TDTS 22

Selection of gas flows and split ratios during thermal desorption

Selecting minimum and maximum gas flows

Primary (tube) desorption

During primary desorption, the flow through the tube must be at least 10 mL/min. Note that the lower the flow through the focusing trap during primary desorption, the more efficient will be its retention of target analytes – it should not normally be allowed to exceed 50 mL/min.

Secondary (focusing trap) desorption

For efficient desorption, at least 2 mL/min must be used to desorb the focusing trap, and it should not normally be allowed to exceed 75 mL/min. All of this flow can be directed to the GC analytical column, or to a combination of column and split vent.

Notes:

- When analysing high-boilers (> n-C_{20}), use much faster desorption flows through the hot tube (>50 mL/min) and at least 10 mL/min through the focusing trap.
- Some flow drift will be observed if needle valves are set below 2–3 mL/min.

Selecting split ratios

Split ratios for UNITY instruments may be set between zero (splitless) and 10,000:1. The split ratio required for a particular analysis will be dependent on (a) the analyte mass in the sample tube, (b) the analytical column capacity and (c) the sensitivity of the GC detector.

(a) Calculating analyte masses in the sample tube

In order to determine the required split ratio, it is necessary to know approximately the mass of analyte expected to be retained/collected in the sample tube.

For direct desorption of volatiles from materials, this is most easily determined experimentally from control or real-life samples. It can also be calculated from relevant material specifications where appropriate. For example, if the specification for residual chloroform in cough medicine is 1% w/w, a 20 mg sample will contain 200 µg.

For air monitoring applications the calculations are a little more complex, as they depend on variables such as diffusive uptake rate, pumped volume and molecular weight. Tables 1 and 2 show calculated masses that can be used as a quick reference guide.

Conc.	Diffusive uptake rate (ng ppm^{-1} min^{-1})				
	1.3	1.5	1.7	2.0	2.5
100 ppm	0.624 mg	0.72 mg	0.816 mg	0.96 mg	1.2 mg
10 ppm	6.24 µg	7.2 µg	8.16 µg	9.6 µg	12.0 µg
1 ppm	0.624 µg	0.72 µg	0.816 µg	0.96 µg	1.2 µg
10 ppb	62.4 ng	72 ng	81.6 ng	96 ng	120 ng
1 ppb	6.24 ng	7.2 ng	8.16 ng	9.6 ng	12 ng
100 ppt	0.624 ng	0.72 ng	0.816 ng	0.96 ng	1.2 ng

Table 1: Mass of component collected during 8 h of diffusive monitoring.

Conc.	Molecular weight				
	50	75	100	150	200
1000 ppm	20 mg	30 mg	40 mg	60 mg	80 mg
10 ppm	200 µg	300 µg	400 µg	600 µg	800 µg
1 ppm	20 µg	30 µg	40 µg	60 µg	80 µg
10 ppb	200 ng	300 ng	400 ng	600 ng	800 ng
1 ppb	20 ng	30 ng	40 ng	60 ng	80 ng
100 ppt	2 ng	3 ng	4 ng	6 ng	8 ng

Table 2: Mass of component collected when 10 L of air is pumped into a sorbent tube.

(b) Analytical column capacity

The capacity of an analytical column will depend on its diameter and the thickness of the film of stationary phase. As a general rule, a 0.25 mm i.d. column with a 25 µm film has an approximate sample capacity of 100 ng per component. Wider-bore and thicker-film columns will have a higher sample capacity – up to low micrograms in the case of thick-film (5 µm) columns with 0.53 mm i.d. Narrower-bore and thinner-film columns will have a lower sample capacity of <10 ng per component in some cases.

(c) Sensitivity of GC detectors

The sensitivity of GC detectors depends on both the type of detector and manufacturer, and it is advisable to consult the manufacturer for details. However, the following general guidelines may be useful:

- **Mass spectrometer in full-scan mode:** Modern systems should comfortably be able to detect and quantify a single compound at 10–100 pg.
- **Mass spectrometer in selected ion mode:** Modern systems should comfortably be able to detect and quantify a single compound at 1 pg.

- **Flame ionisation detector (FID):** Typical detection limits 10–100 pg for individual hydrocarbons.
- **Electron capture detector (ECD):** Highly selective detector. Used for halogenated solvents. Detection limits are well below 1 pg for compounds such as carbon tetrachloride and some halogenated pesticides.
- **Thermal conductivity detector (TCD):** General-purpose, low-sensitivity detector. Typical detection limits are in the order of 10 ng.

Calculating split ratios

Once the mass of analyte expected, the detection limits of the system and the analytical capacity of the column are all known, then an overall split ratio can be calculated.

For example, if the expected mass of analyte on the sample tube is 50 µg and the analytical column capacity is 100 ng, then a total split ratio of at least 500:1 is required to prevent column overload, *i.e.* <0.2% of the sample must be transferred to the column.

One of three different split modes can be utilised:

(a) Zero split (splitless operation)

Unusually among thermal desorbers, UNITY can operate in the splitless mode in conjunction with narrow-bore (0.32 mm i.d.) columns, as the minimum flow required through the focusing trap during trap heating is 2 mL/min.

Notes:

- During tube desorption the desorb flow must be set to at least 10 mL/min to provide enough flow through the sample tube for efficient thermal desorption.
- During tube desorption the desorb flow should not far exceed 50 mL/min, or there may be a risk of breakthrough from the focusing trap.

During splitless operation:

Flow through tube during tube desorption = Desorb flow

Flow through trap during tube desorption = Desorb flow

Flow through trap during trap heat = Column flow

(b) Single-split operation

During single-split operation the split may either be open during tube or trap desorption. The advantages of having the split open on the way into the trap (inlet split) are:

- A relatively fast flow can be used through the tube to facilitate desorption while, at the same time, the flow passing through the focusing trap is kept low to aid retention and focusing of analytes
- The focusing trap is not overloaded with solvent or analytes – the UNITY focusing trap is designed for optimum desorption speed/efficiency, and is deliberately small and fast-heating. Split discrimination and/or peak splitting may be observed if the trap is allowed to become overloaded with volatile solvent or water.

Notes:

- During tube desorption, the flow through the hot tube must be set to at least 10 mL/min to provide enough flow through the sample tube for efficient thermal desorption.
- During tube desorption, the 'desorb' flow (*i.e.* the flow through the focusing trap) should not exceed 50 mL/min, or there may be a risk of breakthrough from the focusing trap.
- During tube desorption, the desorb flow should not be less than 2 mL/min, to ensure efficient sweeping of analytes onto the trap sorbent.
- The flow through the trap during trap heat should not exceed 75 mL/min.

During single-split operation:

Flow through tube during tube desorption = Desorb flow (+ Split flow if selected)

Flow through trap during tube desorption = Desorb flow

Flow through trap during trap heat = Column flow (+ Split flow if selected)

$$\text{Split ratio} = \frac{\text{Desorb flow}}{\text{Split flow + Desorb flow}}$$

OR

$$\text{Split ratio} = \frac{\text{Column flow}}{\text{Column flow + Split flow}}$$

(c) Double-split operation

During double-split operation the split is open both during tube desorption and trap heating.

Notes: (As for single split operation).

During double split operation:

Flow through tube during tube desorption = Split flow + Desorb flow

Flow through trap during tube desorption = Desorb flow

Flow through trap during trap heat = Split flow + Column flow

Split ratio = Inlet split × Outlet split

$$= \frac{\text{Desorb flow}}{\text{Split flow + Desorb flow}} \times \frac{\text{Column flow}}{\text{Column flow + Split flow}}$$

Gas flow through the analytical column

Gas flow through the analytical column ('column flow') should always be optimised for chromatographic separation of the analytes of interest, and not for thermal desorption. Typical capillary column flows range from 0.5 mL/min for 100 µm i.d. columns, to ≥10 mL/min for 530 µm columns. UNITY offers maximum split ratio versatility with columns that operate most effectively at >10 psi and flows between 1–4 mL/min.

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