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Short communication

High-pressure liquid chromatography with direct injection of gas sample

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ABSTRACT

The conventional method of using liquid chromatography to determine the composition of a gaseous mixture entails dissolving vapors in a suitable solvent, then obtaining a chromatograph of the resulting solution. We studied the direct introduction of a gaseous sample into a C18 reversed-phase column, followed by separation of the components by HPLC with UV detection. Since the chromatography was performed at high pressure, vapors readily dissolved in the eluent and the substances separated in the column as effectively as in liquid samples. Samples were injected into the column in two ways: a) through the valve without a flow stop; b) after stopping the flow and relieving all pressure. We showed that an injectable gas volume could reach 70% of column dead volume. When an injected gaseous sample volume was less than 10% of the column dead volume, the resulting peaks were symmetrical and the column efficiency was high.

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1. Introduction

Gas chromatography is the most commonly used technique to determine the composition of a gaseous mixture. However, there are times HPLC is used; for example, to determine phenols, aldehydes and phosgene in the air [1]. In all of these methods air is passed through the solvent and the resulting solution is analyzed by HPLC. To the best of our knowledge, only one study describes a direct gaseous sample injection into an HPLC column to measure the concentration of methane, ethane and propane [2]. The authors used silica gel as a stationary phase and liquid nitrogen as an eluent at a temperature of −196 °C. There is also one study in which air was directly injected into a glass column with a reversed-phase sorbent [3]. A photographic approach was used for visualizing the air transport during elution, and the authors found different types of flow involved in the process. However, in this study elution took place at low pressure (1 bar), which undoubtedly affected the speed of air dissolution in the mobile phase. Therefore, we believe yet-unexplored processes were taking place in the column with the gas sample at high pressure. Direct injection of a gaseous sample into a column and its subsequent analysis by HPLC under normal conditions has not yet been performed. In this study we explored the direct injection of vapor into a chromatographic column and showed the applicability of reversed phase HPLC with UV detection in determining the gaseous phase composition and the concentration of substances.

2. Experimental section

2.1. HPLC instrument

A "MiLiChrom A-02" chromatograph equipped with autosampler and multiwavelength detector (Institute of Chromatography "EcoNova", Ltd., Novosibirsk, Russia) [4]. Double-channel vacuum degasser "DEGASi" Compact Degasser (BIOTECH, Sweden) were used for degassing of eluent. For manual sample injection without the flow stop we used the valve with the injection loop of 20 μl (model A1357, Knauer, Germany). Separation was done on column 2 x 75 mm with reversed-phase ProntoSIL-120-5-C18 AQ (Bischoff Chromatography, Germany), column temperature 35°C, cell volume 1,2 μl, cell length 1,6 mm, 5 mM $HClO_4$ in water as eluent A, methanol or acetonitrile as eluent B.

2.2. Gaseous samples preparation

Samples were prepared as follows: 50 μl was placed in an autosampler vial, vials were tightly sealed with polyethylene caps and incubated for 15–20 min at room temperature to establish

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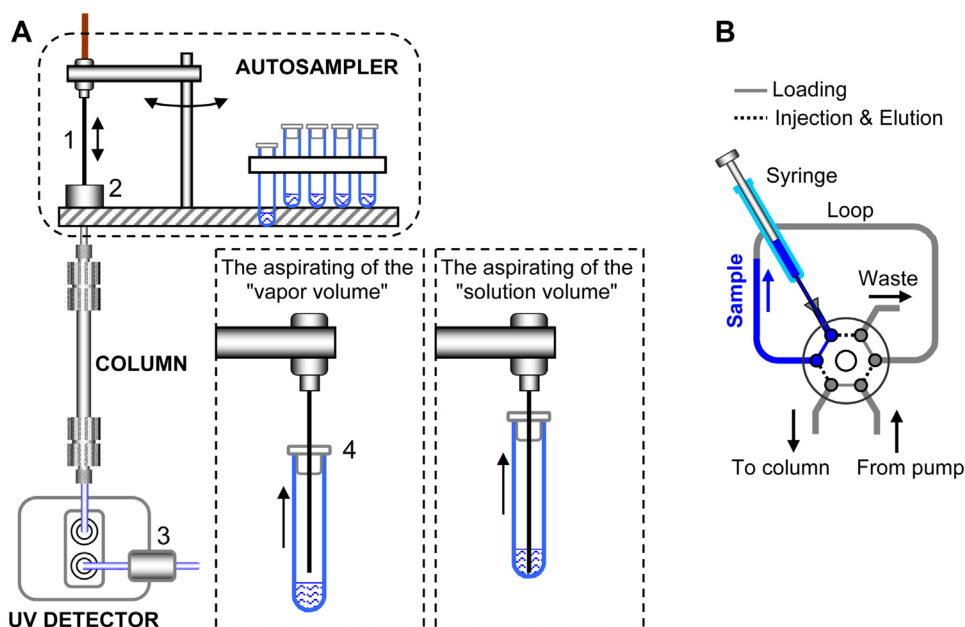

Fig. 1. (A) Sample collection from an autosampler vial. 1—injection needle; 2—injection port; 3—flow-through back pressure regulator; 4—polyethylene cap. (B) The scheme of a gaseous sample injection into the column with the injection valve.

the equilibrium vapor concentration. Vial volume is 250 μl. The autosampler was modified by drilling a vial port, which meant samples were taken from the vials automatically via an autosampler needle and placed above the liquid (Fig. 1A). Samples were also taken manually with a syringe for manual injection through the injection valve (Fig. 1B).

3. Results and discussion

3.1. Injection of the gaseous sample into a column with the eluent flow stop

Before sample injection pumps A and B stopped, the injector needle was lifted from the injection port and system pressure was zeroed. The needle was placed above the vial, lowered, inserted through the cap, and the gaseous sample was aspirated into the needle with pump A. The needle then lifted, returned to the "injection" position, lowered into the injection port, and was sealed. Subsequently, pumps A and B were switched to run mode, the sample was injected into the column, and elution began. As pressure quickly increased, the gaseous aliquot compressed and dissolved in the eluent. To prevent formation of bubbles in a detector cell, the flow-through back pressure regulator was installed to provide the excessive pressure of 0.2–0.4 MPa in the cell. The typical chromatogram is shown in Fig. 2A. In our case, the autosampler was modified by drilling a hole, but the same result could also be obtained by reprogramming. The chromatogram of the same substances dissolved in methanol is given in Fig. 2B. The chromatograms appear very similar, but in Fig. 2A the pressure plateaued later because the sample was gaseous.

Using the chromatogram in Fig. 2B for calibration, we calculated the concentrations of solvent vapors from the chromatogram in Fig. 2A as the following: pyridine—5 μg/ml; chloroform—24 μg/ml; benzene—67 μg/ml; toluene—32 μg/ml. The efficiency of the column was calculated using the toluene peak in both cases as 5800 theoretical plates, and the toluene peak symmetry calculated at the level of 10% of its height was 0.88.

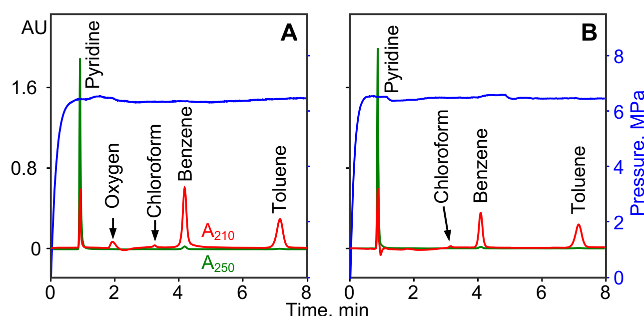

Fig. 2. The chromatogram of compounds in gas phase (A) and liquid phase (B). A) The composition of the gas phase above the mixture: pyridine:chloroform:benzene:toluene (1:1:1:1) (v/v). The aliquot of gaseous sample was 5 μl. (B) The sample was methanolic solution of pyridine (6 μg/ml); chloroform (30 μg/ml); benzene (40 μg/ml) and toluene (25 μg/ml). Sample volume was 5 μl. The eluent was 55% methanol. The flow rate was 200 μl/min. Detection at 210 nm and 250 nm.

The volume of the injected gaseous sample can be more than 50% of column dead volume. As shown in Fig. 3, even when oxygen sample volume was 100 μl (66% of the column dead volume), the resulting peak was quite symmetrical. It should be noted, however, that when sample volume exceeded 2 μl, column efficiency dropped. This is primarily due to column overload. It is known that the critical load for conventional reversed-phases is about 10 μg of substance per 1 g of sorbent [5]. Our column contains 0.2 g of sorbent, so when the oxygen sample volume is 2 μl (3 μg or 100 mmol), column load exceeded 15 μg/g.

The sensitivity of the oxygen analysis with UV detection is quite low, but it can be increased many times using an electrochemical detector. The sensitivity of the determination of oxygen achieved in [6,7] was 98 fmol.

It is evident in Fig. 4 that the oxygen peak area on the chromatogram linearly correlated with the volume of the injected sample up to 50 μl, the latter corresponding to about 30% of the column's dead volume.

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