

Sample Re-collection on the TurboMatrix 650 ATD Thermal Desorber



Introduction

The TurboMatrix™ 650 ATD is the most sophisticated of the PerkinElmer® family of five Thermal Desorber models. It incorporates technology, allowing a portion of desorbed sample vapor to be re-collected rather than injected into the gas chromatograph, providing a second sample. This sample, which would otherwise be lost through sample splitting, can now be re-collected onto the original or a fresh sorbent tube to enable a subsequent analysis.

This functionality is useful in situations where the sample contains both high-level and low-level concentrations of analytes.

In such cases, the ability to re-collect sample allows the sample analysis to be repeated using a different split ratio.

Another key benefit of sample re-collection on the original or different tubes is that analysis can be repeated by an independent laboratory for audit or litigation reasons.

Furthermore, automatic re-analysis is possible because the re-collected sample is on the same magazine. This approach also minimizes the cost of both labor and the requirement for a second autosampler magazine with additional tubes to make the re-collection.

Key Benefits

- ▶ Allows quantitation of tubes that may contain high and low analyte levels in a single unattended analytical run
- ▶ Provides automatic re-analysis without user intervention
- ▶ Minimizes costs both in labor and the requirement of a second autosampler magazine
- ▶ Allows analysis to be repeated by an independent laboratory for audit or litigation reasons

Principle of operation

Figure 1 shows the pneumatics inside the TurboMatrix 650 ATD. The rotary valve (*RVA*) on this model uses an electronic actuator to allow rotation of the valve to any of 8 possible positions. This valve is positioned to allow part of the vapor

produced during trap desorption to enter the transfer line/column and part of it to pass through a sample tube and out to a solenoid valve (*ESV1*) and electronic mass flow controller (*MFC3*). In principle, *MFC3* acts in the same way as the outlet split control – except that

now a sample tube is in-line with the split-flow path. Consequently, the analyte vapors that would otherwise be lost in the outlet splitter can now be re-collected on a sample tube.

The tube used for the re-collection can either be the original tube that introduced the sample into the trap or a fresh (previously conditioned) tube can be loaded to make this re-collection. In both cases, the sample and re-collection tubes share a single internal tube magazine. The TurboMatrix 650 ATD magazine is labeled to indicate the destinations of the re-collected sample when using fresh tubes, as shown in Figure 2.

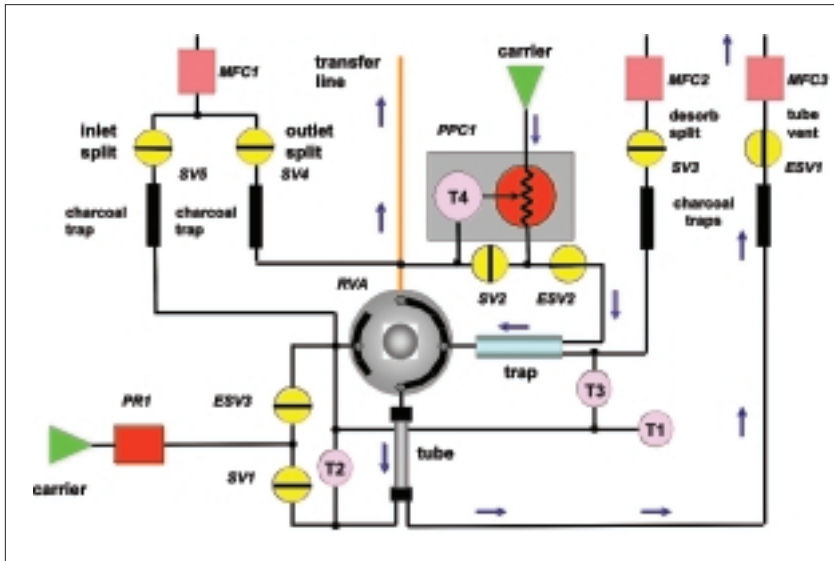


Figure 1. Pneumatic diagram of the TurboMatrix 650 ATD with *RVA* in sample re-collection position.



Figure 2. TurboMatrix 650 ATD magazine showing a label associating sample tubes and re-collection tubes.

Instrument setup for sample re-collection

It is easy to set up an analytical method using the TurboMatrix touch-screen interface for sample re-collection. The user chooses the thermal desorption conditions as for any normal analysis, but the operating mode is now selected as shown in Figures 3-5, depending on whether the sample will be re-collected on the original tube or on a fresh one.

Calculation of sample re-collection

The amount of sample vapor re-collected on a tube will depend on both the inlet split ratio and the outlet split ratio (or more correctly, the ratio of the re-collection flow rate to the column flow rate). As any sample vented through the inlet split will be lost from the system, it is expected that inlet splitting will not normally be applied in order to maximize recovery onto the re-collection tube.

Equation 1 may be used to calculate the sample fraction that would be expected to pass into the re-collection tube. The remainder would be lost either during inlet splitting (if applied) or through introduction into the GC column for the initial analysis.

$$R = 100 \cdot \left(\frac{F_d}{F_d + F_i} \right) \cdot \left(\frac{F_r}{F_r + F_c} \right) \text{----- Equation 1}$$

Where:

R is the percent of sample re-collected onto the tube

F_d is the flow rate of gas into the trap during tube desorption

F_i is the flow rate of gas exiting the inlet split during tube desorption

F_r is the flow rate of gas into the re-collection tube during trap desorption

F_c is the flow rate of gas into the column

Equation 1 describes the fraction that is re-collected and it also represents the ratio between the peak areas of the re-collected chromatogram to the initial chromatogram, if analyzed under exactly the same conditions.

Experimental

To demonstrate the efficacy of this sample re-collection technology, a standard gas mixture of benzene, toluene and xylenes (BTEX) was

introduced into a tube. This tube was analyzed using the conditions given in Table 1. The re-collected sample was analyzed under the same conditions.

Results

Table 2 shows a comparison between the observed peak-area ratios for the two chromatograms and the expected ratios calculated using Equation 1. Very good agreement is demonstrated between the experimental and predicted results.

In instances where the re-collection flow rate is much higher than the column flow rate, only a small amount of the sample will enter the GC column and most will be

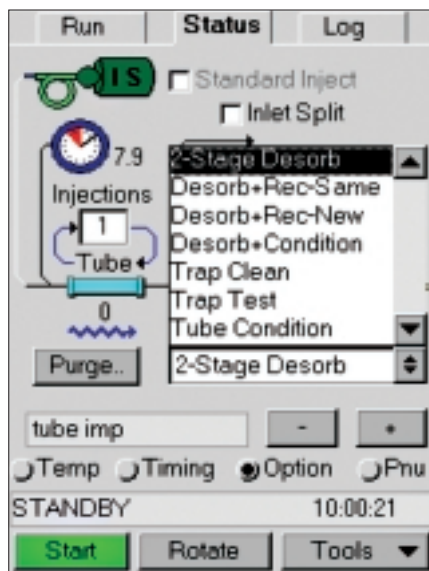


Figure 3. Screen display showing available operating modes.

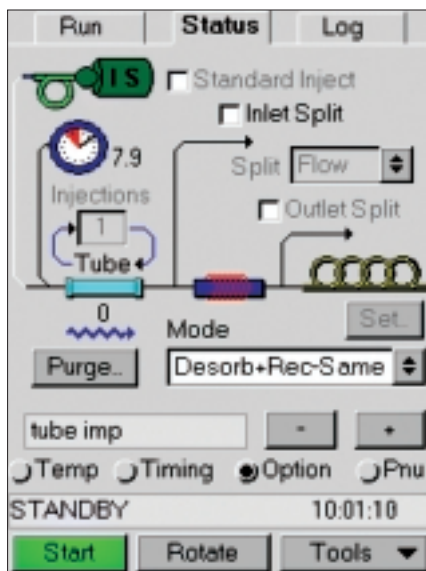


Figure 4. Screen display showing selection of mode to re-collect sample vapor on original tube.

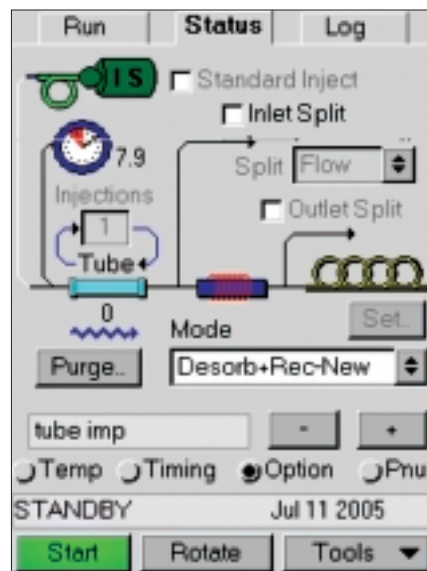


Figure 5. Screen display showing selection of mode to re-collect sample vapor on fresh tube.

re-collected onto a tube. It now becomes possible to repeat the analysis many more times. Figure 6 (page 5) shows the overlaid chromatograms of 19 replicate analyses of a tube loaded with gasoline vapor, according to the conditions given in Table 3. These data are particularly impressive because of the large number of repeat runs that were conducted without any obvious degradation in the chromatography.

One special concern was that successive analyses might demonstrate a discrimination effect as a result of non-linear splitting of the sample vapor during trap desorption. To investigate whether this was occurring with the technology being used here, several peaks were chosen throughout the chromatography shown in Figure 6 – labeled as Peaks 1 to 11. The peak areas were ratioed against the peak area for Peak 5 in each chromatogram. These ratios are given in Table 4 (page 5).

Peaks 1, 2, 6, 9 and 10 are not fully baseline resolved, which may contribute to integration errors and a slightly higher %RSD than for the other peaks.

Note that the relative areas of all the peaks are consistent throughout the sequence of analyses. If there was a discriminatory effect, then a progressive change in peak area would be observed. This data clearly shows that this method, using mass flow controllers and PPC regulators for sample re-collection, does not exhibit mass discrimination.

Table 1. Experimental Conditions Used for BTEX Sample Re-collection Tests.

Valve temperature:	250 °C	Trap low:	-5 °C
Tube oven temperature:	280 °C	Trap high:	350 °C
Transfer line:	250 °C		
Purge time:	1 min	Primary desorb:	5 min
Cycle time:	15 min	Secondary desorb:	3 min
Carrier pressure:	12 psig	Desorb flow:	20 mL/min
		Re-collect flow:	20 mL/min
GC oven:	50 °C (hold for 2 min) then 9 °C/min to 110 °C (0 hold time)		
Detector:	Flame ionization - 250 °C - Range: 1 - Attenuation: 4		

Table 2. Comparison Between Experimental and Predicted Peak-Area Ratios.

	Benzene	Toluene	Ethylbenzene	o,p- xylene	m- xylene
Standard	148991	170832	193878	385604	193572
Re-collected	142854	165531	188891	371894	186047
Calculated re-collection	141896	162697	184646	367242	184354
% Re-collected	95.9	96.9	97.4	96.4	96.1
% Expected re-collection	95.2	95.2	95.2	95.2	95.2

Table 3. Experimental Conditions Used for Gasoline-Sample Multiple Re-collection Tests.

Valve temperature:	250 °C	Trap low:	-10 °C
Tube oven temperature:	280 °C	Trap high:	350 °C
Transfer line:	250 °C		
Purge time:	1 minute	Primary desorb:	5 min
Cycle time:	45 minutes	Secondary desorb:	3 min
Carrier pressure:	12 psig	Desorb flow:	20 mL/min
		Recollect flow:	50 mL/min
GC oven:	35 °C (hold for 5 min) then 5 °C/min to 150 °C (hold for 5 min)		
Detector:	Flame ionization - 250 °C - Range: 1 - Attenuation: 4		

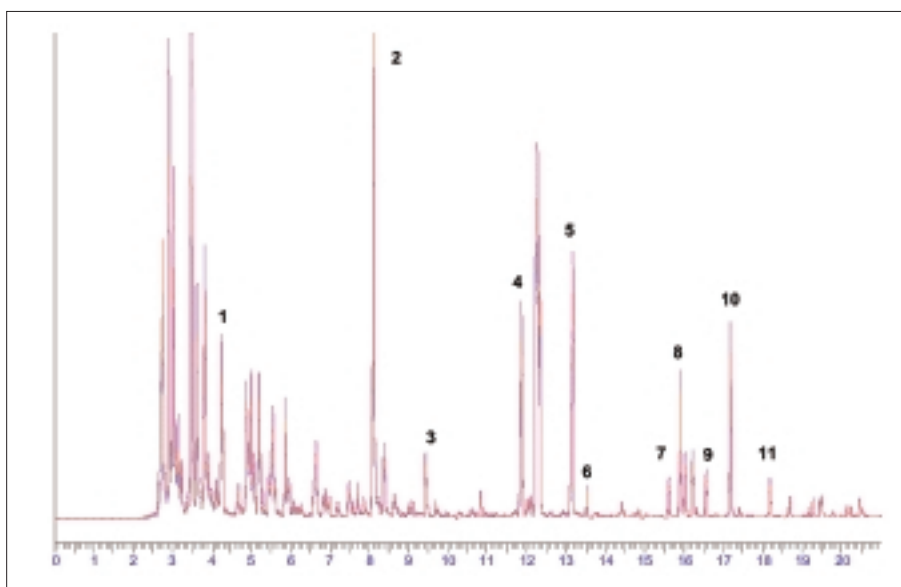


Figure 6. 19 repeat chromatograms from a single tube loaded with gasoline vapor.

Besides providing the ability to allow a second (or multiple) re-analysis of a sample, this technique also allows the sample to be run under different conditions. One application could be to run the sample at a high split ratio and follow it with a re-analysis at a lower ratio to enable both high and low concentration analytes to be determined within the same sample, greatly expanding the dynamic range of the analysis without additional sample preparation.

The next experiment used a series of injections with changing re-collection/split flows and re-collection

Table 4. Areas of Selected Peaks Ratioed Against the Area of Peak 5 (Results are Expressed as Percentages).

	Peak 1	Peak 2	Peak 3	Peak 4	Peak 6	Peak 7	Peak 8	Peak 9	Peak 10	Peak 11
Run 1	71.36	246.16	28.69	84.18	10.96	15.86	57.99	16.59	76.49	16.49
Run 2	72.73	266.62	28.39	84.78	10.47	15.74	57.50	16.35	73.57	16.10
Run 3	68.62	261.39	28.36	83.96	10.51	15.76	57.41	16.35	73.53	15.96
Run 4	65.36	246.12	28.85	84.32	10.56	15.81	57.72	16.34	73.80	16.12
Run 5	65.92	268.54	29.06	84.28	10.72	15.73	57.50	16.25	73.69	16.12
Run 6	66.60	246.72	28.87	84.35	10.83	15.72	57.36	16.13	73.13	16.04
Run 7	67.03	246.30	28.88	84.12	10.59	15.75	57.43	16.52	73.28	16.02
Run 8	70.74	247.33	28.73	82.90	10.22	15.75	57.36	17.14	73.20	16.11
Run 9	67.93	256.45	29.05	83.57	10.29	15.84	57.93	17.43	74.36	16.36
Run 10	67.13	244.57	28.86	83.94	10.21	15.74	57.54	16.60	73.34	16.20
Run 11	67.29	246.17	28.98	82.57	10.68	15.76	57.55	16.67	72.62	16.21
Run 12	74.53	246.17	29.11	83.96	10.19	15.71	57.33	16.57	72.10	16.05
Run 13	67.98	246.04	28.68	82.56	10.19	15.75	57.49	16.66	75.53	15.96
Run 14	68.64	246.57	28.72	84.05	10.13	15.77	57.41	16.65	73.22	16.09
Run 15	68.98	246.42	29.08	83.87	10.20	15.77	57.44	17.65	73.36	16.00
Run 16	71.70	245.86	29.00	84.00	10.13	15.78	57.49	16.75	72.32	16.20
Run 17	72.36	262.31	28.75	83.74	10.15	15.77	57.37	16.77	72.77	15.98
Run 18	70.61	245.78	28.98	83.87	10.21	15.77	57.51	16.77	71.90	16.11
Run 19	72.45	261.92	28.75	83.36	10.20	15.81	57.58	16.87	73.55	16.28
Mean	69.37	251.44	28.83	83.81	10.39	15.77	57.52	16.69	73.46	16.13
RSD %	3.80	3.30	0.73	0.71	2.54	0.24	0.31	2.29	1.49	0.87

on the same tube. Figure 7 shows a chromatogram of an initial sample split flow of 100 mL/min and overlaid is the chromatogram of the re-collected sample at a split flow of 5 mL/min. The lower split-flow rate provides enhanced peak response.

Conclusions

The robustness of the technique has been demonstrated in various ways, notably:

1. RSD data showed that peak-area ratios from 11 peaks in a gasoline sample do not change significantly with each successive re-collection, confirming that PPC mass flow controllers in the TurboMatrix 650 ATD maintain a very non-discriminatory splitting performance.
2. The ability to run a sequence of samples with different split ratios allows quantitation of tubes that may contain high and low analyte levels in a single unattended analytical run.

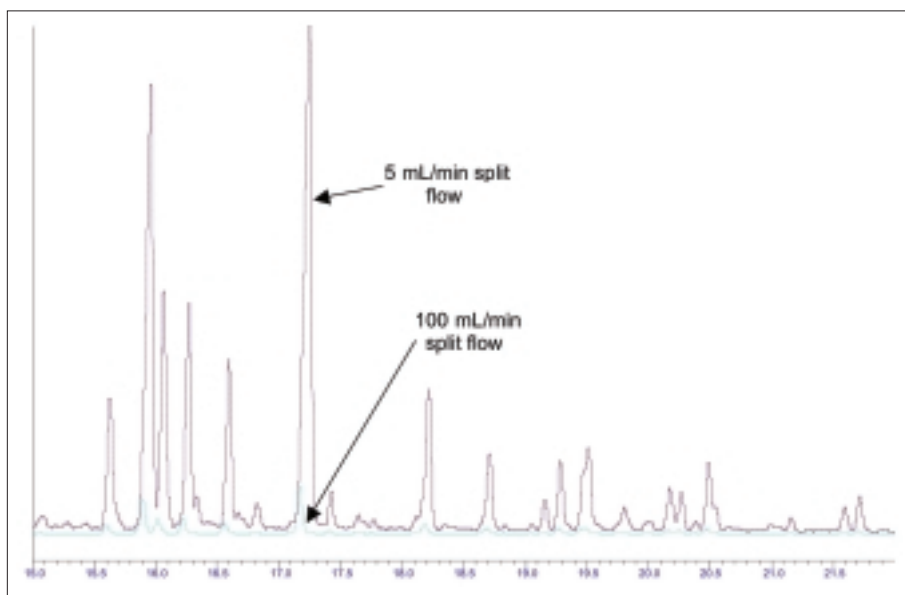


Figure 7. Gasoline sample run with 100 mL/min re-collection flow rate and then the re-collected sample run with 5 mL/min re-collection flow.

Since the same magazine is used to hold the re-collected sample, a sequence can be built that will automatically re-analyze a sample without the need for operator intervention. This technique minimizes the cost of both labor and

the requirement of a second auto-sampler with additional tubes to make the re-collection.

Overall, sample re-collection is a key feature, providing increased confidence in your results.