Automated TD Sample Prepararion of Calibration Standards

Application Note
General

Author:

Michael Apsokardu
Xiaohui Zhang

Abstract
This application note demonstrates quantitative sample preparation of calibration standards using the CDS 7550S automated thermal desorber. The internal standard loop of the 7550S is utilized here to automate the process of preparing calibration standards onto pre-conditioned thermal desorption tubes.

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.

Here the CDS 7550S automated Thermal Desorber incorporates a sample concentration feature, which is designed to assist in sample preparation of calibration standards. Sample concentration works successively adding one more aliquots of standard gas directly from a sample loop of a known volume.

Experiment Setup

A CDS 7550S automated thermal desorber with the internal standard and Peltier options. In concentration mode, calibration standard is added directly to the sample tube.The calibration standard that was used was a pre-mixed 1 ppmv gas used for EPA TO-15 containing 65 analytes (Restek PN 34436). This was done for four total samples in which one, two, three, and four aliquouts of standard gas were added to each tube. The volume of the sample loop is 5 mL. After the standard was added into each tube, the sample tube was returned the autosampler rack where the tube was stored until all calibration standards were prepared. Once all samples were prepared, the VOCs were desorbed from the thermal desorption sample tube to the analytical focus trapped electronically cooled by a Peltier unit. The sample tube was manufactured by Camsco and packed with Carbograph 1/ Carbograph 2/Carboxen 1000 (P/N SU644-4).

GC-MS Setup

The extract analysis was performed on a Shimadzu GC-2010 Gas Chromatograph with a splitless injection port interfaced to a Shimadzu GC-MS QP2010 (Kyoto, Japan) and a 30m x 0.25mm x 1.4µm Restek Rtx®-VMS GC column. GC-MS parameters are shown below.

The GC-MS method is described below. Ions used for quantification of each standard were selected by those recommended by EPA TO-15. The MS was tuned successfully using DTFPP.

7550S Thermal Desorber:

Valve oven:	245 °C
GC transfer line:	250 °C
Tube purge flow:	60 mL/min
Pre-heat time:	15 s
Tube Rest temp.:	37 °C
Tube Dry purge temp.:	37 °C
Tube Dry purge time:	0.1 min
Tube Desorb temp.:	330 °C
Tube Desorb time:	8 min
Primary sample tube:	Camsco P/N SU644-4
Trap Rest temp.:	-20 °C with Peltier
Trap Desorb temp.:	300 °C
Trap Desorb time:	2 min
Trap Type:	Tenax TA
Peltier transfer line:	250 °C

GCMS QP-2010

GC conditions:

Oven temp.:	35.0 °C
Injection temp.:	240 °C
Injection mode:	Split
Column Flow:	1.01 ml/min
Split Ratio:	40.0
Temp. program:	35.0 °C hold 4 min
	10.0 °C/min to 90.0 °C
	20.0 °C/min to 150.0 °C
	30.0 °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

Results and Discussions

In total, the 7550S thermal desorption system was used for automated preparation of sample tubes loaded with 5 mL aliquots 1 ppmv gas standard one, two, three, and four times. Each time the loop is loaded, 10 ng are delivered from the loop to the tube. This corresponds to a concentration of 1 ppbv of analyte in an air sample, assuming 5 L of total air are sampled. The chromatogram in Figure 1 was acquired from analysis of the TO-15 gas standard containing 65 analytes after the tubes was loaded with two aliquots of standard.

For each sample tube, the response for each analyte was extracted to generate a four point calibration curve for each standard. Each sample tube was run in replicates of 3. The R^2 values for each analyte are shown in Table 1 and are listed in order of their retention time on the GC column. The measured for repeated standard additions to the same sample tube.

response for each analyte was linear and the average %RSD was 1.5%.This indicates that standard is precisely controlled by the sample loop and quantitatively delivered to the sample tube

Conclusions

This application note has showcased the application of the 7550S for automated prepartion of calibration standards by introducing gas phase standard onto a clean thermal desorption tube via the sample loop. The response was found to be linear for all 65 compounds contained within the TO-15 standard gas. The amount of standard delivered to the tube is prescisely controlled by the sample loop and then quantitatively delivered from the sample loop to the clean sample tube. This feature will provide greater flexibility to users looking for an automated method for preparing of calibration standards in gas phase sampling studies done by TD-GC-MS.

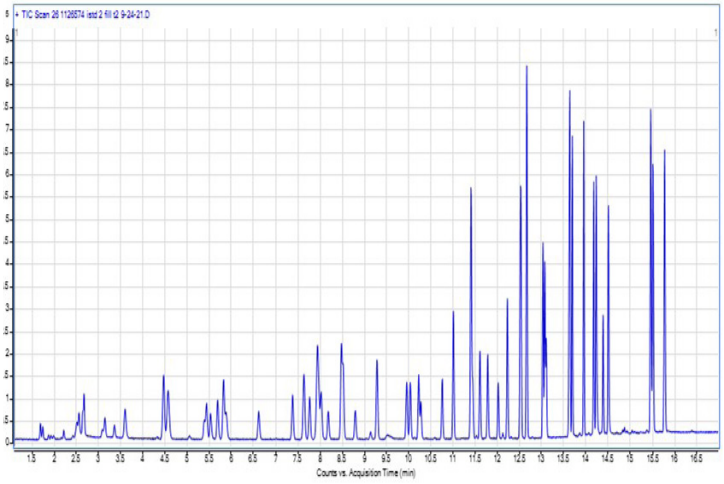

Figure 1: Chromatogram from of TO-15 gas with two 5 mL aliquots of standard gas loaded onto pre-conditioned thermal desoprtion tube.

Table 1: R^2 and %RSD for 65 compounds contained within the TO-15 standard gas. The R^2 is representative of a four point calibration curve with each point on the curve performed in replicates of three.

	R^2	%RSD
propylene	0.9640	1.7
dichlorodifluoromethane	0.9956	0.44
1,2-dichlorotetrafluoroethane	0.9780	2.9
chloromethane	0.9612	4.25
vinyl chloride	0.9967	0.3
1,3-butadiene	0.9720	1.79
bromomethane	0.9768	3.11
chloroethane	0.9533	6.12
trichlorofluoromethane	0.9971	0.15
1,1-dichloroethene	0.9982	0.13
ethanol	0.9894	1.49
carbon disulfide	0.9927	0.91
1,1,2-trochlorofluoroethane	0.9983	0.19
acrolein	0.9208	12.82
isopropyl alcohol	0.9928	0.88
methylene chloride	0.9941	0.47
acetone	0.9766	2.89
trans-1,2-dichloroethane	0.9995	0.06
hexane	0.9614	5.87
methyl tert butyl ether	0.9265	7.56
1,1-dichloroethane	0.9803	2.27
vinyl acetate	0.9516	8.72
cyclohexane	0.9299	12.85
chloroform	0.9562	7.74
carbon tetrachloride	0.9801	3.48
ethyl acetate	0.9909	0.98
tetrahydrofuran	0.9961	0.34
1,1,1-trichloroethane	0.9986	0.17
2-butanone	0.9966	0.51
heptane	0.9997	0.03
benzene	0.9838	2.48
1,2-dichloroethane	0.9930	1.15
trichloroethylene	1.0000	0
1,2-dichloropropane	0.9991	0.14
bromodichloromethane	0.9997	0.05
methyl methacrylate	0.9988	0.1
1,4-dioxane	0.9955	0.42
cis-1,3-dichloropropane	0.9991	0.12
toluene	0.9997	0.01

Table 1con.: R^2 and %RSD for 65 compounds contained within the TO-15 standard gas. The R^2 is representative of a four point calibration curve with each point on the curve performed in replicates of three.

	R^2	%RSD
tetrachloroethene	0.9992	0.1
4-methyl-2-pentanone	0.9993	0.07
trans-1,3-dichloropropene	0.9973	0.08
1,1,2-trichloroethane	0.9997	0.05
dibromochloromethane	0.9972	0.29
1,2-dibromomethane	0.9989	0.16
2-hexanone	0.9990	0.04
chlorobenzene	0.9993	0.06
ethylbenzene	0.9994	0.02
m-xylene	0.9992	0.08
p-xylene	0.9992	0.08
o-xylene	0.9992	0.08
styrene	0.9994	0.07
bromoform	0.9993	0.09
1,1,2,2-tetrachloroethane	0.9993	0.06
4-ethyltoluene	0.9569	7.65
1,3,5-trimethylbenzene	0.9990	0.06
1,2,4-trimethylbenzene	0.9906	1.45
1,3-dichlorobenzene	0.9916	1
1,4-dichlorobenzene	0.9523	6.85
benzyl chloride	0.9940	0.73
1,2-dichlorobenzene	0.9959	0.56
hexachlorobutadiene	0.9906	0.62
1,2,4-trichlorobenzene	0.9762	1.99
naphthalene	0.9948	0.23