Molecularly Imprinted Polymers For Detection Of Explosives In Gas Phase Approach For The Detection of TNT In Cargo Containers

Moritz Heil

Fraunhofer ICT, Joseph-von-Fraunhofer-Str. 7, 76327 Pfinztal, Germany

Abstract

In this work, adsorption properties of TNT molecularly imprinted polymers (MIPs) with different functional monomers are characterized using Langmuir and Freundlich isotherm. Affinity constants and pre-exponential factors are calculated for the two models. Langmuir model is applicable in gas phase adsorption on MIPs which is different from adsorption in liquid phase. The MIPs investigated here use TNT as template and acryl amide (AA), methacrylic acid (MAA) and methacrylamide (MAAM) as functional monomers.

Introduction

Molecularly imprinted polymers are widely used in a variety of different matrices to extract target substances [1]. Most of these applications use MIPs for adsorption in liquid phase [2] [3] [4] [5], only very few report the use MIPs in gas phase environment [6] [7]. To characterize MIPs regarding their adsorption properties in the gas phase, a combination of thermo desorption, gas chromatography and time of flight mass spectrometer is used.

For detection of explosives in cargo containers, large volume flows are needed which leads to large MIP particle diameters. Therefore the MIPs are designed as core-shell-shell-particles:an inert glass core, providing the necessary size (approx.. 1 mm), a first shell that allows fast heating of the MIP particle by microwave absorption and a second shell consisting of MIP providing the actual adsorption capability. Since the core and the first shell are not contributing to the adsorption process, characterization of the MIP shell describes the adsorption properties completely. In this study, a core of SiO_2 covered by MIP is used for characterization.

Experimental

Synthesis

The MIP consists of an EGDMA backbone that uses acryl amide (AA), methacrylic acid (MAA) or methacrylic acid amide (MAAM) as functional monomer - purchased from Fluka, Merck and Röhm Pharma respectively - with 2,4,6-trinitro-toluene from Dyno Nobel Norway as template. Polymerization is started using Azo-bis-isobutyronitrile (AIBN) from Fluka. SiO_2 (Kieselgel 60 from Fluka) serves as an inert core material. Chloroform (Roth) is used as solvent and polyethylene glycol (PEG 4000 from Merck) as surfactant. To increase adhesion of MIP on the SiO_2 core, a coating of 5 mass-% of Synthalat A 1633 (Synthopol) and Desmodur N75 MPA (Bayer) has been applied on the core particle. TNT is recrystallized before use; all other substances are used as-received. Synthesis is carried out in a 6 L vessel under argon. 142.8 g PEG is dissolved in 2.8 L water in the vessel. 6.74 mmol template (1.53 g TNT), 169 mmol EGDMA (33.46 g), 26.9 mmol of the functional monomer (1.91 g AA, 2.29 g MAA or 2.31 g MAAM) and 1.5 mmol (1.89 g) AIBN are solved in 85.7 mL chloroform. 50 g of the coated SiO_2 were added and stirred at 200 rpm. Organic mixture (chloroform with template, EGDMA, monomers and AIBN) is added dropwise. After addition, temperature is brought to 62 °C for 24 h under argon flow. MIP particles are filtered and washed at least three times with hot water, chloroform and acetone respectively. TNT is extracted by supercritical CO_2 (Dionex SFE 703, 15 MPa, 50 C, 3 h, 6 kgh^{-1}).

Analytical setup

For characterization of TNT adsorption properties, a nitrogen gas flow is spiked with TNT. This is achieved by placing a heated segment, that contains TNT coated glass spheres, in the gas flow. The MIP particles are placed in the nitrogen flow (in a thermal desorption unit, "Tandemdesorber") where TNT can be adsorbed by the MIP. After adsorption, the particles are heated and adsorbed TNT desorbs into a gas flow that is redirected through a gas chromatograph (GC) for splitting up different components and a time of flight mass spectrometer (MS-TOF) for identification and quantification. All gas leading parts are made of stainless steel and coated with SilcoNert® to minimize TNT adsorption on the walls. Figure 1 shows the experimental apparatus. Calibration is done by feeding pure TNT into the system via a sideway to allow establishing a solid base for identification and quantification. An exemplary mass spectrum of TNT is given in Figure 2. The mass fragment 210 is used for quantification because it is the predominant mass fragment of TNT at 70 eV ionization.
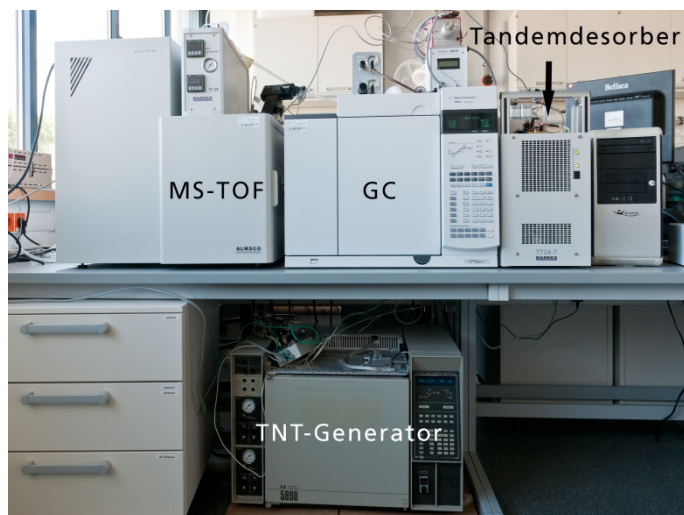
Figure 1: Experimental setup for characterization of TNT adsorption properties. The TNT spiked nitrogen comes from TNT-Generator and is adsorbed at the Tandemdesorber. GC and MS-TOF are used for analysis.

Calibration has shown adsorption of TNT on the walls of gas leading parts. The applied coating is not fully preventing adsorption of TNT so this has to be taken into account for quantitative analysis. To compensate, following model is applied:

The TNT generator is assumed to create a constant concentration C_0 of TNT in the nitrogen stream. Adsorption, that is assumed to be of Langmuir type, takes place on the walls of the system.
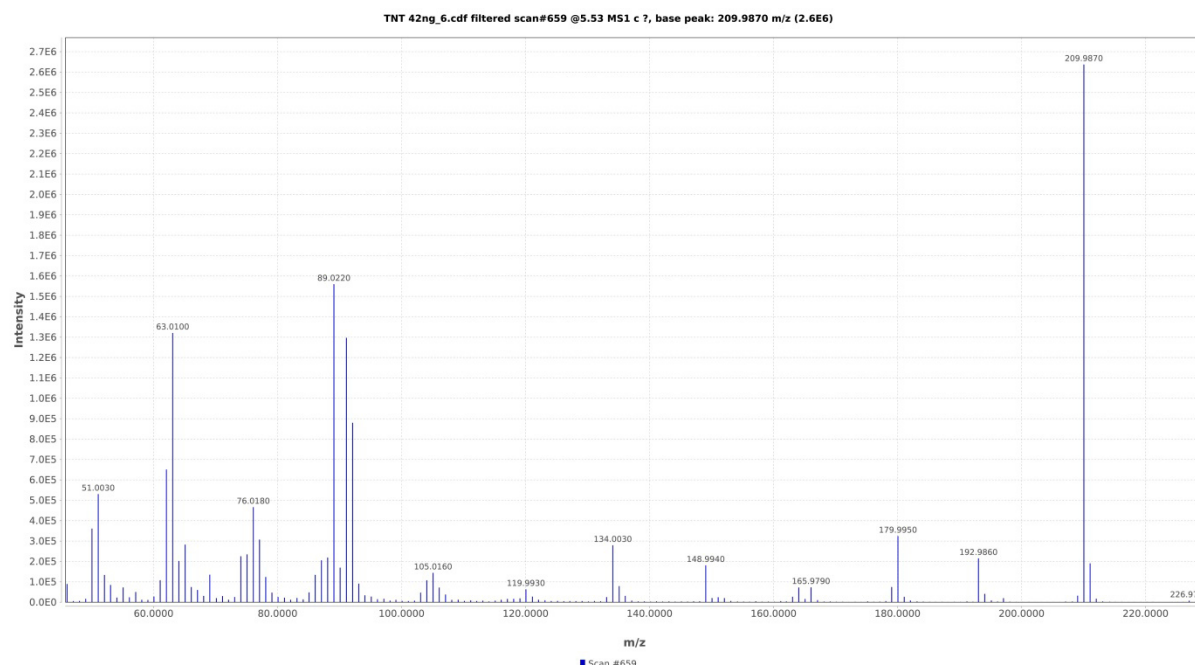

Figure 2: Mass spectrum of TNT. Ionization is 70 eV ionization, main fragment is 210 m/z. The spectrum is very consistent with those of the NIST mass spectra database.

Adsorption kinetic is assumed to be first order with a reaction rate k and the number n of the measurement, so the number of free adsorption sites is

$$N(n) = N_{max} \cdot \exp(-k \cdot n)$$

Equation 1: Model for TNT adsorption sites on walls

Since the walls of the system are kept at a constant temperature adsorption and desorption are in equilibrium. The overall amount of TNT adsorbed at the walls grows with subsequent measurements. The upper limit is the total amount of TNT that can be adsorbed by the walls. To determine the amount of TNT that is available for adsorption in the MIPs it is necessary to calculate the amount of TNT that is adsorbed in this specific measurement. This is calculated [2] by using Equation 1 and the affinity constant K:

$$B(n) = \frac{N(n) \cdot K \cdot C_0}{1 + K \cdot C_0} = \frac{N_{max} \cdot \exp(-k \cdot n) \cdot K \cdot C_0}{1 + K \cdot C_0}$$

Equation 2: Basic Langmuir model for TNT adsorption (in this case: on walls).

Using Equation 2, the free TNT that is available for adsorption on the MIP is given as:

$$C(n) = C_0 - B(n) = \begin{cases} 0 & ; B(n) \geq C_0 \\ C_0 \left(1 - \dfrac{N_{max} \cdot \exp(-k \cdot n) \cdot K \cdot C_0}{1 + K \cdot C_0} \right) & ; B(n) < C_0 \end{cases}$$

Equation 3: Calculated amount of TNT available for adsorption

Since the TNT concentration should be identical for different measurements series, the respective adsorption parameters for TNT adsorption on the walls have been calculated as $N_{max} = 4.79 \cdot 10^7 \, a.u., K = 3.1 \cdot 10^{44} \, a.u.^{-1}, k = 0.0062$. The resulting amount of TNT is shown Figure 3.

The measurement-dependent concentration of TNT can be used to fit the TNT adsorption curves on MIPs using the Langmuir model of Equation 2 of the Freundlich isotherm:

$$B(n) = a \cdot [C(n)]^m$$

Equation 4: Basic Freundlich isotherm. a is the pre-exponential factor and m is the heterogeneity index.

Normally the use of Langmuir model is not allowed for the description of MIP adsorption due to the presence of several types of binding site with different properties [2]. However, in the gas phase adsorption, non-imprinted control polymers showed no adsorption of TNT. This means, that there is no unspecific adsorption, hence only one type of binding site. The heterogeneity index of Equation 4 is therefore expected to be very close to 1.
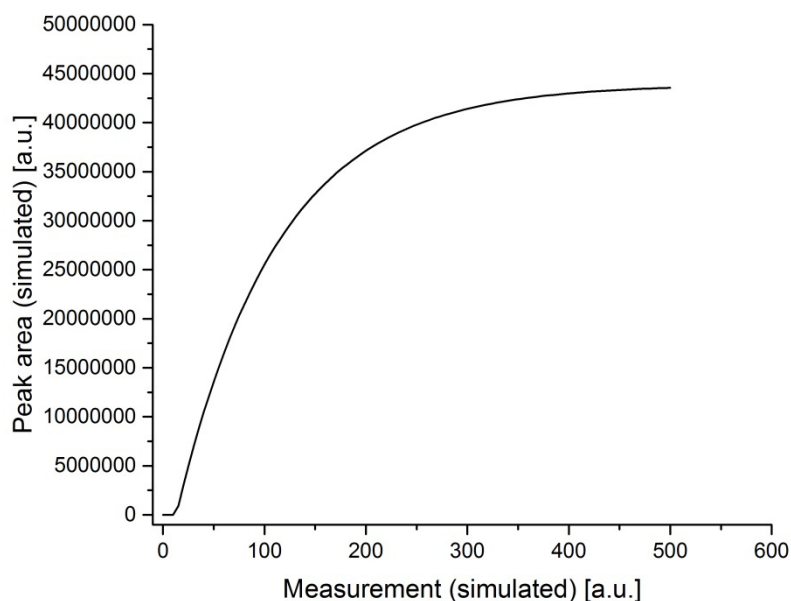
Figure 3: Simulated amount if TNT available for adsorption. The amount is measured in peak area units of the mass spectrum. The curve is simulated using the parameters mentioned in the text.

Results and Discussion

Figure 4 shows an exemplary curve of TNT adsorption. Each measurement is performed as a double. There is a difference between the measurements which might come from different conditions of flow in each sample. This would lead to different contact times and adsorption time. The mean of two curves is calculated and used for further analysis.

The three investigated functional monomers are acrylamide (AA), methacrylic acid (MAA) and methacrylamide (MAAM). Only AA and MAA are investigated in depth, because MAAM does not seem to adsorb TNT at all and is therefore disregarded. The adsorption characteristics of the two remaining monomers are shown in Table 1 for the two models.
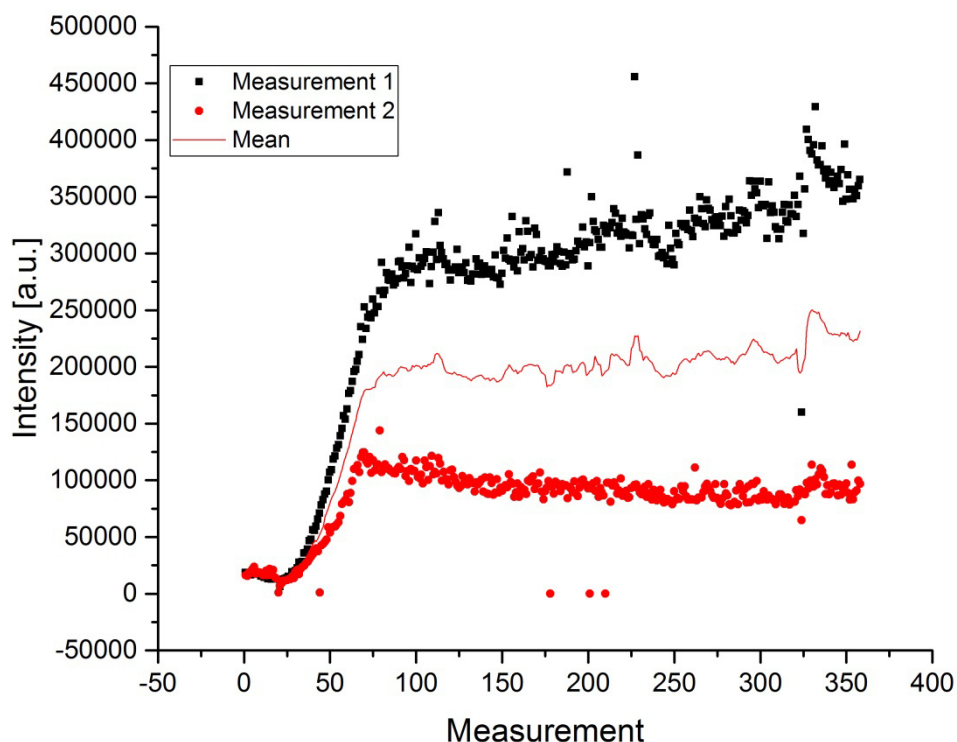
Figure 4: TNT adsorption on an imprinted polymer using AA as functional monomer. The mean of two measurements is calculated and used for further analysis.

Table 1: Kinetic parameters describing adsorption of TNT using Langmuir and Freundlich isotherm for two different monomers. For comparison, results obtained with Tenax as standard adsorption material are included.

Monomer	Langmuir	
	Adsorption sites [ng / 100 mg MIP]	**Affinity constant [ml / a.u.]**
MAA	$7.8 \cdot 10^7 \pm 1.9 \cdot 10^{10}$	$2.8 \cdot 10^{-11} \pm 6.8 \cdot 10^{-9}$
AA	$2.4 \cdot 10^5 \pm 3.0 \cdot 10^3$	$2.2 \cdot 10^{-7} \pm 2.8 \cdot 10^{-8}$
Tenax	$4.9 \cdot 10^7 \pm 2.8 \cdot 10^7$	$4.2 \cdot 10^{-9} \pm 2.5 \cdot 10^{-9}$
Monomer	**Freundlich**	
	Pre-exponential factor	**Heterogeneity index**
MAA	$1.3 \cdot 10^{-3} \pm 1.1 \cdot 10^{-3}$	1.00 ± 0.05
AA	$4.8 \cdot 10^{-3} \pm 1.4 \cdot 10^{-2}$	1.0 ± 0.16
Tenax	$1.1 \cdot 10^{-1} \pm 4.7 \cdot 10^{-2}$	1.0 ± 0.02

Conclusion

Selective adsorption of TNT from the gas phase using MIPs has been shown. Non-imprinted polymers did not adsorb TNT so the adsorption is entirely specific. Therefore only specific adsorption sites seem to exist. The unspecific adsorption sites that are reported from liquid phase application cannot be confirmed in this work. It is unclear if this is a property of gas phase application of MIPs in general or of this specific MIP system. Langmuir and Freundlich isotherm were used to describe adsorption behavior. Both models lead to similar results while Freundlich isotherm confirms the existence of homogeneous adsorption sites.

References

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