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Solid Phase Microextraction (SPME) combined with TGA as a Technique for Guest Analysis in Crystal Engineering

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A method has been developed to extract evolved guest molecules from a TGA exhaust stream using solid phase microextraction fibers SPME). The study was conducted using a known hydrogen bonded framework consisting of $Zn(HPDCA)_2*(H_2O)_2$ and o-tolidene which has been shown to contain guest molecules. These guests co-crystallize inside the 1-D channels formed during the self-assembly of the hydrogen bonded framework. Single guest as well as mixed-guest-containing host frameworks have been analysed using this method. Guest molecules extracted in this fashion were successfully characterized using gas chromatography and mass spectrometry without the necessity of coupled TGA/GCMS.

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Introduction

Here we report the use of a combination of thermogravimetric analysis (TGA) and solid phase microextraction fibers (SPME) to determine the identity of guest species that are freed from molecular framework hosts, as well as the temperature at which the guests evolve. While SPME has been used in other disciplines (such as for food and pesticide analysis), it has so far not been used by crystal engineers for identification of guest species. This method may be useful for those who do not have ready access to tandem TGA/GCMS for guest analysis.

Background

Examples of supramolecular frameworks held together through charge assisted hydrogen bonding have been previously made in our laboratory using Cu(II), Co(II) and Ni(II) complexes that contain peripheral carboxylic acid functional groups.[1] The diamine frameworks are based on previous work in which mono-amine structures formed close-packed layered compounds.[2] Use of diamines affords very robust hydrogen-bonded frameworks having channels that are desirable for the study of host-guest chemistry.[3] Studying frameworks of this nature is compelling as they have the potential to be used for gas storage, separations or potential catalysts.[4,5,6] It has been shown that networks can be formed that contain guest molecules by combining equimolar amounts of Zn(2,4-pyrdinedicarboxylic acid)$_2$ and 3,3'-dimethylbenzidine (o-tolidene) (Fig. 1).[3]

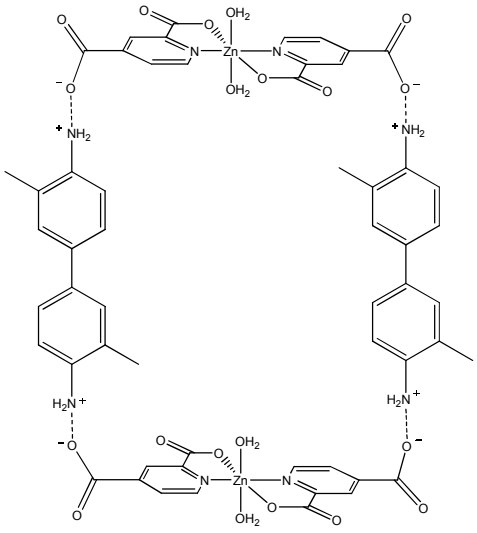

Fig 1. Representation of the zinc complex plus dimethylbenzidene which forms the layers and pillars of the framework.

These frameworks reproducibly form hydrogen-bonded lamellar networks similar to those reported for other charge-assisted hydrogen-bonded frameworks, such as guanidinium sulfonates or trimesic acid plus amines.[7,8] Crystalline

frameworks become host-guest materials when bridging hydrogen bonded components are used as pillars.[5,9] In our case, the zinc(II) dicarboxylate combines with diammonium pillars, which are far enough apart to allow small molecule guests, such as toluene and hexanol, to be present in channels.[3] The walls of the channels are close packed, so that molecular transport can occur only in 1D (significant for e.g. transport across membranes, Fig. 2).

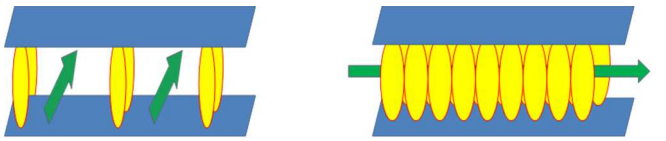

Fig 2. Diagram of 1-directionality of the channels within the hydrogen bonded framework where the guest molecules reside

We have shown the framework to be stable to guest removal and re-uptake, and are interested in guest selectivity when multiple guests are in competition with each other in solution. Therefore, a technique which not only shows the change in weight upon guest loss (TGA) but also the identity of the guest that evolves in certain temperature ranges is ideal.[10] However, for labs not equipped with tandem TGA/MS, this can be a challenge.[11,12]

In the past, several techniques have been used to determine the identity of guest molecules in host-guest crystalline materials. If the crystals are soluble in a suitable solvent, the guests can be identified by e.g. ^{1}H NMR.[13] The guest can also be analyzed from the prepared solution as well as the growth solution by gas chromatography.[14,15] Previously our group has extracted the guest molecule from headspace using a gas tight syringe and it was then analyzed using GCMS.[6] Some have reported that a combination of TGA and DSC can be used to determine the host/guest ratio or the dominant guest from prepared competition reactions.[16] It has been shown that the guest can be removed, and the crystal re-solvated with another guest or combination of guests by dipping the crystal and allow solvent guests to permeate the system.[17] When the samples are not soluble in organic solvents, as in the case of MOFs, a variety of techniques can be used, but in fact the MOFs tend to lose guests without heating. In one case, a MOF was digested in basic methanol (NaOH) and UV-Vis absorption was used to determine the concentration of guest dyes in the resulting solution. In the same study, guest uptake into the MOF suspended in a mother liquor solution reduced the concentration of bromoarenes in the mother liquor. The reduced concentration was determined by gas chromatography.[18]

Our previous research on the $Zn(HPDCA)_2*(H_2O)_2$/o-tolidine framework (Compound **1**) focused on the synthesis of the framework itself and characterization through methods such as TGA, single crystal X-ray diffraction and powder X-ray diffraction. The guest was identified by heating the host/guest solid in a closed container fitted with a septum, and by sampling the headspace with a syringe.[19,20,21] Injecting the gas into a GC or GCMS allowed the characterization of the guest separate from the TGA analysis.

An analyte extraction technique used by researchers in other disciplines, for example water treatment facilities, forensic laboratories, and artificial flavoring developers, is SPME. Using an approach outlined in the literature, we hypothesized that SPME could be used for guest detection by sampling off-gas from the TGA furnace exhaust port.[22,23]

SPME was invented in 1989 by Janusz Pawliszyn.[24] Pawliszyn noted that a modified silica fiber using thermal desorption can eliminate the problems associated with solid phase extraction (SPE) while still retaining the advantages of SPE, which had proved to save lab and analysis time and eliminated the need for the use of solvents in the extraction process.[25] Prior to the introduction of SPME, SPE was the alternative to liquid-liquid extraction, because in SPE analytes are absorbed from the sample onto a modified solid support. However, in 1990 SPE required that expensive and time consuming modifications be made to existing analytical instrumentation. Modifications would have to be made to the GC injector, or a desorption module would be needed.[26] SPE had other complications including large variations in the quality of SPE cartridges made by different manufacturers. SPE cartridges were made of plastic, which allowed it to absorb other analytes, giving greater opportunity for interference. SPME, on the other hand, can be seen as an extension of laser desorption from fused silica fibers, since they are made from fused silica fibers which have been coated with a specific thickness of polymer in order to extract analytes from headspace or aqueous solution.[27] The insertion needle is made of metal, so unlike the SPE cartridge, the entire coated section of SPME fiber is exposed to the high temperatures of the injection port. Proper thermal desorption technique prevents carry over between samples.

SPME analysis has two fundamental steps to the technique. In the first step, the analytes are partitioned between both the sample matrix and the extraction phase. This is followed by desorption of those analytes into the analytical instrument, typically an injection port. It is currently and commonly used manually with GC, GCMS, HPLC and LCMS instruments with no additional changes made to the instrument other than a 23 or 24 gauge injection liner (GC applications, dependent on the needle size). If available, SPME can be used with a headspace autosampler.

Since SPME is mostly used as a headspace method, it is only able to analyze the molecules which are in equilibrium between the analyte in the sample, in the headspace above the sample and in the polymer coating on the fused silica fiber. While there is an equilibrium step, it need not be exhaustive. The rate determining step of SPME is either diffusion of the analyte from SPME polymer film surface into its inner layers or evaporation of the analyte from the condensed phase to the headspace of a sealed container.[28] Depending on the nature of the polymeric coating of the fiber, SPME can be used to detect hydrophobic or hydrophilic compounds and, in some cases, a modest mixture of the two. A recent review of SPME outlines how the technique has evolved in use and applications.[24]

For liquid polymeric coatings, the level of analyte absorbed by the coating is directly related to the concentration of the analyte in the sample.[29]

$$n = \frac{K_{fs} V_f C_0 V_s}{K_{fs} V_f + V_s}$$

where n = mass of the analyte
C_0 = Initial concentration of analyte in the sample
K_{fs} = partition coeffiecient for analyte between coating and sample matrix
V_f = volume of coating
V_s = volume of sample

More extensive work has been done however to explain the theory and practice of SPME.[28,30,31] It has been demonstrated that an SPME fiber could be placed directly into the exhaust port of a TGA.[22,23] The exhaust can contain volatile and semi-volatile molecules which have been released from the sample within the TGA furnace. These molecules are then absorbed by the SPME fiber, which is then placed into the injection port of a GCMS and desorbed for analysis. Using SPME in this fashion can have significant cost savings compared to the expense of coupling MS to a TGA.

As the guest molecules used in our host/guest framework have different characteristics (aromatic compounds, long chain alkyl alcohols, etc.) it is important to use SPME fibers that absorb a wide range of molecules. In fact, SPME has a wide range of detection applications. SPME has been used to detect aroma compounds, halogenated volatiles in food, C2-C10 fatty acids in water, sulfur compounds, essential oils in hops, xylenes in palm oil, benzene and toluene in vegetable oil, stereoisomers in pulegone enantiomers, flavors in vodka, methylcyclopentadienyl manganese tricarbonyl in beverages, pesticides in wine, trichloroanisole in wine, organophosporus pesticides, selenium compounds, PCBs, methylmercury in fish, and insecticides and pheromones to name a few.[32,33-46]

The particular coatings used in making the SPME fibers define which guests can be absorbed. The fibers have been modified through the use of metal fibers comprised of either platinum, stainless steel, or copper metal rather than fused silica due to the increased mechanical strength.[47] New coatings have been developed by building metal organic framework (MOF) coatings onto the metal wires. These new MOF coatings can be highly porous and thus increase sensitivity as well as selectivity compared to commercial coatings. These modified coatings have been used to detect benzene derivatives, organochlorine pesticides and other analytes of interest.[48,49,50,51]

In crystal engineering, especially with host/guest systems, obtaining a good quality crystal can be a painstaking and lengthy process. Once a crystal has grown, decisions must be made on how to analyze it. The addition of SPME to the crystal engineer's tool kit allows for a non-destructive way to analyze small amounts of guest molecules as they evolve from a stable host framework. This allows the crystal to be further analyzed for any changes in internal arrangement and structure once the guest has been removed, rather than requiring dismantling of the framework in order to analyze the guests. SPME used in conjunction with TGA allows the identification of guests that evolve over certain temperature ranges. Both are of interest when considering host-guest frameworks that are stable to hundreds of degrees Celsius.

Experimental

SPME fibers were purchased from Sigma Aldrich Chemical Company (Supelco). The 100 µm polydimethyl siloxane (PDMS) coated SPME fiber (Supelco, Cat# 57300-U), 7µm PDMS coated SPME fiber (Supelco, Cat#57302) and the 85µm polyacrylate (PA) coated SPME fiber (Supelco, Cat# 57305) were used. $ZnCl_2$ (≥97%) was purchased Fisher Scientific. Toluene, m-xylene, and 1,3-diethylbenzene were reagent grade and purchased from Sigma Aldrich. O-Tolidine (≥97%) was purchased from Sigma Aldrich Chemical Company. 2,4-pyridine-dicarboxylic acid (98%) was purchased from AK Scientific. Methanol was reagent grade from Sigma Aldrich Chemical Company. Dimethylformamide (anhydrous, 99.8%) was purchased from Fisher Scientific. TGA plots were collected using a Thermal Advantage TGA Q50 (TA Instruments) and TA Universal Analysis software was used to generate plots and analyze the output data. PXRD patterns were collected on a Rigaku Ultima IV X-ray diffractomer containing a CuKα source (λ =1.54051Å) and viewed with MDI Jade 9 software. An HP gas chromatograph 5890 and HP gas chromatography mass spectrometer 5988A were used to collect all chromatographic data. For GC/GCMS method development, the isolated crystals were placed inside of a 20mL GC headspace vial (Xpertek, PJ. Cobert, Cat#954040) with a high temperature rated septa within the cap (Xpertek, PJ. Cobert, Cat#952237). All chemical reactions were carried out under ambient conditions.

Synthesis of 1·guest

The Zn (II) metal complex was synthesized by combining $ZnCl_2$ (0.0146 moles, 2g) in 40mL of D.I. water and 2,4-pyridinedicarboxylic acid (0.0293 moles, 4.9g) in 400mL of a 1:1 ratio of D.I. water and methanol. The resulting suspension was filtered through a Buchner filter funnel and paper filter. The white slurry was washed with D.I. water until the mother liquor tested pH neutral. The product was allowed to dry on the funnel and then air dried overnight. The resulting product was $Zn(HPDCA)_2*(H_2O)_2$. The $Zn(HPDCA)_2*(H_2O)_2$ (0.06 moles, 0.025g), and 3,3'-dimethylbenzidine (0.06mole, 0.012g) were separately dissolved in 2mL each of methanol. The two methanol solutions were then mixed together and stirred and a 1:1 mixture of water (1mL) and DMF (1mL) was then added. The guest molecule, in this case toluene, was added in excess. In most instances, the guest molecule(s) was added to a 15mL glass vial and the methanol solution of components of the

framework were added on top. Crystals of the neutral framework [**1**,(3,3'-dimethylbenzylidinium)($Zn(PDCA)_2$*($H_2O)_2$)] then grew from the resulting solution. The **1**·toluene crystals are brownish-red haystacks. Once crystal growth had ceased, the resultant crystals were washed in the glass vial with methanol (1x), then acetone (2x) and then dried under vacuum to remove any remaining surface residues which might bias the results. Samples were then analyzed using powder x-ray diffraction scanning from 2° to 40° in 2θ.[2]

Chromatographic Methods

In order to determine the GC/GCMS parameters, **1**·toluene (0.010g) crystals were heated to 200°C, which evolved all of the guest molecules being tested (temperature from TGA data). 200°C was also used as the upper limit because **1** decomposes at around 215°C. The 100 µm PDMS-coated SPME fiber was inserted and was allowed to absorb the guest molecules in the headspace for a period of two minutes. The SPME fiber was then placed into the injection port of a GCMS and the mass data was collected for each of the eluted species. No traces of acetone or methanol were seen in the MS data, though sometimes DMF would elute around 2.00 minutes in the chromatogram. DMF seems to co-crystallize in small amounts. The standalone GC was only used for initial aspects of **1**·toluene analysis. The GC oven temperature was initially 30°C for 3.0 minutes, then ramped to 150°C at a rate of 20°C/min and held for 1.0 minute. The injection port temperature was 250°C. The total analysis time was 10.50 minutes. The retention times were slightly longer since the GC used an 15m SPB-1 column, 10µm film thickness, 0.2mm ID, bonded, 100% dimethyl siloxane stationary phase. GCMS guest determinations were performed using an 11m HP-1 Ultra column, with a 0.2mm I.D x 0.33µm film.

SPME Coupled TGA

For SPME/TGA analysis, the coated SPME fibers were used to identify toluene, m-xylene and 1,3-diethylbenzene guests. Using the SPME fibers, we were able to isolate each of the guests from the TGA exhaust port while **1**·guest was heated. The TGA provided insight into the temperatures at which the guest molecules were evolving out of **1** (Fig. 3). Using a similar method to that of Biswas et al, an SPME fiber was used in conjunction with the TGA in order to discern the guest molecule being evolved from the framework.[19,20] The TGA was programmed to jump to 40°C and perform an isotherm for three minutes. Although, no evidence of residual toluene had been found from room temperature head-space injections, this step was purposefully done to ensure that no residual solvent was left on the surface of the crystal. Once the isotherm was complete, the SPME fiber was placed in front of the TGA exhaust port. The plunger on the fiber holder was depressed so that the SPME fiber fully extended into the exhaust port, but did not touch the inside of the port walls. A heating ramp began and the temperature was increased at a rate of 10°C/min. The fiber was allowed to absorb the off-gas from the TGA until 145°C, past the peak seen in the TGA graph expected to be toluene. The fiber was quickly transferred to the GC and inserted into the injection port where the SPME fiber was allowed to desorb and the guest molecule eluted through the SPB-1 column. **1** continued to ramp to a final temperature of 550°C.

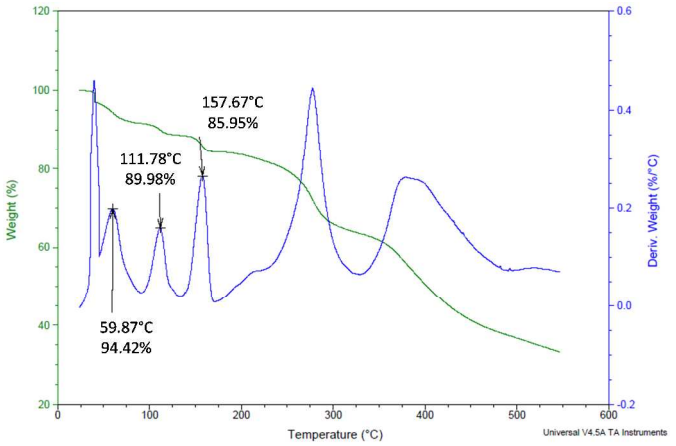

Fig 3. TGA plot of $Zn(HPDCA)_2$*($H_2O)_2$ plus o-tolidine framework containing toluene guest from 40°C to 550°C at a heating rate of 10°C/min.

1·m-xylene/1,3-diethylbenzene were tested in the same manner as **1**·toluene using the TGA/SPME method. The crystals used here were part of a series of competition reactions in which the guest molecules were added at different mole fractions over a series of 11 experiments. For this determination, the framework was assembled using the same previously mentioned synthetic pathway, however; mole fractions of m-xylene (X_A = 0.4) and 1,3-diethylbenzene (X_B = 0.6) were placed in the growth solution rather than a single potential guest molecule. As the crystal grows, the preferred guest will be the predominant species in the host cavities. Once the brownish/red haystack shaped crystal was isolated from the growth solution, the crystals were washed, dried and then placed in the TGA for analysis. In same manner as the toluene experiment, the crystal was held isothermally for a period of three minutes to ensure that no residual solvent was left of the surface of the crystal. Once the isothermal period was complete, an SPME fiber with 85µm PA coating was placed in front of the exhaust port and the fiber exposed. A PA SPME fiber was chosen since its response factor is an order of magnitude larger than that of 100µm PDMS for xylenes. The same TGA program was run for all three samples. The fiber was quickly transported to and inserted into the GCMS rather than the stand alone GC in order to differentiate between the guests.

Results and Discussion

Analysis of **1**·toluene: The crystals were analyzed using SPME fibers to absorb guest molecules from the TGA, with both GC alone and GCMS. In the GC analysis, the resultant chromatogram showed a sharp peak at 4m 27s (Peak Area = 555187). To ensure that the toluene was being detected, a stock solution of toluene in methanol was run to determine the retention time under the current GC conditions. Toluene eluted with a sharp peak at 4m 25s (Peak Area = 4518843). This confirmed that toluene was not only evolving from the framework, but being captured by the SPME fiber from the exhaust gas of the TGA.

In the GCMS analysis, the fiber was inserted into the GCMS and allowed to desorb. A peak was seen at 2m 61s (Peak Area = 1313133) and the corresponding fragmentation pattern was consistent with toluene (NIST database). The retention time changed due to the shorter column length. To our knowledge this would be the first example of an SPME fiber extracting guest molecules from a hydrogen-bonded framework using TGA off-gas.

The TGA plot shows a very gradual onset for the weight change, so a different technique was used to determine a more definitive temperature range for guest evolution. In this case the sample was placed in a vial equipped with a septum, and heated to a precise temperature using a heating block. The vial was placed in a well of a heating block set to 40°C. The sample was allowed to heat for 10 minutes. During the last two minutes, the fiber was exposed to the headspace and then inserted into the GCMS and allowed to desorb at 250°C. There was no evidence found in the chromatogram, nor the mass spectrum data of toluene evolving from the host. The temperature of the block was increased by 10°C until 120°C was reached (Table1).

Table 1. Measured peak areas for 1• toluene detection during a step-wise temperature gradient

Heating Block Temperature (°C)	Peak Area (Abundance)	Post Purging Peak Area (Abundance)
40	ND	
50	ND	
60	383405	
70	960345	
80	1950212	
90	602539	
100	779687	
110	326116	126836
120	1712765	ND

It can be seen that the onset temperature where toluene first becomes detectable is around 60°C. For each temperature set point tested a new clean new vial was used and a fresh crystal sample was tested. The average crystal weight was 20mg for each of the samples. The only guest peak that appeared throughout this temperature range was identified as toluene, whose retention time was based on standard injections. The peak area fluctuated as several 7µm PDMS fibers were used in this series. The 7µm fibers tended to be more fragile than the other fibers used in previous experiments. The overall concentration of the guest should be increasing with temperature rise as more guest molecules are evolved. Other experiments have shown dimethylformamide present in the chromatography. It is not surprising since DMF is part of the crystal growth solution and some may become co-crystallized as well. The peak area for DMF was calculated to be 3.28% of the peak area value for toluene when DMF was present.

The temperature of the multi-well heating block was again set to 120°C and sampled using the same procedure as before. The SPME syringe was immediately inserted into the GCMS and allowed to desorb while the sample vial was cooled to room temperature using a stream of compressed air. Once the sample was cool, the vial was purged with nitrogen for 1 minute. The cap was replaced and the vial positioned back on the heating block at 120°C. The SPME fiber was then exposed to the headspace for 10 minutes. After 10 minutes, the fiber was removed and inserted into the GCMS. No guest was detected at 120°C after purging. The temperature was then reduced to 110°C and the heating, cooling, purging and injection cycle was repeated. The toluene guest was detected after the purge when the temperature of the block was 110°C (Table 1). The presence of the guest in the headspace post purging tells that at lower temperatures, not all of the guest is released. There is potential for partial release of the guest within a specific temperature range. The crystal could then be held for period of time while part of the initial guest concentration is stored and released at a later date.

While the purge cycle sheds some light on the release of the guest from the framework, there is still a tail from the TGA plot around 130°C. The TGA/SPME method had to be revisited to be sure of the final temperature of guest release. An 85µm polyacrylate fiber was used for this test because it has lower detection limits for toluene than PDMS. The PA fiber has higher response factor than 7µm PDMS or even 100µm PDMS. Peaks will have a higher area count in the GC chromatograph. As can be seen in the Table 2, the peak area does increase during exposure.

Does the amount of guest loss based on TGA weight change correspond to the peak area shown in the GCMS study? To answer this question, the weight difference from the TGA for the temperature range of 100-130°C was plotted against the peak area. Here we see a linear response with an R^2 value of 0.9957 (Figure 4). Considering how the guest was sampled, the linearity is impressive, demonstrating that the SPME technique is not only qualitative, but also can determine relative quantities

Table 2. Measured data for **1**•toluene from the TGA and GCMS using 85µm PA SPME fiber

Crystal Wt (mg)	Initial Temp of Fiber Exposure (°C)	Peak Area (Abundance)	Residence Time (Mins)	TGA, Wt Diff (%) 40-145°C	TGA, Wt Diff (%) Extraction Temp to 145°C
22.565	40	1313133	10.5	12.25	12.25
24.970	100	1004544	4.5	11.55	5.626
24.366	110	679366	3.5	11.83	4.030
21.337	120	389800	2.5	11.97	2.687
23.017	130	151190	1.5	11.65	1.494
22.577	140	173877	5	14.98	3.141

of guests. Having the ability to have the off-gas sampled from the TGA and correlate this with a change in concentration can have significant impact on future studies. It would be interesting to detect the overall concentration of guest for each TGA event. While sampling, there was no disturbance of the TGA itself, thus yielding usable TGA data as well as GCMS data. An attempt was made to use a gas tight headspace syringe in order to sample the off-gas from the TGA and compare the results to the SPME fiber. Not only was there no evidence of the guest in the chromatogram, but a large noise signal could be seen in the TGA when the gas sample was pulled. Using the headspace syringe contaminated the TGA data whereas the SPME fiber left no trace that any sampling had been performed.

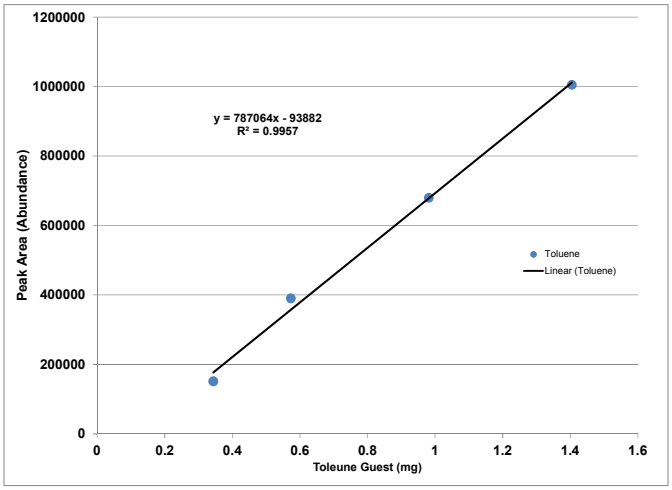

Fig. 4. Plot of toluene guest TGA weight versus peak area

Analysis of **1**· m-xylene/1,3-diethylbenzene: Competition studies between two guest molecules can reveal what types of guest molecules will be dominant inside of the framework. Using crystals from an ongoing competition study between m-xylene and 1,3-diethylbenzene, it was determined whether the SPME fiber could absorb multiple guest molecules from the TGA off-gas. The same extraction conditions were set on the TGA as the toluene system using the 85µm PA coated fiber. The GCMS parameters were used to determine which of the two possible guests were absorbed by the fiber. Two distinct peaks appeared in the mass spec. The ratio of the areas of the peaks for the two guest molecules show 1,3-diethylbenzene as the dominant guest molecule. More work would have to be done in order to display direct correlation between the TGA/SPME results and head-space analysis results. If the correlation held true, it would create a simple and cost effective method for analyzing multiple guest molecules.

Conclusions

We have demonstrated that SPME fibers can be a useful tool for analyzing, both qualitatively and quantitatively, guest molecules evolved from crystalline frameworks, either by headspace analysis or from TGA off-gas. The non-destructive nature of SPME headspace analysis allows for the framework to remain intact so that the crystal may be used for other studies. This is a great advantage over methods which dissolve the entire crystal. SPME requires little sample volume for analysis, which is also useful in host/guest crystal systems that are hard to obtain. Using SPME in tandem with the TGA offers an effective option for analyzing guest molecules in conjunction with separate events observed by the TGA, but without the high coupling costs that tandem TGA/GCMS brings. SPME sampling does not contaminate the TGA plot data by creating noise which would make it difficult for accurate weight difference calculations. This method can also help identify guest molecules that might otherwise appear too disordered in XRD. We have shown that not only will SPME assist in detection of a single guest but also multiple guests from TGA off-gas. It may be possible in the future to isolate separate TGA events to determine the guest from each event.

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Notes and references

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Electronic Supplementary Information (ESI) available: The supplemental information contains a general description of the experimental methods, powder XRD patterns, the original chromatography, peak area tables and mass spectrometer fragmentation pattern data. See DOI: 10.1039/b000000x/

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