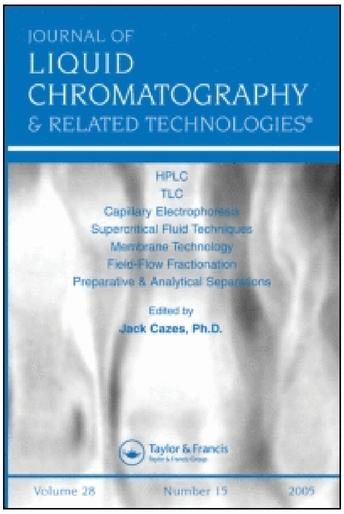

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ADDITION AND MEASUREMENT OF METHANOL IN CARBON DIOXIDE MOBILE PHASE FOR SUPERCRITICAL FLUID CHROMATOGRAPHY

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ABSTRACT

A simple method for the addition of methanol to supercritical CO_2 is described. Carbon dioxide, the most widely used mobile phase in supercritical fluid chromatography, is a relatively non-polar fluid, and hence addition of small amounts of polar modifiers could be necessary to migrate polar solutes. In this paper, a new mixing device was developed, in which high porous stainless steel filters were used to generate methanol-modified carbon dioxide mobile phase. When supercritical CO_2 goes through the mixing device, the modifiers held within the small pores of filters can be dissolved in the pressurized supercritical fluids. High porous stainless steel filter with 2μm porosity was used in our mixing device. To measure the amount of methanol dissolved in supercritical CO_2 after the mixing device, a fuel cell type modifier sensor, which was made by depositing gold and platinum on a porous plastic disc was used.

INTRODUCTION

In 1962, the idea of using dense gases for the transport of nonvolatile substances through a chromatographic column was independently conceived and reduced to practice by Klesper et al.[1] in a simple chromatographic apparatus using porphyrins as the eluates.

The method is called supercritical fluid chromatography(SFC). During its relatively short existence, supercritical fluid chromatography(SFC) has become an attractive alternative to GC and LC in certain industrially important applications. SFC gives the advantage of high efficiency and allows the analysis of non-volatile or thermally labile mixtures.

The density of the mobile phase in SFC is about 200 to 500 times the density observed in gas chromatography. The effect of shorter intermolecular distances and the resultant increase in molecular interactions is an enhanced solubilizing capability of the solvent towards various solutes. Compounds of much higher molecular weight than the ones which the gas chromatography allows can therefore be chromatographed. However, the most commonly used mobile phases in SFC are all relatively nonpolar fluids. Carbon dioxide, the most widely used fluid, is no more polar than hexane[2] even at high densities. Solute polarity should be between that of the stationary phase and the mobile phase in order to have a well behaved separation. Few real-world samples contain only non-polar solute, so a major objective of research into SFC has been directed toward increasing the range of solute polarity that can be handled by the technique. To bring the SFC technique into routine use, mobile phases that are more polar than the commonly used carbon dioxide are necessary.

The main limitation of the most often used mobile phase, CO_2, is its limited ability to dissolve polar molecules, even at very high densities. Other possible neat fluids such as NH_3[3] are often reactive, flammable, or toxic. Alternatively, the characteristics of the supercritical fluid mobile phase can be varied by the addition of miscible compounds to the primary fluid. The term "modifier" is generally used for the second component of the mobile phase. The solubility of the solute in the supercritical phase can be influenced a lot by adding modifiers to the mobile phase. Therefore, the polarity range of polar compounds that can be separated by SFC can be greatly extended by the addition of polar modifiers to supercritical CO_2.

The use of modifiers has been reported by Jentoft and Gouw[4] and by Novotny et al.[3] The latter authors showed that adding 0.1% isopropanol to n-pentane as the mobile phase decreases the observed K values for many

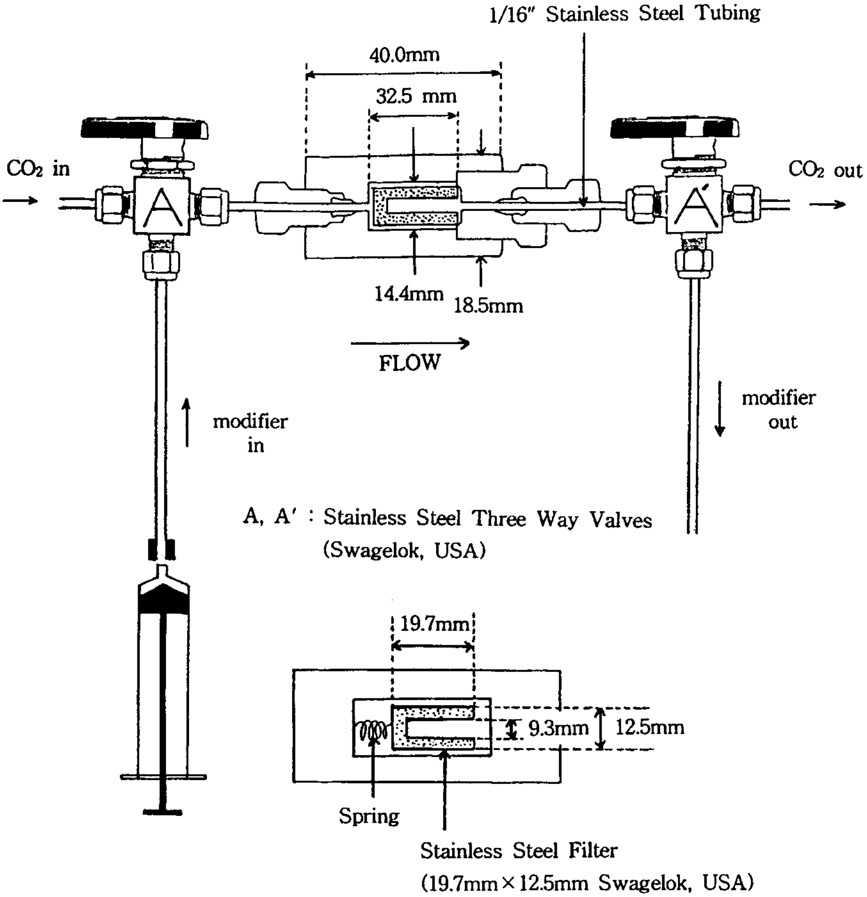

Figure 1. Mixing device.

polynuclear aromatic hydrocarbons by 20-35%. Thus the addition of modifiers (generally organic solvents) to supercritical mobile phase changes the polarity of the mobile phase and also leads to deactivation of the column packing material.

Several workers[6,7,8] have reported the influence of modifiers on peak shape, selectivity, and retention time in capillary and packed column SFC. One of the simple and effective ways for the addition of modifiers to supercritical fluid mobile phase is to use a saturator column[9,10] which is usually a silica column saturated with polar modifiers. In our laboratory,[11] μ-Porasil column saturated with polar modifiers has been used successfully as a saturator column for a while. A serious disadvantage with this system is that the amount of modifiers dissolved in the mobile phase varies as mobile phase passes through the saturator column since a modifier holding capacity of the silica column is limited. Therefore, we attempted to develope a new device to maintain the amount of polar modifiers dissolved in supercritical fluid constant for a longer period of time.

In this paper, a stainless steel filter with 2 μm porosity was used to generate methanol modified CO_2 mobile phase, and the results were compared to those of saturator column.

EXPERIMENTAL

A Lee Scientific Series 600 supercritical fluid chromatography was used with a 100μm ID × 20m capillary column (SB-biphenyl-30, film thickness 0.25 μm). This system was equipped with a timed split injector and a flame ionization detector. SFC grade CO_2 (Scott Specialty Gases) was used as a basic mobile phase. Experimental conditions for SFC separations were as follows: supercritical CO_2 at 110°C, pressure programmed from 170 atm to 400 atm at 5 atm/min, frit restrictor with a initial linear velocity of 5.5 cm/sec. High porous stainless steel filter (2 μm porosity, 19.7 × 12.5 mm, Swagelok, USA) was used in our mixing device.

The mixing device was saturated with methanol using a 50 mL hypodermic syringe. The mixing device was placed between a pump and an injector. To measure the quantity of modifiers dissolved in supercritical fluid, a fuel cell type modifier sensor (Won-sung Electronics. Inc., Incheon, South Korea) was designed and made by depositing gold and platinum on a porous plastic disc.[13] The sensor output was recorded on a strip-chart recorder (Knauer, Berlin, Germany).

RESULTS AND DISCUSSION

When modifiers are used with supercritical CO_2 in order to chromatograph polar substances, the binary mixture of eluents can contaminate the instrument. Especially, when water or formic acid are used as a modifier, the modifier remaining in a pump, may cause a corrosion of the pump and when methanol is used as a modifier, the residual methanol in a pump can be eluted slowly during the next run.

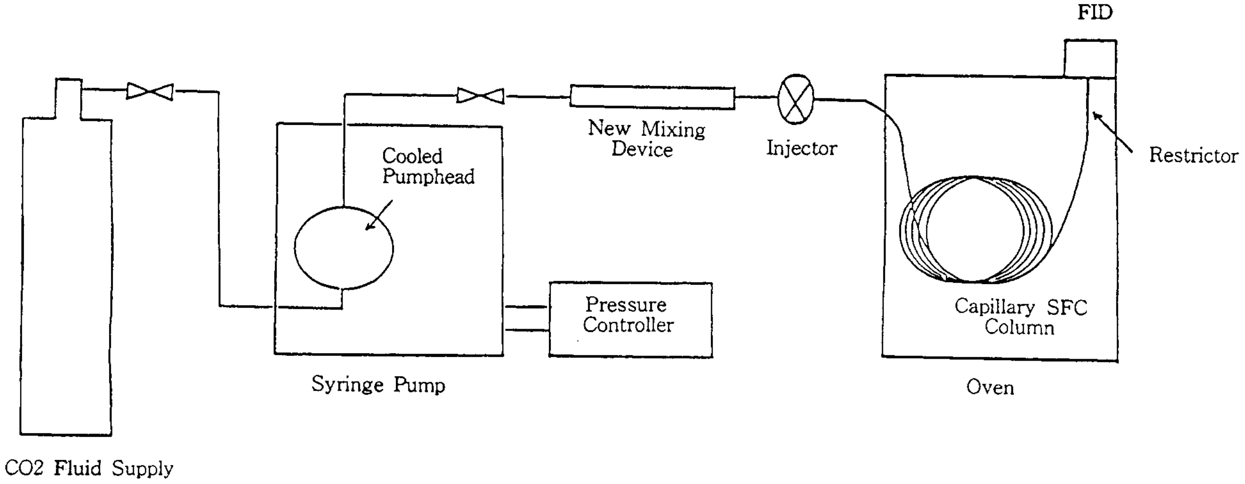

Figure 2. A diagram for adding a polar modifier to supercritical fluid mobile phase.

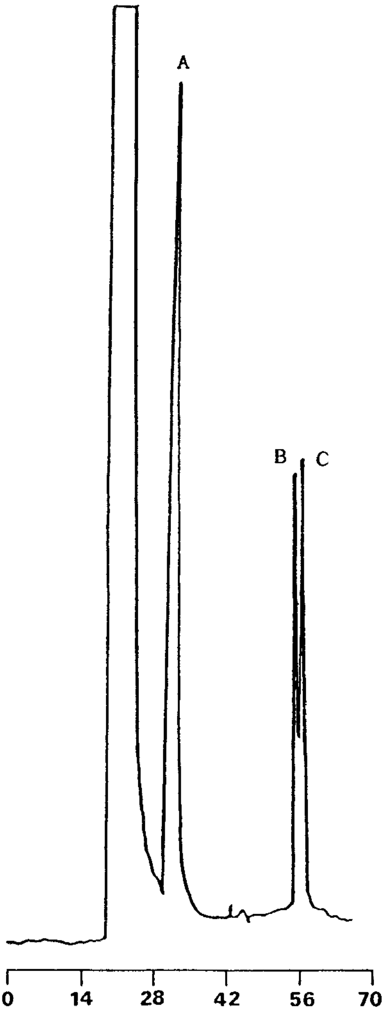

Figure 3. The chromatogram of a mixture of pesticides. Peak A: Methomyl, B: Dimethorph E, C: Dimethorph Z.

This may affect the time to achieve chemical equilibrium for the following separations, and also many modifiers can diffuse in the laboratory and contaminate the air in the laboratory. A good way to overcome these problems is to use a saturator column[9,10] to add polar modifiers to supercritical CO_2.

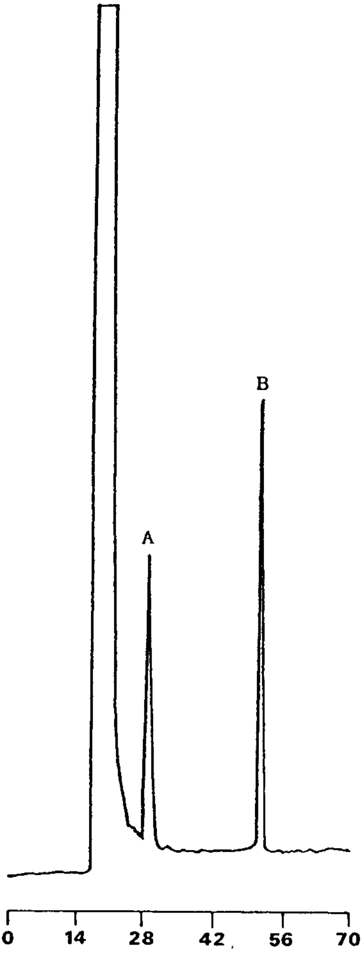

Figure 4. The chromatogram of a mixture of pesticides. Peak A: Carbofuran, B: Alanycarb.

In our previous paper,[11] water was used as a modifier and μ-Porasil column was used as a saturator column with a system design similar to Engelhardt's.[9] With this design, a polar modifier(water) can be added to pressurized CO_2 fluid after the pump, and thus no modifier remains in the pump. However, when dealing with the use of a saturator column, it should be mentioned that a serious problem always arises. The problem is a bad reproducibility of the amount of modifier dissolved in the supercritical CO_2.

Table 1

The Structure of Peak in the Chromatograms

Chromatogram	Peaks	Commercial Name	Chemical Name
	A	Methomyl	S-methyl N-(methyl-carbamoyloxy) thioacetimidate
Figure 5	B	Dimethomorph E	4-[3-(4-chlorophenyl)- -3-(3,4-dimethoxyphenyl) acrylol] morpholine
	C	Dimethorph Z	4-[3-(4-chlorophenyl)- -3-(3,4-dimethoxyphenyl) acryloyl] morpholine
	A	Carbofuran	2,3-dihydro-2,2-dimethyl benzofuran-7-yl methylcarbamate
Figure 6	B	Alanycarb	Ethyl(Z)-N-benzyl-N-[[methyl(1-mthylthioethyl ideneamino-oxycarbonyl amino]thio]-β-alaninate

When the same experiments were repeated several times, it was very difficult to obtain reproducible results in the chromatograms since the amount of modifier in the mobile phase does not stay constant with time.[12] For these reasons, a new mixing device (Fig 1) was developed, in which high porous stainless steel filter was used to hold a large amount of methanol. Methanol in the saturator columns[9,10,11] is held on the stationary phase by hydrogen bonding, but it is held physically inside small pores of filters with this device. After being saturated with methanol, the device is placed between a pump and an injector (Fig 2).

With this design, supercritical CO_2 is delivered from the pump to the device which is saturated with methanol. When supercritical CO_2 goes through the device, methanol held within the small pores of the filter can be dissolved in the pressurized supercritical fluids.

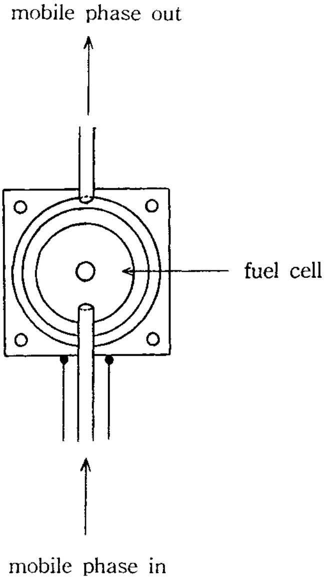

Figure 5. Modifier sensor.

Thus nonpolar supercritical CO_2 can have the characteristics of polar mobile phase because it can absorb the polar solvent, that is, MeOH. Therefore, after passing the mixing device, supercritical CO_2 is changed to new mobile phase with different polarity, and it is possible to separate polar samples using this new mobile phase.

An experiment to separate some polar samples (insecticides and fungicides) with this new mobile phase was performed. Fig 3 and 4 are chromatograms for mixtures of insecticides and fungicides obtained using a mixed mobile phase (supercritical CO_2-methanol). In contrast to the experiment in which only CO_2 was used as mobile phase, excellent separations were obtained. When only CO_2 was used for these samples, unseparated and very broad peaks were observed in about 35 min.

The addition of a small amount of methanol to supercritical CO_2 reduced the retention and improved the peak shapes. The phenomena are in accord with the results reported by Blilie and Greibrokk.[5] The structure of each peak is shown in Table 1.

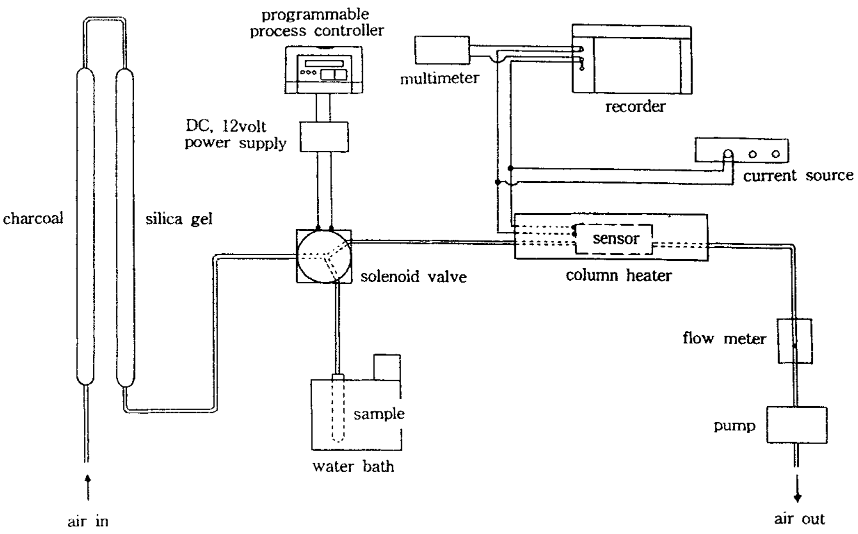

Figure 6. An arrangement of water content measuring device.

To measure the amount of methanol dissolved in supercritical CO_2 after the mixing device, a modifier sensor which consists of a fuel cell made by depositing gold and platinum on a porous plastic disk was used. This fuel cell has the advantage that it can be made more sensitive than any other type of methanol sensors. In a fuel cell, it has been suggested[13] that the reaction taking place is :

$$CH_3OH \rightarrow CH_2OH + H^+ + e$$
$$CH_2OH \rightarrow CH_2O + H^+ + e$$

The electrons produced pass through a resistor and it is the potential across this resistor which is amplified and measured. The measured potential was used as a measure of the water content of the environment surrounding the sensor.

Fig 5 shows a cross-section of the modifier (methanol) sensor used in this work. The entire modifier-measuring device was assembled together, as shown in Fig 6. A constant-current (d.c.) source was used to supply a current of about 0.1 μA to the sensor. The potential of the fuel cell was changed according to the methanol content of the supercritical CO_2 fluid, and the voltage difference between the two wires was recorded and measured.

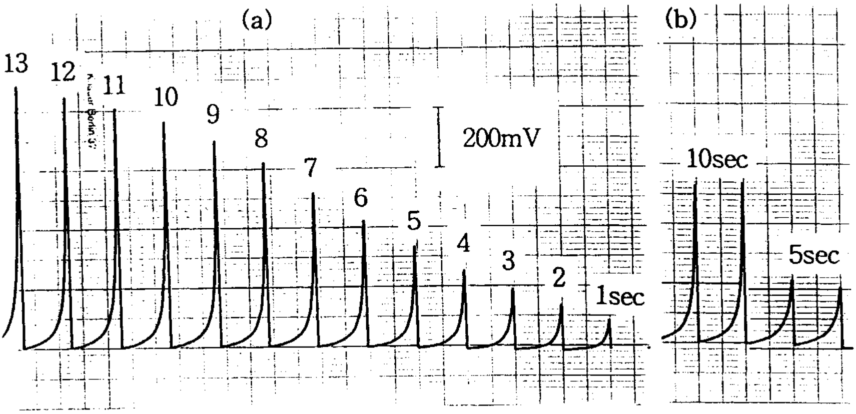

Figure 7. Relative peak height at different time intervals (flow rate 0.5 dm^3min^{-1} temperature: 20°C. (a) For air saturated with methanol and (b) for carbon dioxide fluid saturated with methanol.

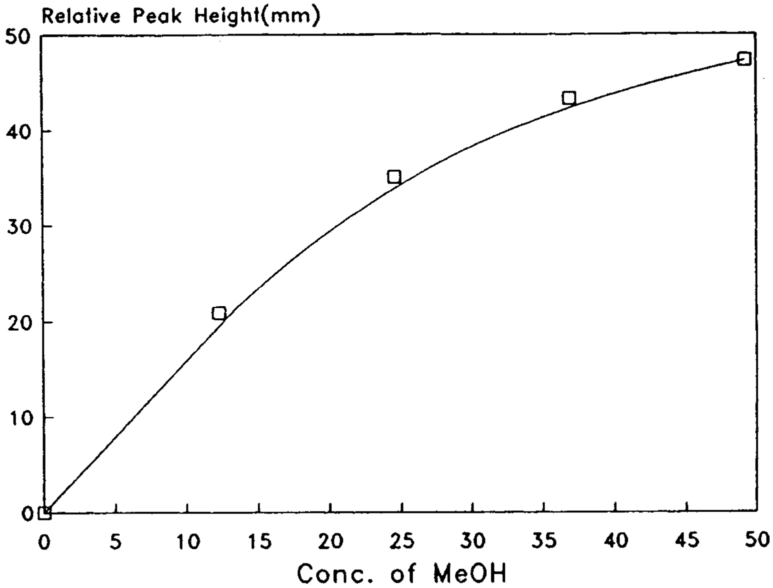

Figure 8. Sensor response with various concentration levels of methanol. (12.3, 24.6, 36.9, 49.2 x 10^{-4} M, at 23.0°C).

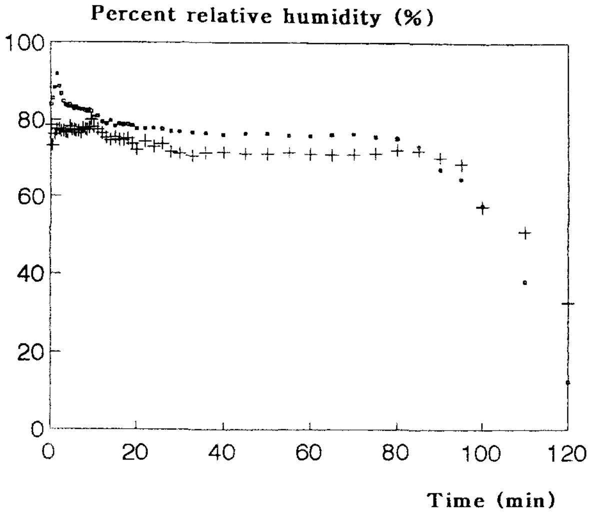

Figure 9. Measurement of the methanol content is supercritical CO_2 as a function to time at (+)100 and (□) 200 atm.

Fig 7 shows chromatograms for the injection of (a) air saturated with methanol, and (b) supercritical CO_2 fluid saturated with methanol, through the mixing device at different time intervals. Air saturated with methanol was generated by passing air, with bubbling, through methanol contained in two sequential bottles, and was injected directly into the sensor through a three-way solenoid valve (Radio Shack, Fort Worth, TX, USA). The determination of methanol in CO_2 after passage through the mixing device was performed on-line, i.e., supercritical CO_2 fluid was injected through a C14W loop injector, and the sensor was placed directly after the mixing device.

By using the data (Fig 8) on the correlation of peak height with concentration of methanol, the methanol content of supercritical CO_2 fluid, after passage through methanol saturated mixing device, could be determined. From the data in Fig. 7(b), the amount of methanol dissolved in supercritical CO_2 was measured as 6.8%(V/V) or 16.4×10^{-4} M at a pressure of 25.33MPa(250atm).

With our mixing device, the time period of keeping a constant concentration of methanol was longer (about 30 minutes) than with the saturator column i.e., μ-Porasil column (about 10 minutes, Fig 9). This is probably due to the fact that with the saturator column, methanol is held by hydrogen bonding on -OH functional group of the stationary phase and with our mixing device, methanol is spread out into small pores of a stainless filter. After 30 minutes, the mixing device must be refilled with methanol for practical use.

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