HD-Type Syringe for Reproducible Headspace Gas Chromatography

Abstract

Hamilton offers a High Dynamic (HD)-type headspace syringe for gas chromatography (GC). The new design allows sample injection with high reproducibility at varying temperatures and temperature drops. The performance of the syringe has been tested with a standard mixture of halogenated hydrocarbons.

Introduction

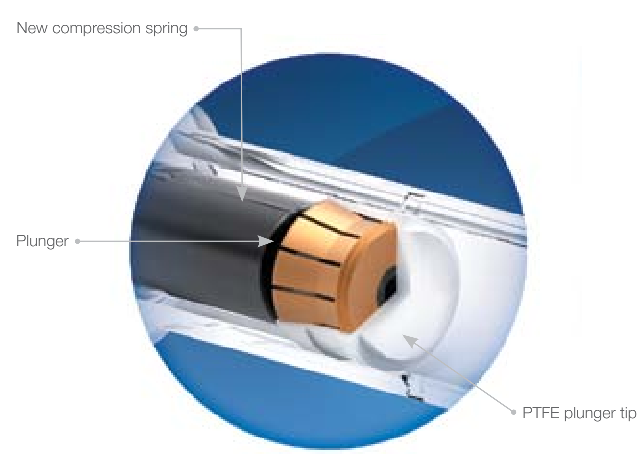
The reproducibility of headspace GC results has been an issue.[1,2] Possible reasons why headspace GC analysis is prone to errors include: 1) exact sampling and dosing of gases is tedious. Unlike solids and liquids, gases have neither fixed volume nor shape and are molded completely by the container in which they are held. 2) Partition coefficients (e.g., ratio of the analyte equilibrium concentration in the gas phase volume and the liquid phase volume) of the analytes in the headspace are usually unknown.

It is especially important in routine analysis 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 headspace GC are also a reason why often internal standards are used for a quantitative analysis.[3]

One source of error in headspace GC is the exact dosing of the sample volume into the injection system. The injection syringe plays the key role of delivering a sample volume as accurate and precise as possible. Conventional headspace syringes employ an O-ring sealed plunger carrying a PTFE tip which seals toward the internal surface of the syringe barrel. This design possesses limited adjustment properties 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 headspace syringe plungers is common when the plunger experiences temperature changes. Hamilton's HD-type syringe addresses this problem with a newly designed spring supported sealing (Figure 1). The metal spring compensates for the thermal expansion of the PTFE tip and exercises a constant temperature, independent contact force toward the glass surface. The sample plunger technology is also successfully used for the ITEX syringes.[3]

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

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.



HAMILTON

Materials & Methods

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

Table 1. List of compounds in the standard mixture.

Reference Number	Compound	RT/Min
1	Freon 11	1.50
2	Freon 113	1.66
3	Dichloromethane	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

Instrumentation: 2.5 mL CTC HD-type syringe (p/n 203084) was used for all experiments. An injection volume of 250 µL was used throughout. A CTC Combi PAL® 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 (50 m, 0.32 mm, 1.8 µm) was used, hydrogen (200 kpa) was used as carrier gas. The over temperature was 80 °C isotherm; the total runtime of the GC program was 8 minutes. The clarity (data-apex) software was used for data analysis.

Results & Discussion

The dosing accuracy of the 2.5 mL CTC HD-type syringe was tested by repeated headspace 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) and tetrachloroethylene (8) 5.56%. The results demonstrate the unsurpassed reproducibility of the HD-type syringe for headspace analyses over conventional syringes.

Table 2. Repeated headspace 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	2,839.66	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 headspace syringe was also tested by repeated headspace 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 were between 1.20 – 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 demonstrate the excellent reproducibility of the injection volume provided by the headspace syringe and indicates an optimal sealing performance of the HD-type plunger even after a temperature stress is applied.

Figure 2 shows 10 overlaid chromatograms with a syringe temperature of 100 °C (red) and 10 overlaid chromatograms with a syringe temperature of 60 °C (blue), demonstrating injection volume reproducibility at varying temperatures.

User Benefits

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

Figure 2. Overlay of gas chromatogram obtained at different syringe temperatures (60 °C blue traces, 100 °C red traces).

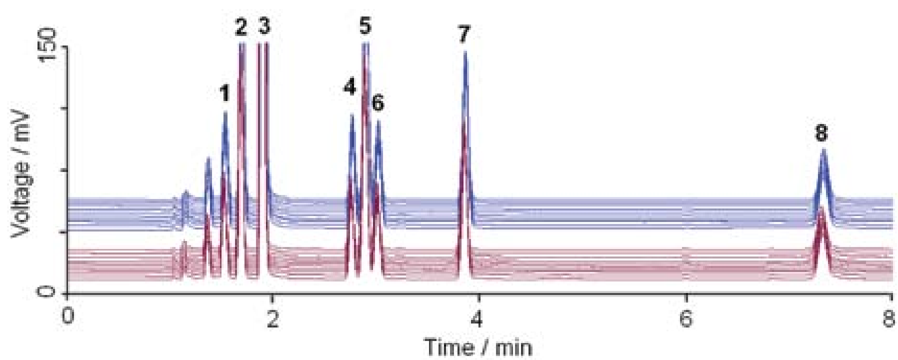


Table 3. Relative standard deviations determined for injections (n = 10) at 100 °C and 60 °C. The delay time between 100 °C to 60 °C was 15 minutes.

Compound	1	2	3	4	5	6	7	8
Avg. Peak Area (100 °C)	351.37	925.35	4,877.65	360.76	1,056.90	379.39	733.20	423.56
RSD (100 °C)	2.02	1.94	1.98	2.18	2.04	1.45	1.82	3.50
Avg. Peak Area (60 °C)	421.81	1,105.34	5,874.51	433.46	1,271.18	450.24	861.56	465.81
RSD (60 °C)	1.27	1.20	1.31	1.54	1.43	1.41	1.67	2.06

References

1. Static Headspace — Gas Chromatography: Theory and Practice — 2nd Edition 2006: B. Kolb, L.S. Ettre, John Wiley & Sons, Inc., Hoboken, New Jersey

2. L.S. Ettre, LC_GC North America 20, 1120 – 1129 (2002)

3. CTC Analytics, Zwingen, Switzerland

Acknowledgements

Beat Schilling from BGB Analytik (Adiswil, Switzerland) is thankfully acknowledged for this collaboration and advice.

Lit. No. L20083 — 05/2012

HAMILTON

Web: www.hamiltoncompany.com
USA: 800-648-5950
Europe: +41-81-660-60-60

Hamilton Americas & Pacific Rim
4970 Energy Way
Reno, Nevada 89502 USA
Tel: +1-775-858-3000
Fax: +1-775-856-7259
sales@hamiltoncompany.com

Hamilton Europe, Asia, & Africa
Via Crusch 8
CH-7402 Bonaduz, GR, Switzerland
Tel: +41-81-660-60-60
Fax: +41-81-660-60-70
contact@hamilton.ch

To find a representative in your area, please visit hamiltoncompany.com/contacts.