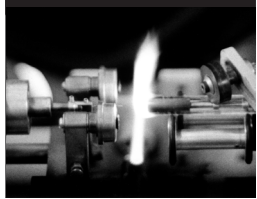


HD-syringe for reproducible headspace gas chromatography

Application Note



Abstract

HAMILTON Bonaduz AG has recently introduced a High Dynamic (HD)-type headspace (HS) syringe for gas chromatography (GC). The new design allows sample injection with high reproducibility at different temperatures and temperature drops. The performance of the syringe has been tested with a standard mixture of halogenated hydrocarbons.

Introduction

The reproducibility of HS GC results often has been an issue.^{1,2} Possible reasons why HS GC analysis is prone to errors include: (I) Exact sampling and dosing of gases is tedious. Unlike solids and liquids, gases have neither fixed volume nor shape and are molded completely by the container in which they are held. (II) Partition coefficients (ratio of the analyte equilibrium concentration in the gas phase volume and the liquid phase volume) of the analytes in the head space are usually unknown.

Especially in routine analysis it is required to evaluate the reproducibility of the sample volume. In terms of the value of the partition coefficient it has been demonstrated that sample volume reproducibility is critical only for low partition coefficient values, whereas for higher values the influence on the reproducibility of analytical results was negligible.¹ The value of the partition coefficient is generally not known, however, and therefore it is always advisable to reproduce the sample volume in duplicate analyses. Reproducibility issues with HS GC are also a reason why often internal standards are used for a quantitative analysis.³

One source of error in HS GC is the exact dosing of the sample volume into the injection system. The injection syringe plays the crucial role of delivering a sample volume as accurate and precise as possible. Conventional HS syringes are composed of rubber O-ring sealed plungers carrying a PTFE tip which is sealing towards the internal surface of the syringe glass body. This design possesses limited adjustment proper-

ties to thermal changes because of different thermal expansion coefficients of the PTFE and rubber O-ring materials and a very long relaxation time of the rubber O-ring. Leakage of conventional HS syringe plungers is common when the plunger experiences temperature changes. To address this prevalent problem HAMILTON Bonaduz AG has recently introduced a High Dynamic (HD)-type HS syringe. The key element of the new HD-plunger design is a newly designed spring supported sealing (Figure 1). This metal spring compensates the thermal expansion of the PTFE tip and exercises a constant, temperature independent contact force towards the glass surface. The same plunger technology is also successfully used for the ITEX syringes.⁴

The reproducibility of HS GC analysis with this new HD syringe was tested with a standard mixture (cf. Table 1) and multiple injections at different temperatures.

Table 1: List of the standard mixture investigated in this study.

No.	Compound	RT / min
1	Freon 11	1.50
2	Freon 113	1.66
3	Dichlormethane	1.87
4	Chloroform	2.73
5	1,1,1-Trichloroethane	2.86
6	Carbon tetrachloride	2.98
7	Trichloroethylene	3.83
8	Tetrachloroethylene	7.32

Experimental Section

Sample preparation: A 1L glass bottle with a septum in the screw cap equipped with a magnetic stir bar was used (Figure 2). The following halogenated hydrocarbons were dissolved in 100 μ L methanol: 2mg Freon 11 (Trichlorofluoromethane), 2mg Freon 113 (1,1,2-trichloro-,2,2,1-trifluoroethane), 20 mg dichloromethane, 2mg trichloromethane, 2mg 1,1,1-Trichloroethylene, 2mg tetrachloromethane, 2mg Trichloroethylene, 2mg Tetrachloroethylene (cf. Table 1). 50mL of deionized water was added to the bottle. The sample mixture was stirred overnight at room temperature before injection.

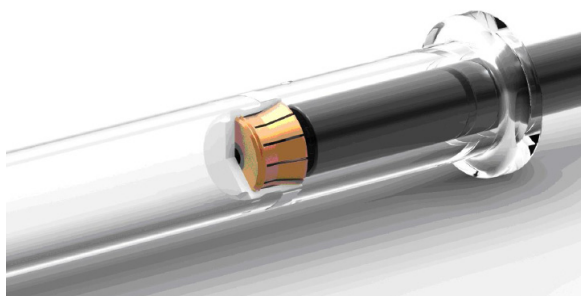


Figure 1: New sealing for the syringe plunger based on a novel metal spring. Enhanced tightness over a large temperature range and temperature gradients have been observed.



Figure 2: 1L glass bottle with a septum in the screw cap used for the HS GC analysis of a mixture of halogenated hydrocarbons.



Instrumentation: A 2.5mL CTC HD syringe (P/N 203084/04) from HAMILTON Bonaduz AG was used for all experiments. An injection volume of 250µL was used throughout. A CTC Combipal autosampler was used together with a Carlo Erba HRGC 5300 instrument equipped with a split/splitless injector (200°C) and a FID detector (200°C). A BGB-624 GC column (50m, 0.32mm, 1.8µm) was used, hydrogen (200 kpa) was used as carrier gas. The oven temperature was 80°C isotherm, the total runtime of the GC program was 8min. The clarity (data-apex) software was used for data treatment.

Results & Discussion

The dosing accuracy of the 2.5mL CTC HD syringe from HAMILTON Bonaduz AG was tested by repeated HS injections of a standard mixture (Table 1). The results of 45 injections at 80°C of the mixture are listed in Table 2. The relative standard deviations (RSDs) calculated for all compounds were in the range of 0.99-5.56%, with Freon 11 (1) 0.99% and Tetrachlorethylen (8) 5.56%. These results suggest that the HD syringe is an excellent choice for repeated injections and routine analysis.

Table 2: Repeated HS injections (n=45) of the sample mixture using Hamilton's new HD-type headspace syringe.

Compound	1	2	3	4	5	6	7	8
Avg Peak Area	248.41	456.24	2839.66	217.34	616.18	221.96	501.02	293.40
RSD / %	0.99	3.87	1.59	1.76	3.33	4.25	3.46	5.56

The performance of the HS syringe was also tested by repeated HS injections (n=10) of a standard mixture keeping the syringe at 100°C and 60°C, respectively. The lag time between cooling down from 100°C to 60°C was only 15 minutes. The relative standard deviations (RSDs) calculated for all compounds are shown in Table 3. The overall RSDs are in between 1.20% and 3.50%, demonstrating the great reproducibility of the setup and the accuracy of the injection volume. The RSDs obtained at 100°C were between 1.45-3.50%. The RSD values obtained after cooling down during 15 minutes from 100°C to 60°C were even lower: 1.20-2.06%. This clearly demonstrates the excellent reproducibility of the injection volume provided by the HS syringe and indicates an optimal sealing performance of the HD-type plunger even after a temperature stress is applied.

Table 3: Relative standard deviations determined for injections (n=10) at 100°C and 60°C. The delay time between between 100°C to 60°C was 15 minutes.

Compound	1	2	3	4	5	6	7	8	
100°C	Avg. Peak Area	351.37	925.35	4877.65	360.76	1056.90	379.39	733.20	423.56
	RSD	2.02	1.94	1.98	2.18	2.04	1.45	1.82	3.50
60°C	Avg. Peak Area	421.81	1105.34	5874.51	433.46	1271.18	450.24	861.56	465.81
	RSD	1.27	1.20	1.31	1.54	1.43	1.41	1.67	2.06

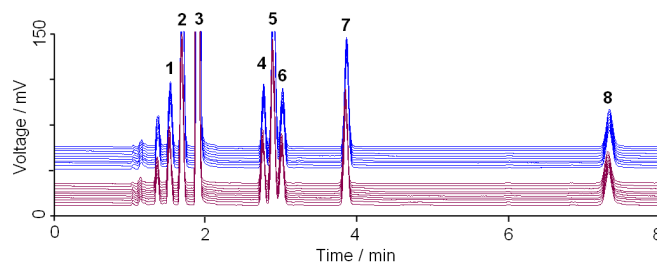


Figure 3: Overlay of gas chromatogram obtained at different syringe temperatures temperatures: 60°C blue traces, 100°C red traces.

An overlay graph is shown in Figure 3 displaying the chromatograms obtained at different syringe temperatures. The 10 injections with the syringe at 100°C are depicted as red traces, and the 10 injections with the syringe at 60°C are depicted as blue traces. Excellent peak shape reproducibility is obtained for the injections at the two temperatures.

User benefits:

- Excellent reproducibility of HS GC analysis for routine work.
- High accuracy and precision of the injection volume and improved lifetime.
- Optimal performance of the HD syringe even at large temperature changes and temperature drops.
- Well suited for HS method development and optimal injection temperature determination.
- Same plunger technology as implemented in ITEX syringes.

References

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