

# Mesoporous Silica: A Suitable Adsorbent for Amines

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**Abstract** Mesoporous silica with KIT-6 structure was investigated as a preconcentrating material in chromatographic systems for ammonia and trimethylamine. Its adsorption capacity was compared to that of existing commercial materials, showing its increased adsorption power. In addition, KIT-6 mesoporous silica efficiently adsorbs both gases, while none of the employed commercial adsorbents did. This means that KIT-6 Mesoporous silica may be a good choice for integrated chromatography/gas sensing micro-devices.

**Keywords** Ammonia · Trimethylamine · KIT-6 · Mesoporous silica · Preconcentration · Desorption

## Introduction

Mesoporous materials are proved to be good candidates for gas sensing purposes as well as for many other applications such as environmentally friendly fuels [1], new generation optical devices [2], biochemical separations, bioactivity control for medical applications [3], catalytic adsorption, and molecular sieves [4–6], which have been reported so far. Due to the large surface area of such structures with nano-size pores, mesoporous materials are considered as a good choice for catalytic systems, supports for sophisticated materials, etc. [7]. Among various mesoporous

materials studied, mesoporous silica has found a great interest due to its promising physical and chemical properties [8–10]. Various types of mesoporous silica have been produced so far; SBA-15 and KIT-6 are now applied as templates for the synthesis of mesoporous metal oxides for chemical sensors, while other structures such as SBA-16 are also under investigation for gas sensing applications [11]. A complete review of the growth method and achieved structures can be found elsewhere [12, 13].

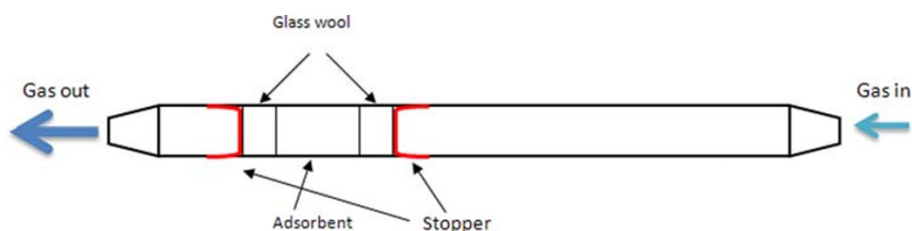
The template is removed during the preparation process, while the remaining material has a large tendency to receive gas molecules at the surface. Gas sensors based on mesoporous materials use this advantage to show their characteristic response to the target gas. One interesting property of a mesoporous material, on the other hand, can be its adsorption capacity, which means that a large amount of the material touching its surface may remain attached to the surface until a high-temperature desorption process is applied. This means that if performed precisely, such structures may also be good candidates for preconcentrating purposes, especially for low-concentration gases. Bruzzonity et al. [14] showed that mesoporous silicates have the potentiality to detect environmental pollutants such as trichloroacetic acid (TCA) and haloderivatives (chloroform, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene) using chromatography systems.

On the other hand, it is known that preconcentration of amines through adsorption/desorption techniques is rather difficult. Adsorption of ammonia on different surfaces has been a subject of investigation since the 1970s, since this material may be attached to the surface through a chemisorption process leaving some residues after the desorption process [15–17]. Therefore, preparing substrates for effective and reversible adsorption/desorption of amines is an important issue. To our knowledge, this article presents

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**Fig. 1** Schematic of the adsorbing assembly



the first results on the application of KIT-6 silica for adsorption/desorption of ammonia ( $\text{NH}_3$ ) and trimethylamine (TMA), which can be employed in integrated gas-chromatographic systems [18].

## Experimental

KIT-6 mesoporous silica was synthesized in acidic conditions using a mixture of Pluronic P123 (BASF) triblock copolymer ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ) and butanol, as reported in literature [10, 19]: 6 g of P123 was dissolved in 220 g of distilled water and 12 g of concentrated HCl (35%). After 6 h stirring at 35 °C, 6 g of butanol was added while stirring for a further 1 h. Then, 12.48 g of tetraethyl orthosilicate (TEOS, 98%, Aldrich) was added and stirred for 24 h at the same temperature. The mixture was hydrothermally treated at 100 °C for 24 h under static conditions and filtered, washed at room temperature with water, dried in air atmosphere, and calcined at 550 °C.

For the gas-adsorption experiments, the KIT-6 powder material has been introduced in a glass tube of 8 mm diameter with silane-treated glass wool (Alltech) inserted on both sides of the material in order to prevent movement of the material inside the tube (Fig. 1). The amount of KIT-6 material introduced was always 0.01 g. The tube was connected to a commercial thermal desorption system (micro-TD, Airsense), which is connected to the computer through a standard 15pin SUB-D connection. Sampling was performed under different conditions described in Table 1.

For comparison, Hayesep P (of Hayes Separations Inc.<sup>1</sup>) and Carboxen 569 (of Supelco<sup>2</sup>) were also purchased and inserted into the glass tubes using the same setup as described for the KIT-6, with the only difference that the amount of KIT-6 used was always 0.1 g.

A portable gas chromatograph (Micro GC 3000, Agilent) with two TCD detectors (for two GC columns that are

**Table 1** Preconcentration settings

Parameter	Set value
Sampling time	60 s
Sampling temperature	30
Desorption temperature	25 °C (for TMA), 100 °C (for $\text{NH}_3$ )
Desorption rate	Maximum (automatically performed by preconcentrating device)

installed and operated in parallel) was configured to be used for detection of the gases concentrated by preconcentrating material. Two standard columns, “Plot A” and “Plot U”, were selected for these investigations as they are said to be the best columns for the detection of amines according to the providers.<sup>3</sup> The process was performed/controlled using Soprano software (ver. 2.7.2) developed by SRA-instruments, which takes the responsibility of the entire process from injection to data recording and analysis.

Ammonia samples (in gaseous form, ca. 300 ppm (v/v)) were prepared from a solution of 25%  $\text{NH}_3$  in water (Fluka), whereas TMA samples (in gaseous form, ca. 1,500 ppm (v/v)) were collected from a solution of 45% TMA in water (Fluka). Samples—kept in 10 mL glass tubes (evacuated before introducing sample gas)—were injected directly to the preconcentrator.

## Results and Discussion

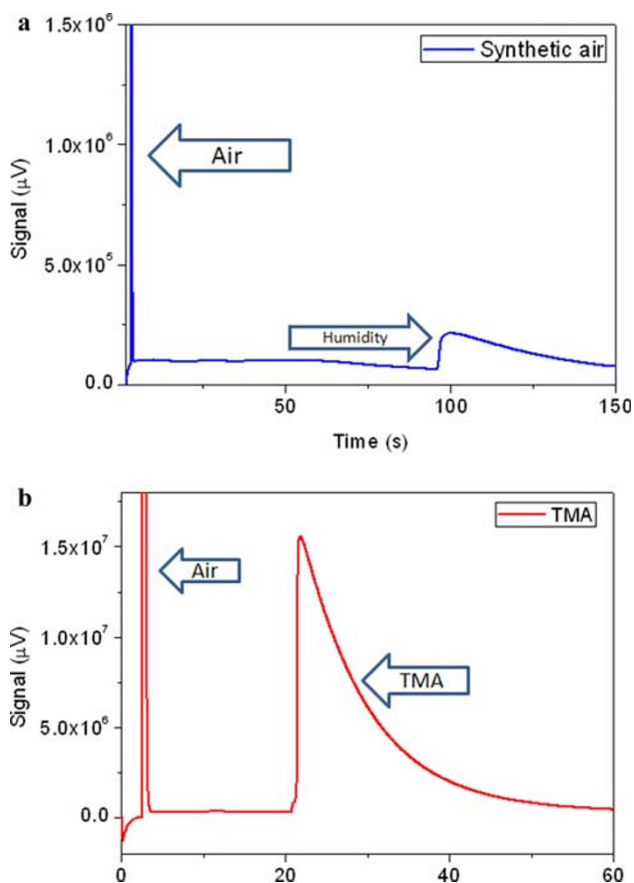
### Device Calibration and Validation of the Setup

Chromatogram of the synthetic air at 100 °C, obtained by the “Plot A” column, is shown in Fig. 2a, where the only

<sup>1</sup> Supelco Hayesep<sup>®</sup> P 60–80 mesh, descriptions: Hayesep is a registered trademark of Hayes Separations Inc. Adequate temperature range is 20–250 °C, particle size 60–80 mesh, compatible with ammonia, alcohols in water.

<sup>2</sup> Supelco Carboxen<sup>™</sup> 569 20–45 mesh descriptions: Carboxen is a trademark of Sigma–Aldrich Biotechnology LP and Sigma–Aldrich Co. Adequate temperature range is –273–225 °C. Particle size 20–45 mesh, compatible with group of permanent gases.

<sup>3</sup> HP-“PLOT U” consists of bonded, divinylbenzene/ethylene glycol dimethacrylate coated onto a fused silica capillary, and is suitable for analyzing hydrocarbons (natural gas, refinery gas, C1–C7, all C1–C3 isomers except propylene and propane);  $\text{CO}_2$ , methane, air/ $\text{CO}$ , water; and polar compounds. In comparison to HP-PLOT Q, HP-“PLOT U” demonstrates greater polarity (RI ethyl acetate 630 vs. 576) and, therefore, different selectivity, better peak shape for some polar compounds like water, and a much lower maximum operating temperature. “PLOT A” is the same as “PLOT U” with one exception: “PLOT A” column is conditioned (by Agilent technologies) to have better sensitivity to amines.



**Fig. 2** Chromatogram of **a** synthetic air, and **b** TMA (presenting peaks of air and TMA) analyzed in “Plot A”. In chromatogram **a** peaks of air and humidity were observed. Passing TMA through preconcentrator (Chromatogram **b**) results in TMA adsorption/desorption with a large peak

detected peaks are air and humidity, with retention times of 3.2 and 103.5 s, respectively. In the case of “Plot U”, a peak corresponding to  $\text{CO}_2$  was also observed with a retention time of 27.1 s (not shown). The existence of the  $\text{CO}_2$  peak can be a result of a small leakage in the sampling line, as our samples are believed to be pure. Moreover, retention times for detected gases are longer than those of “Plot A”, and the signals are extremely weaker since no conditioning has been performed for better response. Henceforth, only the chromatograms of “Plot A” will be discussed hereafter. Meanwhile, it should be noted that due to the fast and automatic injection of the sample gas, the position of the humidity peak may move depending on the time distance between consecutive runs. This can be avoided through controlling parameters such as postanalysis time.

**Preconcentration of TMA**

Under all those conditions indicated in Table 2, the micro GC could not detect the sample gas (45% in Water). The

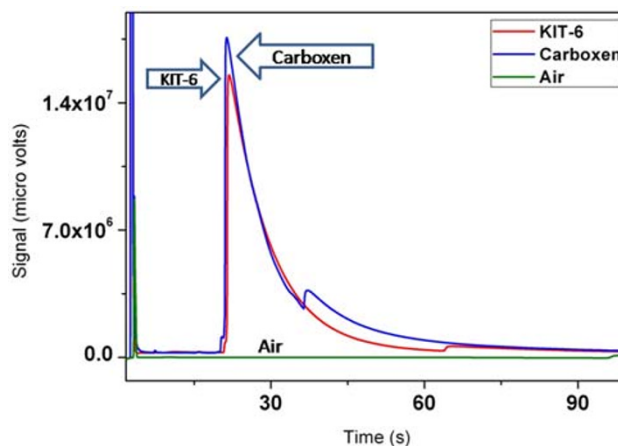
**Table 2** Chromatograph settings

	“Plot A”	“Plot U”
Carrier gas	He	He
Column temperature	100 °C	100 °C
Sampling time	15 s	15 s
Analysis time	Variable (Max. 600 s)	Variable (Max. 600 s)
Column pressure	30 Psi	25 Psi
Sensitivity	High	High

only peaks found were those of air, water and  $\text{CO}_2$  (for “Plot U”). However, using preconcentration, the micro GC was able to detect TMA. Preconcentration parameters are those listed in Table 1 where the sampling time may vary in accordance with the designation of experiments. Desorption temperature was selected to be 250 °C for both Carboxen and KIT-6 silica. The result of using KIT-6 as preconcentrating material at a column temperature of 100 °C is also embedded in Fig. 2b. In this figure, the peak of TMA with retention time of about 22.1 s (for “Plot U”: 60.8 s) can be observed in addition to the peaks of air (the peak of water is not shown because it represents only a small shoulder at this magnification).

Under the same conditions, Carboxen 569 was also found to retain TMA effectively. Results shown in Fig. 3 compare the peaks of TMA for “Plot A” column using KIT-6 and Carboxen.

Comparison of results obtained using KIT-6 with those of Carboxen 569 reveals that both materials show almost the same response in “Plot A” column. This was verified through ratio calculation using the Soprano software. In the case of “Plot U”, however, the results differ to some extent; in fact, KIT-6-concentrated sample reveals a wider



**Fig. 3** Comparison of TMA peaks obtained using KIT-6 and Carboxen 569 detected by “Plot A”. Both KIT-6 and commercial material show the same peak height

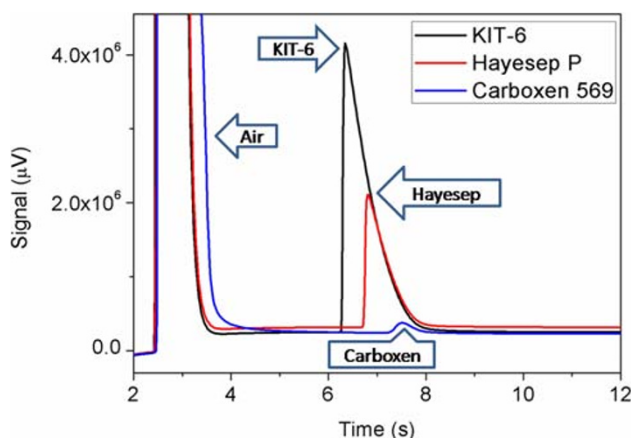
peak when compared to Carboxen 569 but with almost the same height (not shown here).

In the case of amines (especially TMA), it should be considered that high-concentration TMA liquefies at room temperature and this transition makes it difficult to be sensed using existing sensors or gas chromatographs. Moreover and as revealed in chromatograms, the TMA peak may overlap with a wide peak of humidity. This requires effective removal of humidity before injection.

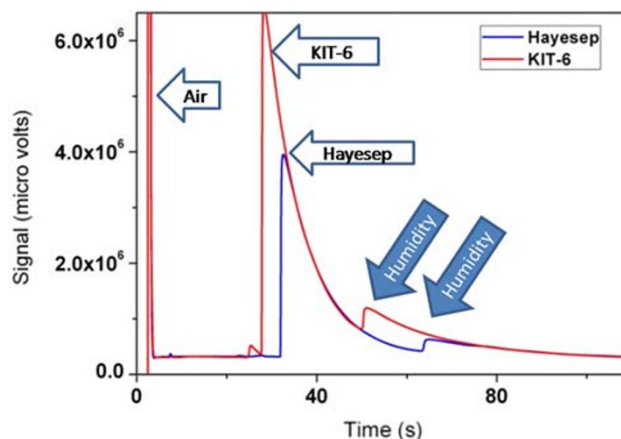
#### Preconcentration of NH<sub>3</sub>

In the case of ammonia, preconcentration parameters were the same as those used for TMA. Here, the chromatograph (“Plot A”) itself was able to detect ammonia, showing a relatively small peak with retention time of 7.5 s at 100 °C (“Plot U”, however, was unable to detect the sample gas without the aid of preconcentrator). Using KIT-6 as preconcentrating material, a large peak was obtained with retention times of about 7.5 (38.2 s for Plot U), as shown in Fig. 4.

Under the same conditions, Hayesep P was found to show lower sensitivity to NH<sub>3</sub>. Figure 5 compares the results for KIT-6 and Hayesep P at 100 °C for 90 s of sampling time. As summarized in Table 3, in comparison to Hayesep P, KIT-6 can concentrate ammonia more effectively where the height ratio and/or area ratio of the peaks is more than 2. One has to take into account that the mass of KIT-6 introduced in the tube is 10 times less than that of Hayesep P and, thus, the effective height ratio would be 2 × 010 times larger. This means that KIT-6 is more likely to work with low concentrations of ammonia. In other words, KIT-6—when compared to Hayesep P—is a better candidate for preconcentration of ammonia, especially when we are dealing with a small amount of gas.



**Fig. 4** Comparison of KIT-6, Hayesep P, and Carboxen 569 for NH<sub>3</sub> preconcentration and “Plot A”. Compared to both Carboxen and Hayesep, KIT-6 shows a much larger signal

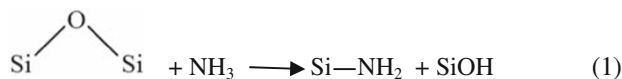


**Fig. 5** Higher response of KIT-6 when compared to refer TMA detection in “relot A”. In addition to TMA, peaks of air, CO<sub>2</sub>, and humidity are also seen. The small peak received just before TMA belongs to the small amount of TMA in the dead volume

Ammonia, moreover, does not show any overlap with the peak of humidity as it was observed in TMA peaks.

#### Adsorption Mechanisms

Chemisorption and physisorption of ammonia on silica surface have been studied already [20–25] where the bonding sites for ammonia have been examined extensively. Griffiths et al. [20] reported that ammonia is chemisorbed on silica surface forming  $\text{NH}_3\text{-O-Si}$  groups. According to Peri [21], reactive strained siloxane sites facilitate the chemisorption of NH<sub>3</sub> resulting in Si-NH<sub>2</sub> groups on silica surface.



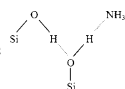
Morrow et al. [22] showed that if this siloxane bridge is unsymmetrical (one Si atom is electron-deficient), then there will be an initial fast reaction followed by a slow reaction involving highly strained sites, which help chemisorption of NH<sub>3</sub> occur at temperatures as low as 20 °C. These strained siloxane rings are normally introduced by applying a force or vacuum treatment of silica at temperatures as high as 800 °C. In the case of mesoporous silica implemented in this work, the calcination temperature has been 550 °C. However, it is very probable that such bridges and rings are formed due to the force applied by surface curvature of nanoparticles. In addition, the existence of water molecules should also be taken into account since they may result in rupture of less-reactive siloxane bridges and form SiOH groups. Moreover,

**Table 3** NH<sub>3</sub> peaks preconcentrated by KIT-6 and Hayesep P detected by Micro GC

		“Plot A”	“Plot U”
KIT-6	Height	39,000	9,000
	Area	24,500	18,500
Hayesep P	Height	18,000	2,000
	Area	9,000	4,000

remaining hydroxyl groups can also react with NH<sub>3</sub> according to Morrow et al. [22].

For physisorption of ammonia on silica, the preferred site has been proved to be the hydroxyl group, which is free to bond to ammonia [23].



### Advantages of KIT-6

One interesting feature of KIT-6, when compared to the commercial materials investigated in this work, can be its functionality for both TMA and ammonia. Carboxen 569 and Hayesep P, as two commercial adsorbent designed for permanent gases and ammonia, respectively, were used for preconcentration of NH<sub>3</sub> and TMA. A comparison of the peaks (Fig. 5) shows that 30 s of TMA preconcentration with “Hayesep P” results in a peak of about half of the one obtained using KIT-6 under the same conditions. For NH<sub>3</sub>, as shown in Fig. 4, results are even more interesting since the preconcentration power of KIT-6 is about 15 times larger than that of Carboxen 569. These findings reveal that although both commercial materials can preconcentrate both TMA and ammonia, none of them is as effective as KIT-6, which shows a high adsorption/desorption when exposed to these gases. This is especially important when dilute gases are targeted by the device.

### Saturation

Adsorption of amines on the surface of adsorbents comes with the saturation problem so that a cleaning/conditioning process is needed in order to detach the molecules from the surface effectively. Depending on the material and the gas to be adsorbed, the cleaning step can require high temperatures. For instance, short-time cleaning of the Carboxen 569 at 250 °C and purging with synthetic air do not result in complete desorption of the attached molecules, and cleaning must be performed in several runs. KIT-6 shows the same problem although it takes more runs to be saturated when compared to Carboxen 569. In the case of KIT-6, 1 h cleaning in air at temperatures of about 500 °C was found to remove the adsorbed material effectively.

### Backpressure

Gas flow through the adsorbent material is an issue taken into account by producers of commercial materials. This necessitates designing such products in the form of large-grain powders. KIT-6, however, is a compact material that may block flowing gas to some extent. Our observations show that if the total assembly is designed accurately, the problem of KIT-6 is minimized as the total amount of the material needed for preconcentration is quite low thanks to its excellent gas-adsorption properties.

### Summary

Mesoporous silica was tested as an adsorbent material for both ammonia and trimethylamine. Compared to commercial materials investigated, KIT-6 was found to be more effective, presenting better concentrating power especially in the case of ammonia, which is difficult to be detected by chromatographic systems at low concentrations. Results show that low concentration amines can also be detected thanks to the high adsorption of the gases on the large surface area of the mesoporous structure. Also, none of the commercial materials studied in this work could show effective sensitivity to both gases, while KIT-6 can adsorb/desorb them efficiently. Two limitations, however, may affect the process: back pressure and surface saturation.

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