeat analysis of samples in the event of problems in the first analytical cycle or for data confirmation.

## Conclusion

This application note has explained how thermal desorption can benefit a wide range of industrial emissions testing applications - offering compatibility with both whole air/gas containers and sorbent tubes and providing quantitative measurement of organic analytes ranging in volatility from $C_2$ to $C_{26+}$ and from ppb to % concentrations. With the recent innovation of SecureTD-Q, it has also been shown that thermal desorption has now overcome its only traditional 'one-shot' limitation.

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* Available on the Markes International website (www.markes.com) (registration required).

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