Ambient Headspace Analysis with the Agilent 7683 Automatic Liquid Sampler

Application

Gas Chromatography

February 1998

Authors

Matthew S. Klee and
Chin Kai Meng
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808-1610
USA

Abstract

Headspace analysis is an attractive alternative to direct injection for samples containing components that might foul the inlet, column, or detector. While usually done with thermostatted samples, many analytical goals can be achieved with ambient headspace sampling using the 7683 automatic liquid sampler (ALS). The benefits are increased sample throughput, less costly equipment, and simplified operation. Examples are presented to illustrate the technique.

Key Words

Headspace, 7683, automatic liquid sampler, ALS, Agilent 6890 Plus, gas chromatograph, GC, blood alcohol, residual solvents, trichloroanisole, BTEX

Introduction

Headspace sampling is complementary to liquid injection (figure 1). It works best on the most volatile components in a sample although its effective range can be increased by heating the sample.

For samples with significant nonvolatile content, headspace sampling offers these advantages over direct injection:

- No contamination of injectors and columns by nonvolatiles
- Reduction in the amount of solvent, which may obscure early peaks
- Increased sensitivity for volatile analytes
- Possible analysis of volatiles in solid as well as liquid samples

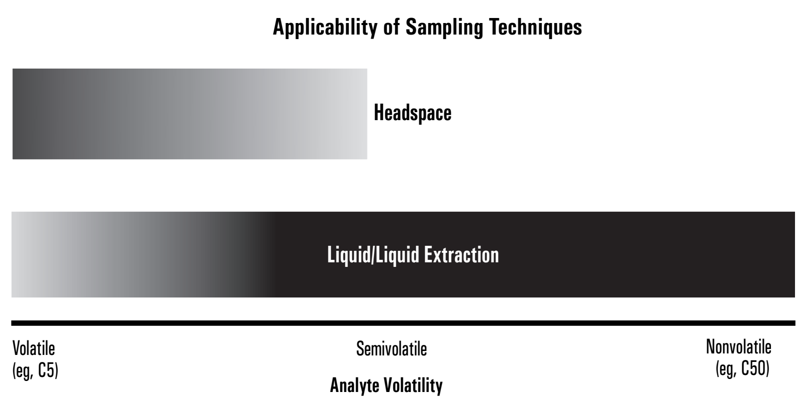


Figure 1. **Micro liquid-liquid extraction and ambient headspace sampling with the 7683 ALS. These techniques are complimentary, cover a wide range of analyte volatilities, and provide very good analytical precision. Ambient headspace analysis is best for volatile compounds, and micro liquid-liquid extraction is best for less volatile analytes.**

The technique depends on the equilibration of analytes between a sample and the air space in a closed container. The amount of an analyte in the air space (the headspace) depends on its concentration in the original sample, the relative volumes of the sample and the headspace, and the partition coefficient of the analyte. The partition coefficient varies with the natures of the analyte and the sample, the pressure in the container, and the temperature.

Sample and container volume are easily controlled, leaving temperature as the main external variable. For the highest reproducibility, the temperature must be closely controlled as well. However, the impact of temperature variation on analytical results may be minimal in some cases:

- When the partition coefficient is only weakly dependent on temperature
- When the temperature effect is insignificant compared to the required accuracy
- When the ambient (laboratory) temperature is well controlled
- When the temperature effect can be reduced using a relative measurement such as when using an internal standard

Often, the laboratory temperature varies only a few degrees during normal working hours. Ambient headspace data obtained under these conditions can yield satisfactory reproducibility and accuracy for many applications.

Ambient Headspace Sampling

Ambient headspace sampling (figure 2) has several advantages over fully automated and temperature controlled headspace sampling:

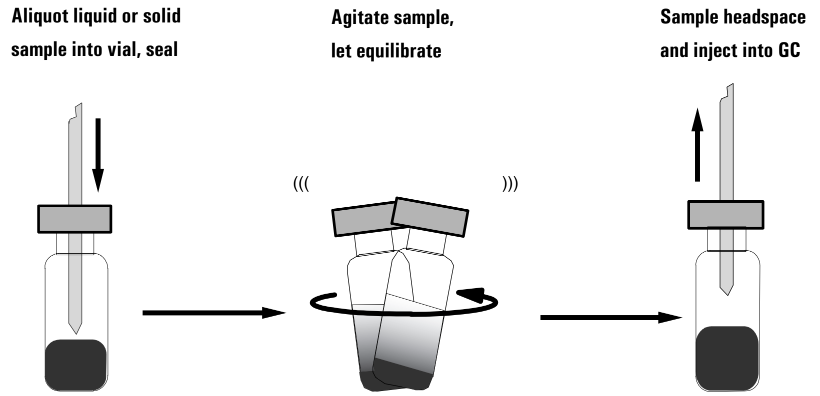


Figure 2. Typical procedure for ambient headspace analysis. Place the sample in the vial, seal the vial, agitate the vial, wait for the sample to equilibrate, and sample the headspace. Concentration of analytes in the headspace depends on their concentration in the original sample, solubility in the sample (lower solubility = higher headspace concentration), temperature (higher temperature = higher headspace concentration), and relative volumes of the headspace and the sample (more sample = higher headspace concentration).

- It can be accomplished with little incremental investment in instrument hardware and software.
- It has few experimental variables that need to be (or can be) optimized.
- It can often be accomplished with a standard gas chromatograph (GC) system configuration.

It does, of course, have some disadvantages:

- Results are sometimes less reproducible than with fully automated and temperature-controlled headspace sampling.
- Sensitivity is often lower (smaller injection volume, lower sample temperature).

Ambient headspace analysis can be quite useful for qualitative analysis. For example, one can screen foods for flavors and aromas, determine and verify chromatographic fingerprints for quality control, and screen water for pollutants.

Several applications are presented to illustrate the potential utility of ambient headspace sampling:

- Alcohols in water/blood
- Residual solvents in pharmaceuticals (USP 467)
- Trichloroanisole (TCA), an off-flavor in wine or wine cork
- BTEX (benzene, toluene, ethylbenzene, xylenes) in water
- Industrial solvents in water

Ambient Headspace Sampling with the 7683 ALS

The 7683 ALS (figure 3) can sample from different heights in the vial, making it suitable for both liquid and headspace sampling. The only special requirement for ambient headspace analysis is the use of a large-volume, gas-tight syringe. The syringe can also be used for large-volume liquid injection with the programmable temperature vaporizer (PTV) and cool on-column (COC) inlet with solvent vapor exit.

- 25-µL gas-tight ALS syringe part number 5183-0312
- 50-µL gas-tight ALS syringe part number 5183-0314
- 100-µL gas-tight ALS syringe part number 5183-204

A typical procedure for ambient headspace analysis with the 7683 ALS is given below. At each step, better reproducibility in sample and standard preparation means more accurate quantitative results. If the goal is qualitative analysis, control of the process is less stringent.

The items in brackets are optional but are important for best quantitative accuracy and/or maximum sensitivity.

1. Place the sample in a vial (do not fill vial more than half full). [Aliquot liquids (recommended volume 0.1 to 1 mL)] [Weigh solids]
2. [Add 0.5 g of Na_2SO_4 to aqueous samples for a salting-out effect.]
3. [Add internal standard to increase quantitative accuracy.]
4. Cap the vial tightly.
5. [Shake (this can be done using the bar code reader that is an option to the sampler tray) to speed equilibration.]
6. Place the sample in the sampler turret or tray, and analyze it.
7. [Control the tray temperature with a liquid circulating bath.]

Typical sampling parameters are listed in table 1.

If the sampler tray is used, it can be thermostatted using a circulating water bath to increase reproducibility and/or to increase sensitivity by heating samples.

Example 1: The Determination of Alcohols in Water/Blood

A common headspace method is the determination of ethanol in blood.

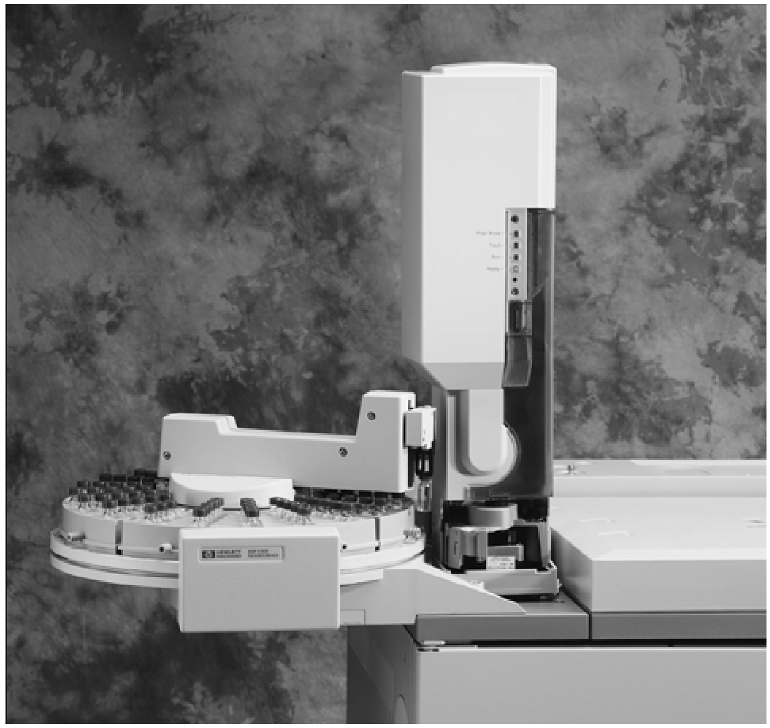


Figure 3. 7683 ALS with capacity for eight 2-mL vials. Also shown are the optional bar code reader (for sample tracking and mixing) and the 100-sample tray. The tray can also be thermostatted via an external water bath through openings on the tray quadrants.

Table 1. Typical Ambient Headspace Analysis Sampling Parameters

Parameter	Typical Choice
Syringe size	50 to 100 µL
Injection volume	25 to 50 µL
Inlet	Split/splitless, PTV, purged-packed, and COC
Liner	Empty, narrow (such as part number 18740-80200)
Split ratio	Splitless
Sample pumps	3 to 5
Sample depth	20 mm
Solvent washes	One to five times in air space above water (wash vial with <2 mL of water)

The high amount of insoluble and involatile material in blood makes direct injection into the gas chromatograph undesirable because of inlet maintenance, column degradation, increased background noise, and sample carryover. To maximize quantitative performance, an internal standard, 1-propanol, is added to the sample prior to analysis. The internal standard helps compensate for temperature, matrix, and sample volume variations.

Figure 4 shows the analysis of 0.1% ethanol and 1-propanol in water as a surrogate for blood. Even a 25-µL injection yields a very good signal-to-noise ratio at the 0.1% level. Table 2 demonstrates the excellent precision achieved even without temperature control.

Example 2: The Determination of Residual Solvents in Pharmaceuticals

Another widely used headspace method is the determination of residual solvents in pharmaceutical formulations such as tablets (USP 467). The tablet is dissolved in water, and its headspace is analyzed. Figure 5 shows a typical headspace analysis of a solution of selected solvents near their regulatory limits.

Injection of solid tablets into a GC would be impractical. Injection of the dissolved tablet is also a problem because of the nonvolatile binders and additives common in pills. Higher sensitivity for the target solvents can be achieved by injecting a large volume of headspace rather than a small volume of solution.

Ambient headspace analysis yields excellent reproducibility (table 3) and sensitivity.

Example 3: Determination of Trichloroanisole in Wine and Cork

Trichloroanisole is formed by microbes on wood and cork. Very low concentrations (sub parts-per-billion) of trichloroanisole can be tasted in wines and can ruin the delicate balance of desired flavors. Therefore, it is important to sensitively detect trichloroanisole in cork before it is used in the bottling process.

One common procedure to analyze cork for trichloroanisole is to leach it out of the cork into a consistent amount of reference wine for a consistent amount of time. Trichloroanisole can then be quantified by extracting the wine with an organic solvent and injecting the

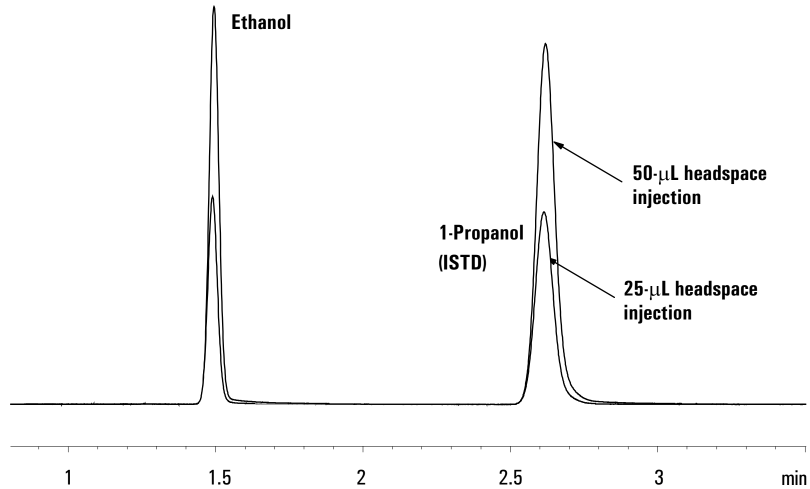


Figure 4. Ambient headspace analysis of 0.1% ethanol and 1-propanol in water. This concentration level equals the legal limit for the concentration of alcohol in blood in many areas of the world. Conditions: 30 m × 530 µm × 1.0 µm HP-INNOWax; Oven: 50 °C isothermal; Inlet: 200 °C, 10 psi, splitless; Detector: FID, 250 °C.

Table 2. Precision of Alcohol Determination by Ambient Headspace (50-µL injections)

	Area %RSD 12 Injections (Six Vials)	Area %RSD 6 Injections (Same Vial)
Ethanol	1.82	0.77
1-Propanol	1.70	0.97

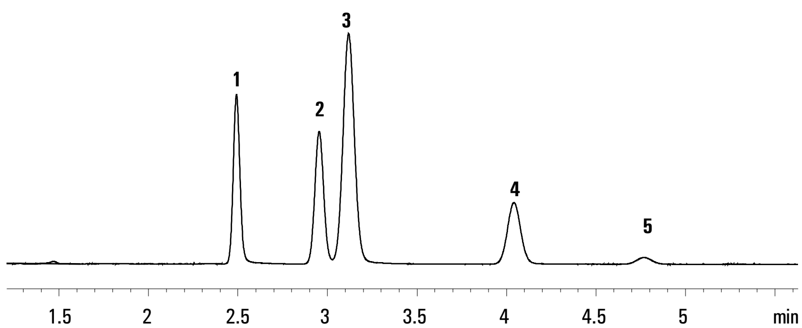


Figure 5. Ambient headspace analysis of USP 467 residual solvents in pharmaceuticals. Peak identifications are given in table 3. Conditions: 30 m × 530 µm × 1.0 µm HP-INNOWax; Oven: 60 °C isothermal; Inlet: 200 °C, 5 psi, splitless; Detector: FID, 250 °C.

extract into the GC, sampling of the wine via solid-phase microextraction (SPME), or analysis of the wine headspace.

Figure 6 shows the combination of ambient headspace analysis with the new Agilent 6890 Micro-ECD. This combination provides a very sensitive and convenient means of analyzing a compound such as trichloroanisole in aqueous samples such as wine.

Example 4: BTEX in Water

This hexad of compounds (benzene, toluene, ethylbenzene, and m-, o-, and p-xylenes) is often used as a marker when tracking gasoline, diesel fuel, and heating oil leaks in ground water and soil. The chromatogram in figure 7 demonstrates detectability at very low levels by ambient headspace sampling.

Example 5: Industrial Solvents in Water

Figure 8 demonstrates ambient headspace analysis of five common solvents at the 0.1% level in H_2O. This application exemplifies a quick and easy means of monitoring plant effluents for trace emissions of industrial solvents in water or for quick screening of waste waters for industrial pollutants. The detection limit for these solvents is about 2 ppm in water.

Table 3. Precision of Ambient Headspace Analysis of Solvents in Water

Peak Number	Analyte	Concentration (ppm)	Area %RSD 6 Injections (Different Vials)	Area %RSD 6 Injections (Same Vial)
1	Methylene chloride	10	1.8	0.7
2	Chloroform	1	3.2	1.5
3	Benzene	2	4.1	3.5
4	Trichloroethylene	2	4.9	5.5
5	1,4-Dioxane	2	4.0	3.2

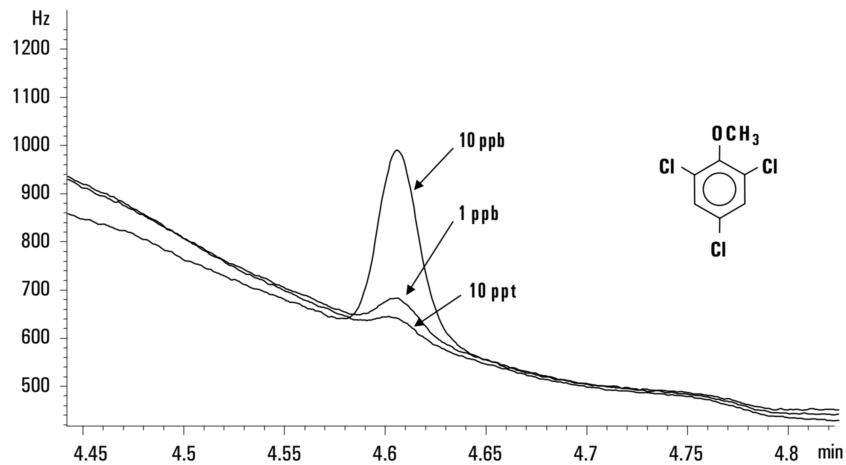


Figure 6. Ambient headspace analysis of trace trichloroanisole in 80:20 water:ethanol. Conditions: 30 m × 530 µm × 0.88 µm HP-5; Oven: 70 °C (0 min), 30 °C/min to 200 °C (2 min); Inlet: COC, oven track; Detector: micro-ECD, 250 °C; Injection volume: 50 µL

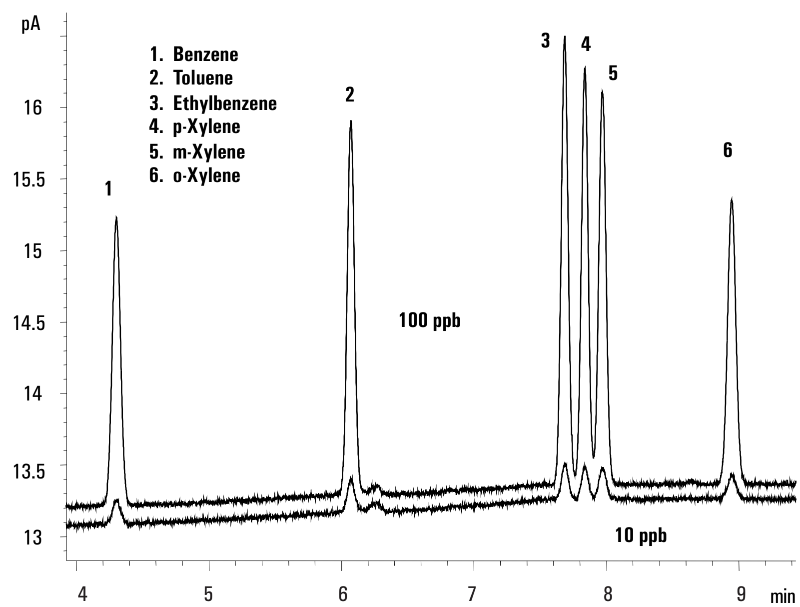
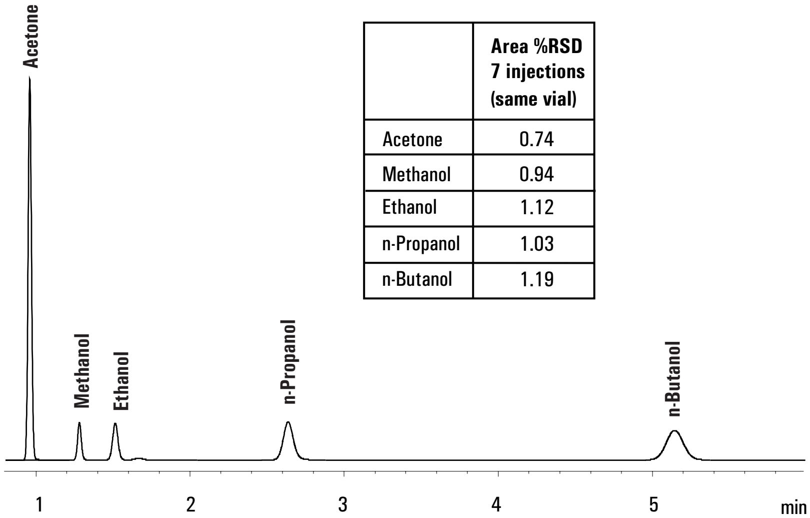


Figure 7. Ambient headspace analysis of 10- and 100-ppb BTEX in water. Conditions: 30 m × 530 µm × 1.0 µm HP-INNOWax; Oven: 40 °C (2.5 min), 10 °C /min to 90 °C (7 min); Inlet: COC, oven track; Detector: FID, 350 °C; Injection volume: 50 µL



	Area %RSD 7 injections (same vial)
Acetone	0.74
Methanol	0.94
Ethanol	1.12
n-Propanol	1.03
n-Butanol	1.19

Figure 8. Ambient headspace analysis of industrial solvents in water (0.1% each). Conditions: 30 m × 530 µm × 1.0 µm HP-INNOWax; Oven: 40 °C (2.5 min), 10 °C /min to 90 °C (7 min); Inlet: COC, oven track; Detector: FID, 350 °C; Injection volume: 50 µL.

Conclusion

Ambient headspace analysis with the Agilent 7683 ALS is a simple and cost-effective way to perform some otherwise difficult analyses. Samples containing water or nonvolatile, late-eluting, or interfering compounds are easily and quickly handled. Qualitative chromatographic fingerprints and sample screening applications require less stringent control of experimental parameters than do quantitative analyses. Quantitative analysis can sometimes be accomplished with ambient headspace analysis, especially if using a properly chosen internal standard.

Printed in the USA 3/2000
5966-1473E

Agilent Technologies
Innovating the HP Way