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Short Communication

A double sealing technique for increasing the precision of headspace-gas chromatographic analysis

Wei-Qi Xie [a,b,*], Kong-Xian Yu [c], Yi-Xian Gong [a]

[a] State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, China
[b] School of Materials Science and Engineering, South China University of Technology, Guangzhou, China
[c] Health Supervision Bureau of Liaoning Province, Shenyang, China

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ABSTRACT

This paper investigates a new double sealing technique for increasing the precision of the headspace gas chromatographic method. The air leakage problem caused by the high pressure in the headspace vial during the headspace sampling process has a great impact to the measurement precision in the conventional headspace analysis (i.e., single sealing technique). The results (using ethanol solution as the model sample) show that the present technique is effective to minimize such a problem. The double sealing technique has an excellent measurement precision (RSD < 0.15%) and accuracy (recovery = 99.1%–100.6%) for the ethanol quantification. The detection precision of the present method was 10–20 times higher than that in earlier HS-GC work that use conventional single sealing technique. The present double sealing technique may open up a new avenue, and also serve as a general strategy for improving the performance (i.e., accuracy and precision) of headspace analysis of various volatile compounds.

1. Introduction

Headspace analysis is a useful technique widely used in the quantification of volatile analytes in samples with complicated matrices, which has been applied in various samples (i.e, residual solvent in drugs, halogenated hydrocarbons in environment, food products and pesticide residues) [1–6]. Because the headspace-based analysis can effectively prevent non-volatile species (e.g., salts and polymers) from entering the GC system, it eliminates many problems caused by contamination, thus can reduce the processes of sample preparation (i.e., column separation, filtration and solvent extraction) [7–13].

In general, the headspace vial is sealed by a septum and a cap, in which the cap is crimped tightly over the septum and the top of the vial [14–17]. However, there exists the problem of gas leakage in the sealed headspace vial, which affects the accuracy and precision of headspace analysis [14]. Additionally, the leakage occurred mainly in the sampling process [14]. Because the driving force for the headspace sampling is the high pressure in the vial pressed by the pressurized headspace auto-samplers (e.g., Agilent, Thermo and DANI), which may cause the high pressure in the vial in the headspace sampling procedure [18]. The high pressure in the vial will inevitable cause the air leakage of the vial when the septa (e.g., silicone rubber septa) is pierced with the needle. Therefore, the accuracy and precision of the headspace analysis will be greatly affected by the air leakage problem in the headspace vial. The leakage problems is a big challenge in the headspace analysis especially in the dual or multiple piercing procedure (e.g., the internal standard method (e.g., a small volume of a liquid sample is added with a syringe through the septum into a closed headspace vial) and the multiple headspace extraction (MHE) analysis) [14].

In the present study, we introduce a new double sealing technique of headspace analysis in order to solve the gas leakage problem. The major focuses were to introduce the gas leakage problem in the conventional single sealing technique and the principle of the present double sealing technique. The optimization of the headspace conditions (i.e., equilibration time and sample volume) were also investigated. Ethanol was used as the model analyte in the investigation and method evaluation in the present study. The new double sealing technique will improve the air tightness of sealed headspace vial, and thus increase the accuracy and precision of headspace analysis.

* Corresponding author at: State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, China.
E-mail address: mswqxie@mail.scut.edu.cn (W.-Q. Xie).

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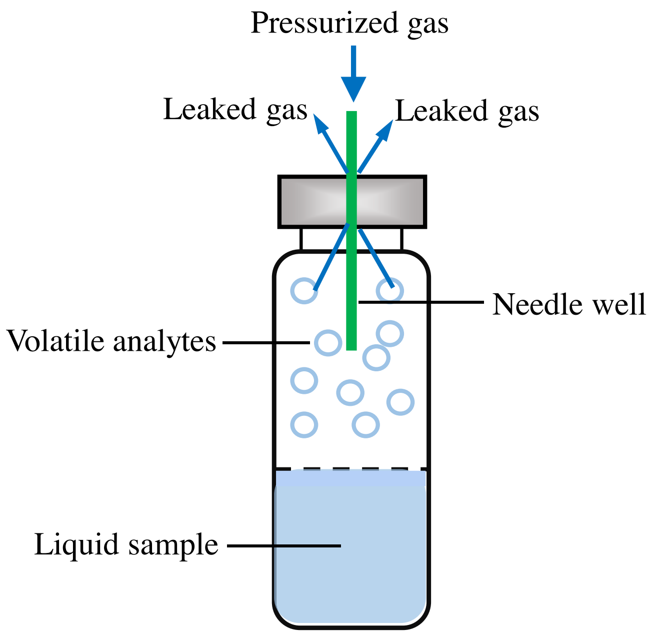

Fig. 1. Schematic of the gas leakage of the headspace vial during the sampling process.

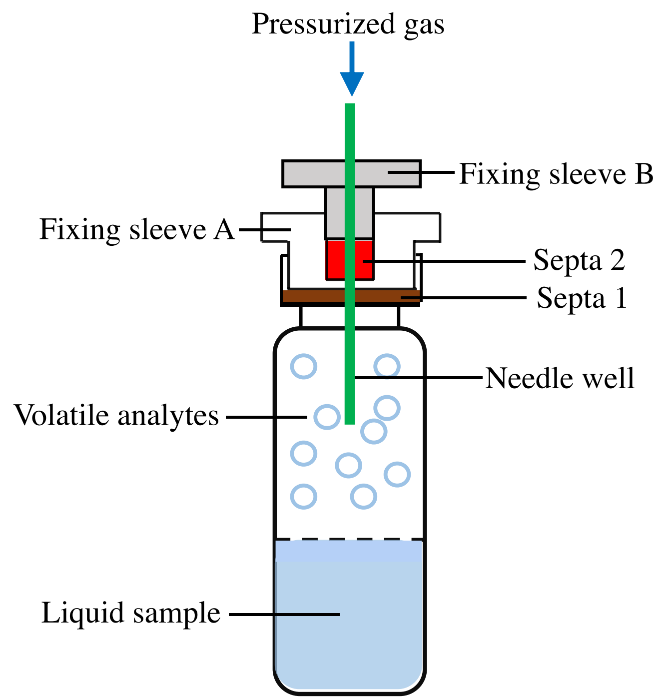

Fig. 2. Diagram of the device for the double sealing method.

2. Experimental

2.1. Materials

All chemicals used in this research were analytical grade and obtained from a chemical supplier (Shanghai Macklin Co., Ltd. (Shanghai, China). A series of standard ethanol solutions (concentrations from 0 to 750 mg/L) were prepared by transferring different contents of ethanol solute to deionized water. The sample solutions were purchased from several different laboratories and factories in southern China.

2.2. Instrument and operations

Headspace gas chromatography measurements were conducted by using an automatic headspace sampler (Thermo HS TriPlus 300, US) and a GC system (Agilent GC 7890A, US) equipped with a flame ionization detector (FID) and a DB-5 capillary column (with an i.d. of 0.53 mm and a length of 30 m) (J&W Scientific, US), operating at a temperature of 30 °C with nitrogen carrier gas (a constant flow of 3.8 mL/min). The operating procedures for headspace auto-sampler consisted of 20 min of high shaking at 70 °C to allow sample equilibration a pressurization pressure of 1.00 bar, a carrier gas pressure of 1.50 bar, a vial pressurization time of 15 s, a sample loop fill time of 10 s, a transfer time of 20 s and a sample loop volume of 3 mL.

2.3. Procedures in the sample preparation

4.0 mL of the ethanol solution was added in a headspace vial (20 mL). Afterward, the headspace vial was sealed immediately by using the rubber septa (using double sealing technique and conventional single sealing technique, respectively) and a cap. The headspace vial was then transferred to the auto-headspace sampler and detected by HS-GC. The headspace equilibration was conducted at 70 °C for 20 min.

3. Results and discussion

3.1. Sealing problems in conventional headspace analysis

The air tightness of headspace vial is a key factor in the headspace measurements, which may greatly affect the accuracy and precision of headspace analysis [14]. However, the main factor affecting the air tightness of headspace analysis is the seal of the headspace vial. In general, the headspace vial is sealed by using a septum and a cap [14], in which the cap is crimped tightly over the septum and the top of the vial. Fig. 1 shows the schematic diagram of the gas leakage from the headspace vial, the driving force for the headspace sampling is the high pressure in the vial pressed by the pressurized headspace auto-samplers (e.g., Agilent, Thermo and DANI), which causes the high pressure in the vial in the headspace sampling procedure. The high pressure in the vial will inevitably cause the air leakage of the vial when the septa (e.g., silicone rubber septa) are pierced with the needle. Therefore, the accuracy and precision of the headspace analysis will be affected Fig. 2.

3.2. Principle of the present double sealing technique

In order to enhance the air tightness of the closed headspace vial, a special device for double sealing as shown in Fig. 3 was designed. It mounts a thick silicone rubber septa (e.g., septa 1, thickness = 5 mm) on the silicone rubber septa (e.g., septa 2, thickness = 1 mm) of a headspace vial. Septa 1 is fixedly and rotarily sealing by a screw opening between fixing sleeve A and B. Additionally, septa 2 is fixedly and rotarily sealing also by a screw opening between the screw-cap and headspace vial. Since septa 1and septa 2 is tightly fixed and fastened to each other, the air leakage from the closed vial caused by the pierced septa 2 can be solved by the tightly fixed septa 1. When the septa 2 is pierced with the needle in the sampling, the tightly fixed septa 1 will prevent the air in the vial form leaking. Therefore, the air leakage problem in the closed headspace vial can be solved effectively by the present double sealing technique.