Automated Sample Recollection by the CDS 7550S Pro Automated Thermal Desorber

Application Note
General

Author:

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Abstract
This application note demonstrates the quantitative, automated recollection of split sample to a clean sample saver tube. This is demonstrated by different split percents on the CDS 7550S automated thermal desorber for a group of VOCs with boiling points as low as -30°C and up to 150°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. Direct liquid injection intot the GC inlet is the most common method of introducing sample onto the GC column. However, in many situations, the analyte identity, analyte concentration, or the matrix are not compatible for GC analysis. To tackle this challenge, various sample introduction techniques, including purge and trap, thermal desorption, pyrolysis, and solid phase micro extraction were developed to introduce analyte onto the GC column to achieve the best separation result.

Among the GC sample introduction techniques, thermal desorption involves heating a thermal desorption sample tube, which is often packed with sorbent(s), to a desired desorption temperature and then purging with inert gas to release volatile organic compounds (VOCs) adsorbed onto the sorbent surface. The purging gas, along with mixed VOC analytes, flows through a heated sample pathway in the vapor phase to reach the GC for separation and detection. The sample splitting technology of thermal desorption instrumentation offers the flexibility to reduce the amount of analyte reaching the GC injection port and extending the dynamic range of the detector coupled to the GC. A concern of sample splitting; however, is that it is a single-shot technique whereby sample going to split is lost out of the split vent not allowing for repeat analysis of a given sample. The option to recollect sample going to the split vent on a clean sample tube has many advantages, including repeat sample analysis, method validation, and acquiring experimental results via complementary detection methods.

Here the CDS 7550S thermal desorber introduces an automated sample recollection feature, also referred to as the sample saver, as a function within the sample split option. The sample saver is combined with sample splitting to analyze quantitative performance of this sample saver function. Seven different VOCs with boiling points up to 150°C are tested at 50% split and 40 mL/min of nitrogen purge flow.

Table 1:

7550S Pro Thermal Desorber:

Valve oven:	250 °C
Tube purge flow:	40 mL/min
Tube Rest temp.:	40 °C
Tube Desorb temp.:	300 °C
Tube Desorb time:	2 min
Sample and Sample Saver Tube:	carbograph 2/carbograph 1/ carboxen 1000
Trap Rest temp.:	-10 °C with Peltier
Trap Desorb temp.:	300 °C
Trap Desorb time:	2 min
Trap Type:	Vocarb 3000
Sample Saver Tube Rest:	40 °C
Sample Saver Tube Heat:	300 °C
Sample Saver Tube Desorb Time:	2 min
Peltier transfer line:	250 °C
GC transfer line:	250 °C

GCMS QP-2010

GC conditions:

Column:	Restek RTX VMS
Oven temp.:	35.0 °C
Injection temp.:	240 °C
Injection mode:	Split
Column Flow:	1.00 ml/min
Split Ratio:	20.0 : 1
Temp. program:	35.0 °C hold 4 min
	10.0 °C/min to 150.0 °C
	50.0 °C/min to 220.0 °C
	Hold 3.10 min

MS conditions:

Ion Source:	200.00 °C
Interface Temp.:	220.00 °C
Start m/z:	35.00
End m/z:	260.00

Experiment Setup

A CDS 7550S automated thermal desorber with the automated sample split / sample saver capability was used for testing. The VOCs desorbed from the thermal desorption sample tube were first split in the 7550S at a user-selected split ratio, which was fulfilled by a mechanism electronically controlled by a mass flow controller (MFC). The portion of the sample split going to the vent was recollected on a clean sample tube before being automatically returned to the original sample tube. Both the primary sample tube and the sample saver tube were manufactured by Camsco and packed with Carbograph 1/Carbograph 2/Carboxen 1000 (P/N SU644-4).

For the other portion of the split, VOCs were adsorbed by a secondary focusing trap, which was electronically cooled by a Peltier module. Sample adsorbed inside the focusing trap was then transferred to the GC injection port. The 7550S and GC-MS parameters are listed in Table 1:

A standard solution of 2000 ng/uL of 502.2 Calibration mix was purchased from Restek. The components of the mixture are listed in Table 2. 1 µL of the stock solution was injected onto a pre-conditioned thermal desorption sample tube and purged with nitrogen at 100 mL/min for 1 min. This thermal desorption tube was then loaded into the autosampler rack of the 7550S for analysis.

Once the sample tube was loaded into the tube heater, a 5mL portion gaseous internal standard was automatically added to the sample tube. The internal standard mixture contains benzene-d6, toluene-d8, and 1-bromo-4-fluorobenzene all with a 2ppmv concentration.

Samples were desorbed from the sample tube to the focusing trap and the clean sample saver tube at 50% split and a purge flow of 40 mL/min. Half of the sample that was collected on the focusing trap and was then desorbed from the trap to the GC-MS. The other half of the sample collected on the clean sample saver tube was then automatically desorbed back to the original sample tube. A second run with the original sample tube was then conducted to desorb the recollected fraction to the focusing trap, without splitting, and then desorbed to the GC-MS for analysis. The quantitative performance of the sample split / sample saver option was assessed by analyzing accuracy and reproducibility of the integrated peak areas. The ratios of the integrated peak areas were expected to match the ratio of the flows, measured with a handheld flowmeter, going to the focusing trap and sample saver tube during sample splitting. Therefore, 100% accuracy is interpreted as the ratios of the integrated peak areas equal the ratio of the flows during sample splitting.

Table 2. Accuracy and %RSD based on the measured split flows to the trap and sample saver tube at 40 mL/min purge gas (n=6).

	Accuracy (%RSD)
dichlorodifluoromethane	102.0 (1.4)
chloromethane	104.5 (1.1)
vinyl chloride	101.7 (1.3)
bromomethane	108.7 (3.9)
trichlorofluoromethane	90.9 (1.5)
benzene-d6	109.7 (4.3)
toluene-d8	112.8 (2.4)
1-bromo-4-fluorobezene	109.5 (4.5)

Results and Discussions

Reproducibility was tested by obtaining % Accuracy (Acc) and %RSD for each of the peaks at a fixed split ratio through multiple runs. Figure 1a is the total ion chromatogram (TIC) overlay from the fraction initially split to the focusing trap and the recollected fraction while Figure 1b is zoomed in on the 5 first eluting VOCs in the chromatogram. Table 2 shows the %Acc and %RSD at 50% split. The %Acc was calculated as the measured fraction of total signal from the sample saver tube compared to the expected fraction of total signal.

From the table above, the data accuracy is within 91 and 113%, as well as an average %RSD of 3.4%. These results demonstrate that, not only is sample quantitatively split, but is also quantitatively captured by the sample saver tube.

Conclusions

This application note has showcased a sample saver function in the 7550S automated thermal desorber. The results show that the sample is quantitatively captured by the sample saver tube following sample splitting. This proves that the 7550S is a versatile thermal desorption instrument that offers a sample recollection mechanism to provide users with enhanced flexibility when performing sample analysis.

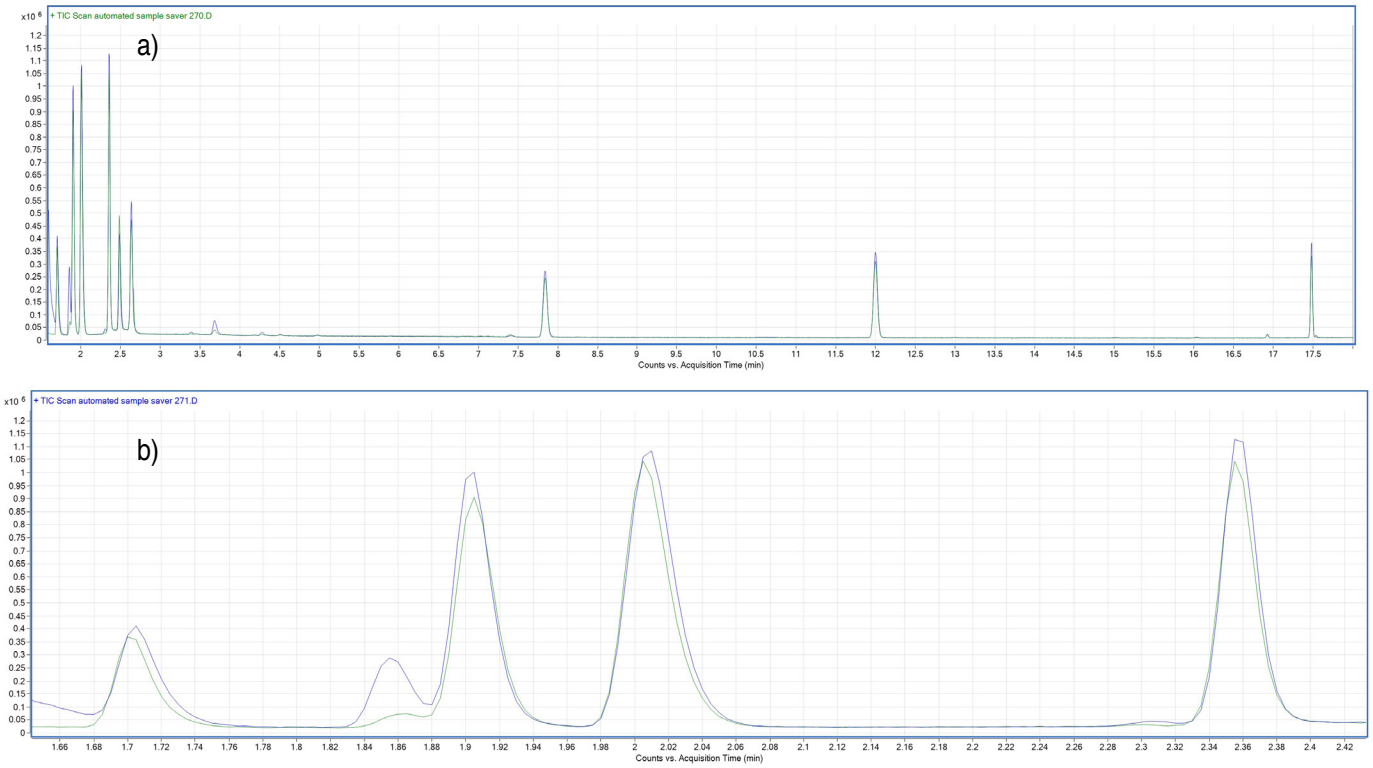

Figure 1a) Overlay of the TIC from chromatograms of the fraction initially split to the trap and the fraction recollected by the sample saver tube and (b) is zoomed in on the five earliest eluting VOCs.