MAF-5

1 Rapid separation of non-polar and weakly polar analytes
2 with metal-organic framework MAF-5 coated capillary
3 column

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ABSTRACT

Metal-organic frameworks (MOFs) have attracted widespread attention due to their unique characters such as high surface area, high thermal and chemical stability, diverse structure topology and tunable pore size. The study first exploited a porous metal organic framework MAF-5 ($[\text{Zn}[(\text{eim})_2]$, Heim = 2-ethylimidazole) as stationary phase for gas chromatography by a novel dynamic coating method. The column efficiency of the 184 silicone@MAF-5 capillary column was up to 9045 plates $\cdot\text{m}^{-1}$ for benzene. The column is very promising for the rapid separation of polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs). And the column showed good reproducibility, retention time, peak area, high resolution, and a wide linear range. The determined thermodynamic parameters and chromatographic retention of all probe molecules on the 184 silicone@MAF-5 column showed the separation of analytes is a complex balance of thermodynamic and kinetic factors.

Keywords: Metal organic frameworks, capillary column, stationary phase, gas chromatography

1. Introduction

Research efforts in capillary gas chromatography have primarily been focused on the adaptable broad spectrum column and a selective stationary phase for a porous layer open tubular column to achieve high-resolution separations [1]. Metal-organic frameworks (MOFs), also known as porous coordination polymers (PCPs), are a new family of hybrid inorganic-organic microporous crystalline materials, which are self-assembled straight forwardly from metal ions and organic linkers via coordination bonds [2,3]. Due to their unique characters such as high surface area, high thermal and chemical stability, diverse structure topologies and tunable pore size, MOFs have attracted great attention in a number of fields, including hydrogen storage [4], gas adsorption and separation [5,6], bioimaging [7], catalysis [8,9], sensing [10], and drug delivery [11]. It is worth mentioning that MOFs have been used for sample preparation and separation in analysis filed [12], especially MOFs were utilized as novel stationary phases [13-22] for capillary gas chromatography (GC) have also been reported.

Gu and Yan firstly reported a MIL-101 (Cr)-coated capillary column for the separation of xylene isomers and ethyl benzene, and high selectivity and resolution were obtained [13]. In subsequent researches, ZIF-8 [14], IRMOFs [15], UIO-66 [16], MOF-CJ3 [17], MIL-100 (Fe) and MIL-100 (Cr) [18], $\text{Zn}(\text{ISN})_2 \cdot 2\text{H}_2\text{O}$ [19], HKUST-1 [20], MOF-5 [21], $[\text{Cu}_2(\text{cam})_2(\text{dabco})]$ and $[\text{Cu}_2(\text{cam})_2(\text{bipy})]$ [22] were also used as stationary phases for the separation of n-alkanes, isomers, natural gas and other compounds.

Metal-azolate frameworks (MAFs) are a class of azolate ligands MOFs which have excellent thermal and chemical stability [23]. MAF-5 ($\text{Zn}(\text{eim})_2$, Heim = 2-ethylimidazole), was rapidly synthesized by simply mixing $\text{Zn}(\text{OH})_2$ and 2-ethylimidazole via acid-base neutralization reaction at room temperature [24,25]. MAF-5 possess zeolite analcime (*ana*) topology with elongated, ellipsoidal cavity ($d = 7.0 \text{ \AA}$, $l = 10.0 \text{ \AA}$) and large porosity. The pore system of MAF-5 with such large channel size is very interesting due to the different ring sizes (diameter 2.2-4.9 $\text{\AA}$ for $\text{Zn}_6(\text{eim})_6$ ring and 4.0 $\text{\AA}$ height, 5.8-9.0 $\text{\AA}$ width for $\text{Zn}_8(\text{eim})_8$ ring). Meanwhile, disordered ethyl groups within the pores provide MAF-5 intense hydrophobic. Thus, the various pore sizes and disordered ethyl groups of MAF-5 assumed to be great potential for enhancing adsorption and separation of molecules with different polarities.

Herein, we utilized 184 silicone elastomer as the protective thin film over MAF-5 to propose a novel dynamic coating strategy to fabricate firm and mechanically stable coating on fused silica capillary column. The capillary column coated with 184 silicone@MAF-5 was successfully applied for the rapid separation of non-polar analytes, linear alkanes and polycyclic aromatic hydrocarbons (PAHs), as well as weakly polar compounds, organochlorine pesticides (OCPs). In addition, thermal stability, McReynolds constants, thermodynamic and kinetic properties of the column were also evaluated.

2. Experimental

2.1. Materials and equipment.

All chemicals and reagents were at least of analytical grade. Benzene (99%), toluene (99%), ethylbenzene (99%), *o*-xylene (99%) were bought from Alfa Aesar (London, England). Naphthalene (99%), acenaphthylene (99%), chrysene (98.9%), benze(a)pyrene (99.9%), benze[g,h,i]perylene (99.3%); *n*-pentane (99%), *n*-hexane (99%), *n*-heptane (99%), *n*-octane (99%), *n*-nonane (99%) and *n*-decane (99%) were purchased from J&K Chemical (Beijing, China). Hexachlorobenzene (HCB) (>97%), trans-chlordane (99.5%), cis-chlordane (99.5%), *o,p*-DDT (>97%), *p,p*-DDT (>97%) and mirex (>97%) were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Dichloromethane and methanol were HPLC grade from Tianjin Chemical Reagent Factory (Tianjin, China). Acetone, cyclohexane, hydrochloric acid and sodium hydroxide were purchased from Guangzhou Chemical Reagent Company (Guangzhou, China). 184 silicone elastomer (base and curing agent) was from Dow Corning (Midland, MI, USA).

GC characterizations of the self-made GC column were carried out on an Agilent HP 6850A gas chromatography with a G2630B flame ionization detector (GC/FID) (Palo Alto, CA, USA). Nitrogen (99.999%) was used as the carrier gas. Untreated fused silica capillary column was purchased from Yongnian Ruifeng Chromatogram Apparatus Co. Ltd. (Hebei, China). A Hitachi S-4300 scanning electron microscope (SEM) (Hitachi, Japan) was used to investigate the surface morphology of the column. The surface images were obtained at 20 kV. A Netzsch-209 thermogravimetric analyzer (TGA) (Bavaria, Germany) was applied to study the thermal stability of the

184 silicone@MAF-5 mixture coating.

2.2. Preparation of MAF-5

Porous MAF-5 with a mean diameter of nanosize pore was synthesized by acid-base neutralization reaction according to a previously reported method [25]. Briefly, Zn(OH)_2 (6 mmol) was dissolved in concentrated aqueous ammonia (25%), then a methanol solution of anazole ligand 2-ethylimidazole was added. After that, a small amount of benzene (5%, v/v) was added into the ligand solution. The reaction time is 5 h for room temperature stirring. Then the mixture was filtered, collected and washed by water and methanol, then dried at 120 °C to obtain white powder as the product.

2.3. Fabrication of the 184 silicone@MAF-5 coated capillary column

Untreated fused silica open tubular column (20 m long $\times$ 0.53 mm i.d.) was filled with 1 M NaOH, sealed at both ends and maintained for 2 h. Thereafter, the capillary was washed successively with ultrapure water for 1 h, 0.1 M HCl for 2 h, and again with ultrapure water until the outflow reached neutrality, finally washed with acetone for 30 min. Then, the treated column was purged with nitrogen at 120 °C overnight. The 184 silicone@MAF-5 coated column was prepared by a modified dynamic coating method in accordance with the method reported by Nikelly et al [26]. Firstly, MAF-5 was well milled to a uniform powder and dispersed in 0.5 mL methanol (6 $\text{mg}\cdot\text{mL}^{-1}$). Then the suspension was introduced into the column under gas pressure, and pushed through the column at a rate of $40\text{ cm}\cdot\text{s}^{-1}$ to leave a wet coating layer on the inner wall. A 1 m long buffer tube was attached to the end of the capillary column

as a restrictor for avoiding acceleration of the solution plug near the end of the column. Finally, the MAF-5 coated capillary column was dried under nitrogen to remove methanol and then conditioned at 250 °C for 2 h. In the next procedure, 0.5 mL of cyclohexane solution of the 184 silicone elastomer (base and curing agent, 10:1, w/w, 4 mg·mL⁻¹) was introduced into the column as the above method. The 184 silicone@MAF-5 column was flushed overnight with nitrogen to remove cyclohexane and then conditioned by a procedure from 50 °C to 270 °C for three times before use. To highlight the separation performance of MAF-5, the amount of MAF-5 is more than that of 184 silicone elastomer.

2.4. McReynolds constants for 184 silicone@MAF-5 capillary column

The polarity is an important factor affecting classifying chromatographic stationary phases in GC. McReynolds constants were employed to describe the polarity of the 184 silicone@MAF-5 column using benzene, 1-butanol, 2-pentanone, 1-nitropropane, and pyridine as test solutes. The five selected solutes represent the extent of intermolecular interactions between the probe compound and the stationary phase [27,28].

3. Results and discussion

3.1. Characterization of the 184 silicone@MAF-5 coated capillary column

3.1.1. Morphology

MAF-5 powder was given by Professor Zhang's group in Sun Yat-sen University, and the confirmation of the structure PXRD (powder X-ray diffraction) pattern of

MAF-5 was shown in previous work [25]. The morphology of 184 silicone@MAF-5 stationary phase was characterized by SEM (Fig. 1). The SEM images showed a cross-section of the short capillary column segments. The 184 silicone@MAF-5 coating on the inner wall was compact and uniform (Fig. 1a) and the thickness of the coating was approximately 1 μm (Fig. 1b).

3.1.2. Thermal stability

Thermal stability was evaluated by TGA test and column bleed test, as shown in Fig.S1, TGA curve exhibited that the 184 silicone@MAF-5 mixture was stable up to 400 °C. To evaluate the maximum operating temperature, the column was heated up to 280 °C to give the column bleed curve (Fig. S2). The result demonstrated that the stationary phase was of high inertness and relatively low bleed. Both TGA and column bleed experiments suggested that 184 silicone@MAF-5 exhibited excellent thermal stability and could be used as GC stationary phases.

3.1.3. McReynolds constants

McReynolds constants of the prepared column were determined using five probe compounds at 120 °C. The average value of the five McReynolds constants was 699, implying that the 184 silicone@MAF-5 coating was of moderate polarity.

3.1.4. Column efficiency

The van Deemter plots of the 184 silicone@MAF-5 coated capillary column, which represent the chromatographic parameters concerning column efficiency, were measured by using a mixture of benzene, toluene, ethylbenzene and *o*-xylene (BTEX) at 180 °C. The van Deemter plots of the 184 silicone@MAF-5 coated column were

shown in the Fig. S3. Minimum height equivalent to a theoretical plate (HETP) were found to be in the range of 0.1-0.15 mm for BTEX. As shown in Table S1, the highest determined column efficiency was 9045 plates·m⁻¹ for benzene and more than 6000 plates·m⁻¹ for the other three analytes.

3.2. Separation performance of the 184 silicone@MAF-5 coated column

The separation performance of the 184 silicone@MAF-5 coated capillary column was evaluated by different analytes including BTEX, *n*-alkanes (*n*-C₅-C₁₀), PAHs and OCPs. As shown in Fig. 2, all of the analytes achieved high resolution on the 184 silicone@MAF-5 column with sharp and symmetric peak shapes except for benzo[*g,h,i*]perylene. Accordingly, the prepared column exhibited excellent separation performance for analytes with different polarity. Moreover, under the considerably large carrier gas flow velocity (8 mL min⁻¹ and 5 mL min⁻¹), PAHs and OCPs were completely eluted using the given temperature program within 10 min and 14 min, respectively. Generally, the elution time for PAHs and OCPs are about 30-45 min on the commercial HP-5MS column (5%-phenyl-methypolysiloxane coating) with gas flow velocity of 1.2 mL min⁻¹. It is likely that the large pore volume of MAF-5 is benefit for improving capacity of the 184 silicone@MAF-5 column, thus the column exhibits excellent separation performance even under such large flow rate.

The injected mass of PAHs and OCPs were changed to investigate the effect of the analytes mass on peak area as well as capacity factor. An increase of analyte mass led to a linear increase of peak area but almost no change in the capacity factor in the range of 0.3-150 ng for PAHs and 0.95-100 ng for OCPs (Table S2 and Fig. S4).

Moreover, as shown in Table S3, the 184 silicone@MAF-5 coated column exhibited good reproducibility for the separation of PAHs and OCPs. The relative standard deviations for five replicate determinations of these analytes were 0.1-0.5%, 1.9-8.3%, 2.0-7.6%, 0.4-1.9% for retention time, peak area, peak height and peak width, respectively. Hence, the 184 silicone@MAF-5 coated column was highly capable of quantitative and qualitative analysis.

3.3. Thermodynamics and kinetics of separation on the 184 silicone@MAF-5 coated column

To get further insight into the energy effect on the retention behavior of the 184 silicone@MAF-5 coated capillary column, van't Hoff analysis were conducted and BTEX were chosen as targets to study the thermodynamic properties of the column in the temperature range of 120-180 °C. The adsorption enthalpy change (ΔH) and entropy change (ΔS) calculated from the van't Hoff plots according to Eq. (1) were summarized in Table 1.

$$\ln k' = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} + \ln \phi \quad (1)$$

$$\text{and} \quad \Delta G = \Delta H - T\Delta S \quad (2)$$

where k' is the capacity factor, R is the gas constant, T is absolute temperature, and ϕ is the phase ratio, which is defined as the volume of the stationary phase in the column (V_S) divided by the void volume of the column (V_0). V_S and V_0 was calculated according to the thickness of the coating (approximately 1 μm) and the column inner diameter (530 μm). The value of k' was calculated according to Eq. (3)

$$k' = \frac{t-t_0}{t_0} \quad (3)$$

where t is the retention time for the analyte and t_0 is the column void time under constant temperature gas chromatographic separation.

The van't Hoff curves showed good linearity (Fig. 3), indicative of no changes in the interaction mechanism in the studied temperature range for the separation of BTEX. The negative values of ΔH and ΔS for BTEX increased with the order of benzene, toluene, ethylbenzene and *o*-xylene, reflecting that side groups on the benzene ring played an important role in the retention of the analyte. The analytes with more or larger side groups were prone to make closer contact with the pore walls, which resulted in not only stronger van der Waals forces and accordingly more negative ΔH , but also more loss of freedom and thus more negative ΔS [15]. The Gibbs free energy changes (ΔG) of the transfer of BTEX from the mobile to the stationary phase were obtained. Clearly, the negative values of ΔG indicated that the analyte transfer process was thermodynamically spontaneous. More negative values of ΔG correlated with a more favorable transfer of the analyte from the mobile phase to the stationary phase, and with longer retention of the analyte on the stationary phase.

The effect of column temperature on selectivity and resolution of the 184 silicone@MAF-5 coated column for BTEX were also investigated (Fig. S5). It was found that as the column temperature increased, the capacity factor k' of all analytes decreased, indicating that an exothermic separation process was involved (Fig. S5(a)). The selectivity of four analytes showed a gentle curve as the column temperature increased, in contrast, the resolution curve showed a sudden drop (Fig. S5(c) and (b)).

It is indicated that a tiny variation of selectivity factor will trigger a significant change on the resolution. Fig. S5(d) showed that symmetry factor of chromatographic peaks of BTEX gradually tended to be 1.0 with the temperature increased.

The separation performance of a GC column is also governed by the ability to distinguish the individual analyte and the interfering compounds [28]. It is usually evaluated by peak broadening. According to the kinetic theory for GC capillary columns developed by Golay, peak shape of analyte depends on longitudinal diffusion and the resistance to mass transfer. Maximal theoretical plates, longitudinal diffusion coefficient (B) and the coefficient of mass transfer resistance (C) for the separation of BTEX on 184 silicone@MAF-5 coated column were shown in Fig. S6, Table S4. As shown, the developed 184 silicone@MAF-5 stationary phase had the smallest plate height for benzene, due to the lowest C in spite of the highest B. It could be inferred that mass transfer should be dominant in the peak broadening for analytes when passing through the column. According to the Eq. 4, the value of H achieves a minimum at a particular flow velocity which is given by $\sqrt{B/C}$ for an isothermal experiment (180 °C). At this flow rate, the resolving power of the column is maximized.

$$H = \frac{B}{u} + C \times u = \frac{B}{u} + C_M \times u + C_S \times u \quad (4)$$

$$H = \frac{2D_M}{u} + \left[\frac{1+6k+11k^2}{96(1+k)^2} \times \frac{d_c^2}{D_M} + \frac{2k}{3(1+k)^2} \times \frac{d_f^2}{D_S} \right] \times u \quad (5)$$

where H is height equivalent to a theoretical plate, u is the linear velocity, k is capacity factor; d_c is the inner diameter of the column (530 μm); d_f is the film thickness (1 μm); C_M and D_M are mass transfer resistance and diffusion coefficient

of the analyte in the mobile phase; C_S and D_S are mass transfer resistance and diffusion coefficient of the analyte in the stationary phase.

The values of D_M for BTEX were much higher than those of D_S (Fig. S7(a)) since the diffusion coefficient of analytes in the mobile phase is a predominant factor for column. C_M and C_S could be considered as measures of the time an analyte needs to transfer between the mobile and the stationary phase. Fig. S7(b) showed the comparison between C_M and C_S for BTEX. It is obvious that both C_M and C_S increased with the increase of elution order of BTEX. The values of C_M and C_S for benzene were smallest which contributed to the narrowest peak width.

4. Conclusion

In this study, we have demonstrated the fabrication of 184 silicone@MAF-5 coated capillary GC column by a modified dynamic coating method. It was easy to generate a compact and mechanically stable layer by using 184 silicone, which was conducive to improve the integrity of the whole coating. High thermal stability of the column stationary phase was observed. Moreover, the 184 silicone@MAF-5 capillary column is very promising for rapid separation of PAHs and OCPs. The prepared column showed good reproducibility (0.1-0.5% and 1.9-8.3% (RSD) for retention time and peak area, respectively), high resolution, great separation efficiency and a wide linear range (0.3-150 ng for PAHs and 0.95-100 ng for OCPs). The determined thermodynamic and kinetic parameters for BTEX indicated the separation of analytes on the prepared column was a complex balance of thermodynamic and kinetic factors. Thus, it is expected that the new 184 silicone@MAF-5 column was potential for the

separation of non-polar and weakly polar compounds.

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Figure Captions:

Fig. 1. SEM images of the thickness of 184 silicone@MAF-5 coating in part of the capillary column (a) scale bar =200 μm ; 184 silicone@MAF-5 deposited on the inner wall of the capillary column (b) scale bar=2 μm .

Fig. 2. Gas chromatograms on 184 silicone@MAF-5 coated capillary column for the separation of (a) BTEX, 150 $^{\circ}\text{C}$; flow velocity: 0.8 mL min^{-1} ; (b) *n*-alkanes, 50 $^{\circ}\text{C}$ (0 min) to 160 $^{\circ}\text{C}$ at 15 $^{\circ}\text{C min}^{-1}$; flow velocity: 0.5 mL min^{-1} ; (c) PAHs, 150 $^{\circ}\text{C}$ (2 min) to 270 $^{\circ}\text{C}$ at 50 $^{\circ}\text{C min}^{-1}$; flow velocity: 8 mL min^{-1} ; Split ratio: 10:1; (d) OCPs, 200 $^{\circ}\text{C}$; flow velocity: 5 mL min^{-1} ; Split ratio: 10:1.

Fig. 3. van't Hoff plots for BTEX on the 184 silicone@MAF-5 coated capillary column.

Fig.1.

Fig. 2.

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371 **Fig. 3.**

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374 **Table 1 Thermodynamic parameters for the separation of BTEX on the 184**
375 **silicone@MAF-5 column**

BTEX	$\Delta H/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta S/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\Delta G/\text{kJ}\cdot\text{mol}^{-1}$	R^2
benzene	-29.5	-46.5	-9.80	0.9980
toluene	-31.8	-46.8	-12.0	0.9995
ethylbenzene	-34.4	-48.7	-13.7	0.9998
o-xylene	-35.0	-48.8	-14.4	0.9999

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