



Quantitative Sample Split by CDS 7550S Automated Thermal Desorber

Application Note

General

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Abstract

This application note demonstrates the quantitative sample split capability of 7550S thermal desorber for a group of VOCs with boiling point up to 218 °C.

Introduction

Gas chromatography (GC) is an analytical technique by separating a mixture of compounds for a downstream detector to identify the chemical composition of each component. In order to obtain quantitative results without overloading the capillary column, modern GC instrumentation adopts the split/splitless inlet (SSI) to vaporize and reduce the amount of the sample passing through the column. This design has some main drawbacks when the sample is introduced by syringe injection, including solvent removal, water management, discrimination of high boiling analytes, poor repeatability of insoluble compounds. To tackle with this challenge, various sample introduction techniques are introduced for GC, including Dynamic Headspace, Purge and Trap, Thermal Desorption, Pyrolysis and Solid Phase Micro Extraction. All of these sample introduction techniques are vaporizing the sample before reaching the SSI to eliminate discriminative split in order to improve the quantification.

Among all the GC sample introduction techniques, thermal desorption involves heating a thermal desorption sample tube, which is packed with sorbent, to a desired desorption temperature and then purge inert gas to release volatile organic compounds (VOCs) adsorbed on the sorbent surface. The purging gas, along with mixed VOC analytes, flows through a heated sample path way in vapor phase to reach the GC for separation and detection. The most popular thermal desorption sample tube has an outer diameter of 0.25 inch and length of 3.5 inch. The VOCs adsorbed in each sample tube could exceed hundreds of micro gram, which is over 3 orders of magnitude greater than the maximum sample capacity allowed from a 0.25 mm inner diameter and 0.25 μ m film capillary column. This amount of sample will overload the column even at the maximum 100:1 SSI split ratio in GC without an auxiliary sample split.

CDS 7550S automated Thermal Desorber has an in-line sample split option to reduce the analyte amount in a range from 1% (100:1 split ratio) to 50% (1:1 split ratio) before reaching the GC. To obtain the quantitative performance of this sample split, seven different VOCs with boiling point up to 218 °C are tested from 2% (50:1 split ratio) to 50% (1:1 split ratio) in 7550S.

Experiment Setup

A CDS 7550S automated thermal desorber with sample split option was used for the test. The VOCs desorbed from the thermal desorption sample tube was first split in the 7550S at a user-select split ratio, which was fulfilled by a mechanism electronically controlled by a Mass Flow Controller (MFC). After the split, VOCs were adsorbed by a secondary focusing trap, where it will be desorbed into the SSI, where the GC sample split is performed. The maximum sample split ratio that could be achieved through this setup is 10,000:1. The 7550S and GC-MS parameters are listed below:



7550S Thermal Desorber:

Valve oven: 220 °C
GC transfer line: 250 °C
Tube purge flow: 16 and 89 mL/min
Pre-heat time: 15 s
Tube Rest temp.: 37 °C
Tube Dry purge temp.: 37 °C
Tube Dry purge time: 1 min
Tube Desorb temp.: 315 °C
Tube Desorb time: 8 min
Sample tube: Camsco EPA 325
Trap Rest temp.: 45 °C
Trap Desorb temp.: 315 °C
Trap Desorb time: 4 min
Trap Type: Camsco TO-17

GC conditions:

Oven temp.: 35.0 °C
Injection temp.: 230 °C
Injection mode: Split
Column Flow: 1.21 mL/min
Split Ratio: 20.0
Temp. program: 35.0 °C hold 2 min
30.0 °C ramp to 245.0 °C
hold 1 min

Mass conditions:

Ion Source: 200.00 °C
Interface Temp.: 250.00 °C
Start m/z: 35.00
End m/z: 160.00

Benzene, toluene, ethylbenzene, m,p-xylene, o-xylene and naphthalene standards were purchased from Sigma-Aldrich. The standards were mixed and diluted in methanol to a final concentration of 400 mg/L for each component as the stock solution.

1 μ L of the stock solution was injected onto a pre-conditioned thermal desorption sample tube through a sample injection accessory supplied with CDS tube conditioner. The methanol was removed by purging the sample tube with nitrogen at 50 mL/min for 4 min. This thermal desorption tube was then loaded into the sample tube rack of 7550S for analysis.

A series of split ratios at 2% (50:1 split), 5% (20:1 split), 20% (5:1 split), and 50% (1:1 split) was used to demonstrate the performance of 7550S sample split function. Two different total purge flow rates, one is slow at 16 mL/min and the other is fast at 89 mL/min, were evaluated respectively to probe the optimum split condition.

Results and Discussions

Reproducibility was first tested by obtaining RSDs of each peak at a fixed split ratio through multiple runs. Figure 1 is the total ion chromatogram (TIC) overlay from 6 runs at 2% split ratio. The RSDs are shown in Table 1 for each component with an average

RSD at 6.4%. Adequate separation and symmetric line shape were observed.

After verifying the basic performance, 7550S was tested at different split ratios. Two total purge flow rates were deployed as 16 mL/min and 89 mL/min. Figure 2 shows the TIC of the 7 components at 4 split ratios under 89 mL/min total purge flow.

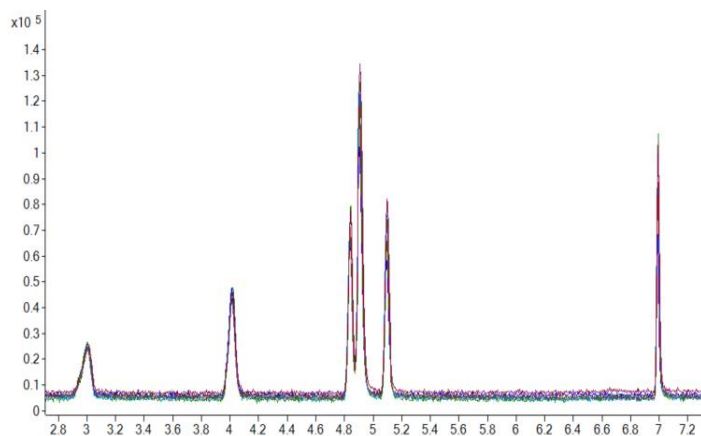


Figure 1: TIC overlay of 6 runs at 2% split ratio.

Table 1: Reproducibility from 6 runs at 2% split ratio.

Compound	Benzene	Toluene	Ethylbenzene	m,p-Xylene	o-Xylene	Naphthalene
RSD (n=6)	4.1%	6.4%	6.2%	6.1%	6.9%	8.8%

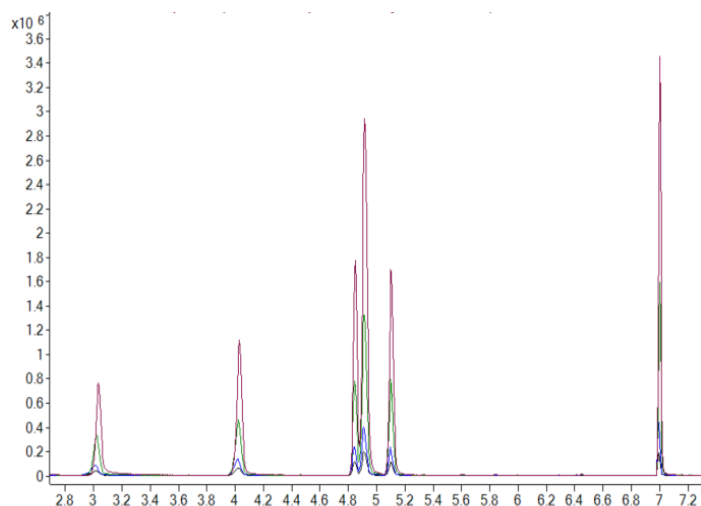


Figure 2: TIC of 6-component VOCs mix at 4 different split ratios of 2%, 5%, 20% and 50% with 89 mL/min total purge flow.

By fitting the peak area vs. split ratio, a calibration curve is drawn in Figure 3 and Figure 4 for the slow and fast total purge flow. Since the concentration is known for each component, the data of accuracy, which is the recovery of calibration, the response factor (RF), and the R^2 of the linear were calculated. Table 2 and Table 3 summarized the calculation for slow and fast total purge flow respectively.

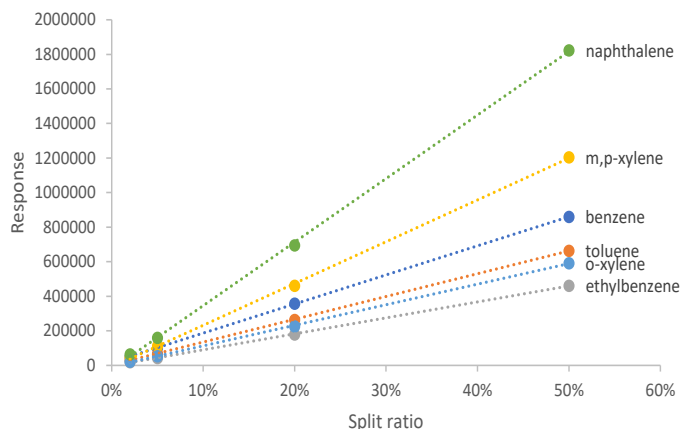


Figure 3: Calibration curve fit with linear regression for 16 mL/min total purge flow.

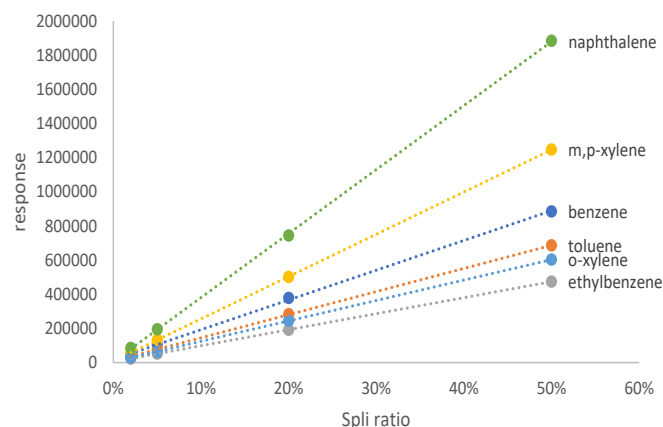


Figure 4: Calibration curve fit with linear regression for 89 mL/min total purge flow.

Table 2: Data of accuracy (%), response factor and R^2 by total purge flow at 16 mL/min.

Split ratio	Mass (ng)	Benzene		Toluene		Ethylbenzene		m,p-Xylene		o-Xylene		Naphthalene	
		Acc	RF	Acc	RF	Acc	RF	Acc	RF	Acc	RF	Acc	RF
2%	8	103	6472	105	4014	110	2451	108	5745	110	2816	107	8080
5%	20	101	5106	98	3443	95	2149	98	5616	96	2659	95	8018
20%	80	101	4463	98	3292	98	2241	97	5754	97	2815	97	8683
50%	200	100	4299	100	3319	100	2305	100	6021	101	2958	101	9118
R^2			1.0000		1.0000		0.9999		0.9998		0.9998		0.9999
RSD			19.4%		9.6%		5.6%		2.9%		4.3%		6.2%

Table 3: Data of accuracy (%) and response factor and R^2 by total purge flow at 89 mL/min.

Split ratio	Mass (ng)	Benzene		Toluene		Ethylbenzene		m,p-Xylene		o-Xylene		Naphthalene	
		Acc	RF	Acc	RF	Acc	RF	Acc	RF	Acc	RF	Acc	RF
2%	8	89	5819	95	4346	98	2903	101	7391	102	3683	102	10733
5%	20	102	5251	101	3862	101	2610	100	6613	98	3189	99	9756
20%	80	104	4725	101	3542	100	2409	99	6264	100	3061	98	9307
50%	200	99	4426	100	3428	100	2368	100	6237	100	3012	100	9418
R^2			0.9998		1.0000		1.0000		1.0000		1.0000		1.0000
RSD			12.1%		10.8%		9.5%		8.1%		9.5%		6.6%

supports that the sample split of 7550S is quantitative. Comparison between Table 2 and Table 3 also suggests that a total purge flow rate near 90 mL/min is an optimized setting which yields better quantitative results.

Conclusions

This application note has showcased a sample split function in the 7550S automated thermal desorber. The hardware consists of a in-line split mechanism controlled by Mass Flow Controller. The results show that this sample split yields quantitative data and proves that the 7550S is a versatile thermal desorption instrument that could handle large sample amount that could overload the capillary column in the GC.

From the table above, the data accuracy within 90%-110%, as well as precision below 20% throughout the different split ratios were observed. The R^2 was also greater than 0.999. This result