GASPHASE DETECTION OF TNT WITH LAYERED IMPRINTED POLYMERS

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1 Introduction

Recent terrorist attacks like the bombing in New York at 11.9.2001, suicide bombings in the middle east or e.g. in London Underground transportation systems in July 2005 show that the today used detection techniques for explosives (Imaging by X-ray, neutron activation techniques, IMS, TeraHz-, MMwave, NQR,) are inadequate and have to be improved as well as new counter-action / detection concepts have to be developed. For the detection of explosives e.g. at airports, for humanitarian demining and in concerns with national security there are needs for inexpensive, rapid, high sensitive and selective sensors.

In this concern mass-sensitive devices coated with substance specific molecularly imprinted polymers (MIP) seem to provide promising low-cost detection devices for use in self-reporting sensor networks for the surveillance of public areas or as on-line / in-line sensors in different vehicle transportation systems (cars, trucks, containers etc.) in order to directly detect and warn for possible terrorist threats by hazardous components.

In former presentations using suspension polymerisation we demonstrated the synthesis of particulate MIPs specific for TNT able to discriminate 2,4-DNT and vice versa /5, 6/. Overall objective of this study was to achieve a direct synthesis of TNT-specific MIPs as thin films using UV polymerisation techniques combined with spray coating. In order to establish a fast screening module for the MIP coatings a so called gaslab 21 should be adapted to a special TNT vapour generator /3/ for online testing of the performance of the MIPs on mass sensitive quartz crystal microbalances, QCMs.

2 The technique of molecular imprinting

The technique of molecular imprinting allows the formation of specific recognition sites in macromolecules. In this process functional and cross-linking monomers are copolymerised in the presence of a target analyte (template). The functional monomers form a complex with the imprint molecule and in the following polymerisation the functional groups are held in position by the highly cross-linked structure. Subsequent removal of the template reveals binding sites that are complementary in size and shape to the analyte. The complex between monomers and template can be formed via reversible covalent bonds or via non-covalent interactions like hydrogen bonds.

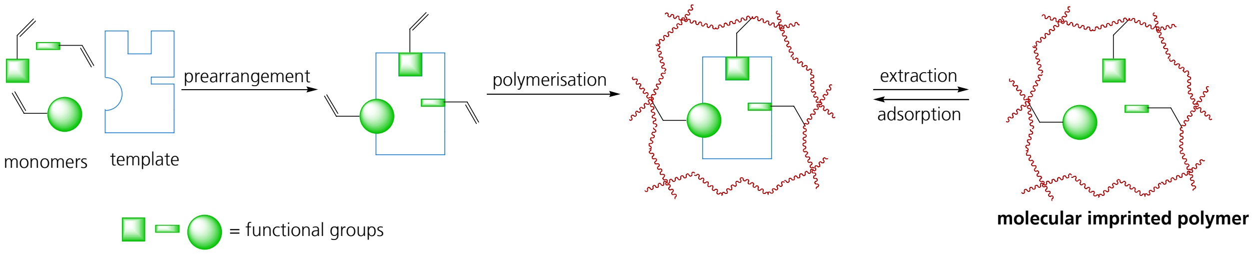
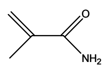
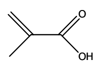
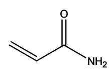
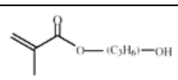
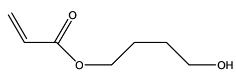


Figure 1: principle of molecular imprinting

For TNT as template it is not possible to use the covalent approach. Furthermore with the non-covalent approach we are able to use a large pool of functional monomers that are commonly used in the field of molecular imprinting. Because of the known problem that nitroaromatics are weak hydrogen bond acceptors /1/ for the synthesis of layered MIPs we used several acrylates with different functional groups as monomers (Table 1) and ethylene glycol dimethacrylate (EGDMA) as cross linking agent.

Table 1: Acrylate monomers tested in this study

Methacrylic amide	MAAM	
Methacrylic acid	MAA	
Acrylamide	AA	
Hydroxypropylmethacrylate	HPMA	
Butandiolmonoacrylate	BDMA	

3 Experimental

3.1 Quartz crystal microbalances

The used quartz crystal microbalances (QCMs) are typical piezoelectric devices cut from whole quartz crystals in a so called AT-cut, resulting in quartz disks with a low temperature dependence of their resonant frequency possessing excellent frequency stability. The quartz disks are clamped and coated with a thin silver and / or gold film forming the electrode. Being used in an electric oscillation circuit they convert acoustic energy into electric energy and vice versa. A special property of QCMs was empirically found by Sauerbrey in the fifties of the last century /4/ . Depending on the quartz crystal dimensions they have a fundamental frequency (5 to 30 MHz) which is proportionally decreased as a mass attachments on the quartz is performed making them ideal for mass sensing (1). Up to a range of about 2 per cent of the quartz mass the function behaves linear while higher mass attachments could still be correlated to the registered frequency decrease.

$$\frac{\Delta f}{f_0} = -\frac{\Delta m}{M} \qquad (1)$$

Δf	=	Change of frequency
f_0	=	Fundamental frequency
Δm	=	Change of the mass
M	=	Mass of quartz

3.2 Spray-coating of QCMs

The synthesis solutions of non-imprinted MIPs are prepared in brown bottles mixing first 10 ml of solvent with the monomers and the cross-linker and secondly dissolving a UV-starter, Irgacure-type from Ciba Specialty Chemicals (ratio of 5 : 1 : 0,1). The solution is once or several times manually sprayed over the QCMs using a spray gun following UV polymerisationwith a point UV-lamp (Dymax, BW50) under nitrogen atmosphere (30 to 120 sec). The polymer layers are shortly washed in the used solvent and dried at air. In the case of imprinted polymers the synthesis solution also contains the target molecules, in this study TNT. As solvent acetonitrile (ACN), chloroform (CH_3Cl) or dimethylformamide (DMF) were used.

3.3 Performance tests of layered MIPs

Performance tests of the produced TNT-imprinted and non-imprinted MIP coatings were realised using a commercial gaslab (ifak, figure 2) in which up to eight QCMs can be measured simultaneously under constant temperature (45°C). Temperature in the gaslab chamber is measured by two PT100 elements. Used quartzes have a diameter of nearly 8 mm and a ground frequency of 10 MHz. Mass increases on the QCM will yield to a decrease of the frequency and vice versa. For comparison reasons TNT-imprinted and non-imprinted polymers of the same type were measured parallel. Typical procedure for screening QCMs is to measure them after short cleaning with solvent for about one hour to determine the ground frequency. After spray-coating the QCMs are again tempered for about one hour to measure the difference to the before measured ground frequency. Based on Sauerbreys formula the thickness of the produced MIP coating can be calculated. Afterwards the TNT vapour treatment starts with online measurements of the decreasing QCM frequency to verify the performance of the MIPs.

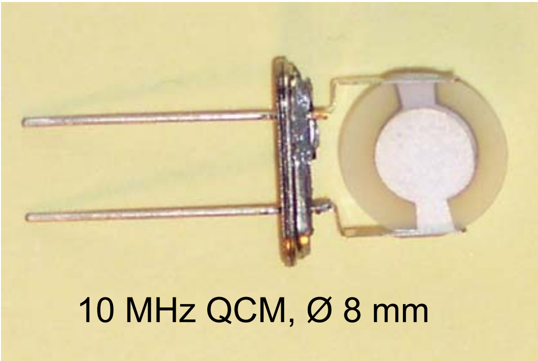


Figure 2: QCM measurement equipment (Gaslab 21) and used 10 MHz quartz crystals

4 Results and discussion

As described in earlier presentations /3, 5, 6/ we already synthesized some particulate MIP materials by suspension polymerisation/2/ which showed much higher adsorption of TNT from vapour than their related non-imprinted polymers. Independent of the used monomer the non-imprinted MIPs only adsorbed very low TNT amounts. As desired the TNT-imprinted MIPs possessed a better ability to bind TNT from the gas phase whereas PMAA showed a more pronounced sensitivity for TNT in comparison to PAA. Preliminary measurements concerning the potential cross-sensitivity of TNT-imprinted MIPs using e.g. 2,4-DNT as test gas provided no measurable absorption amounts as well as DNT-imprinted MIPs did not show measurable affinity for TNT. Produced particles had typical diameters of 10-20 µm and specific surfaces of 200 to 400 m^2/g.

Employment of MIPs as sensor materials is preferably possible as thin film coatings. Necessary or optimized coating thicknesses for the application of MIPs on mass sensitive sensors like e.g. FETs (field effect transducers), SAWs (surface acoustic wave) or micro cantilevers will be in the range of some nanometers to about one micrometer. In principle thin films can be applied to the sensor surface by spray-coating, dipping or spotting followed by UV-polymerisation. In this study we tested manual spray-coating with a commercial artist spray gun. First attempts lead to MIPs which lead to TNT-uptakes in the range of 1 to 2,5 pg per hour needing very long QCM measurement intervals to demonstrate the desired higher adsorption tendency of imprinted materials as shown in figure 3 for two pairs of polymethacrylic amide MIPs. Despite of the long analysis times the used QCM-screening tool was suitable to detect even low differences of the TNT adsorption tendencies of the analysed coated QCMs by nearly constant frequency values of the non-imprinted MIPs and slowly decreasing frequencies for the imprinted polymers.

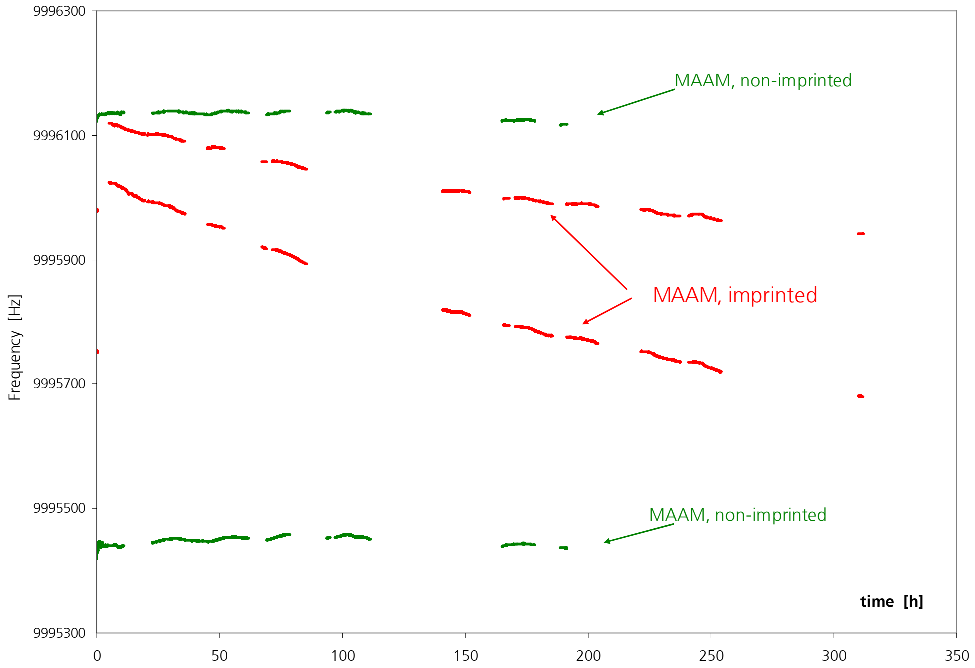


Figure 3: Frequency measurements of four QCMs during TNT vapour treatment produced in the early beginning of direct MIP synthesis via UV-polymerisation of TNT imprinted and non-imprinted PMAAM

Especially the better manual handling of the spray gun as well as the adjustment of the synthesis conditions (N_2-atmosphere, distance of spray gun and UV-point-lamp to the QCM) yielded to improved coatings with higher TNT adsorption properties. As shown in figure 4 typically treatment times under TNT vapour of one to two hours are sufficient to examine the performance of coated QCMs.

Like detected for the particulate MIPs independent of the used monomers the non-imprinted MIP coated QCMs show minor tendencies to adsorb TNT from loading vapour exemplarily shown in figure 5 for PAA, PMAA and PBDMA MIPs synthesized with DMF.

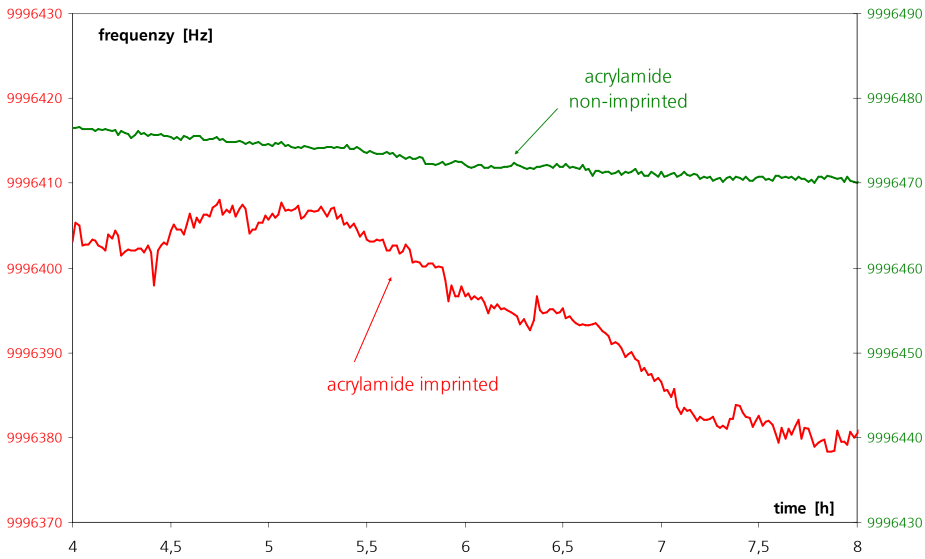


Figure 4: Frequency measurements of two improved QCMs coated with TNT imprinted and non-imprinted polyacrylamide (PAA) during TNT vapour treatment

The production of porous MIP materials with selective binding sites for the template depends on the used solvent due to e.g. different solubility of the contained components, the building tendency of a suitable pre-complex of the latter polymer structure as well as the evaporation of the solvent during the UV-curing of polymer coating. Therefore three different solvents ($CHCl_3$, ACN and DMF) were tested in this study. Physical properties of the solvents are listed in table 2. Chloroform has the lowest boiling point, dielectric constant, ε and dipole moment (μ). Whereas the polarity of acetonitrile and DMF is comparable to each other their boiling points are different and higher than that of $CHCl_3$.

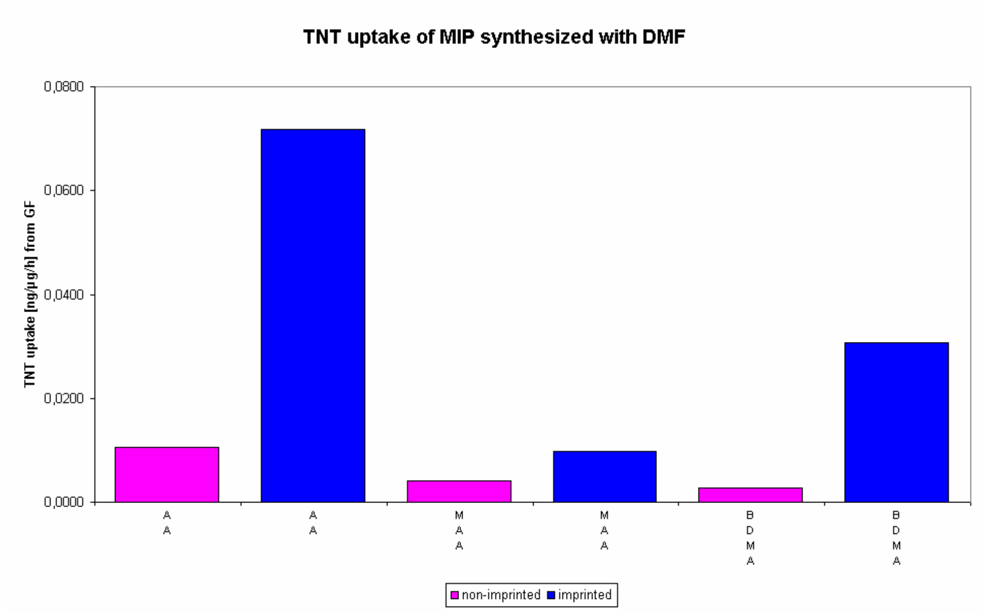


Figure 5: Comparison of TNT-uptake {ng/µg polymer/h] of different QCMs coated with imprinted or non-imprinted polymers (PAA, PMAA and PBDMA) using DMF

Table 2: Selected physicochemical properties of solvents used for UV-polymerisation of layered TNT-MIPs (mp / bp: melting and boiling point in °C, density (*D*) in g/mL at 20 °C, refractive index (n_D), dielectric constant (ε), molar refraction (R_D), and dipole moment (μ) in Debye at 20 °C)

Solvent*	**mp**	**bp**	D^{20}	n_D^{20}	ε	R_D	μ
Acetonitrile	–44	82	0.782	1.3441	37.5	11.1	3.45
DMF	–60	152	0.945	1.4305	36.7	19.9	3.86
Chloroform	–64	61	1.489	1.4458	4.81	21	1.15

The different TNT-uptake of QCMs coated with acrylamide-based imprinted MIPs synthesized with the three different solvents respectively is shown in figure 6. The highest sensitivity for TNT was regarded for the PAA-MIP which was synthesized in the presence of chloroform followed by that of DMF. Despite of the lower boiling point of acetonitrile in comparison to DMF the ACN-based PAA resulted to the lowest TNT sensitivity. Therefore not only the ability of a fast evaporation of the solvent during polymerisationis a driving force for producing higher MIP capacities but also the solubility and other parameters (e.g. wettability of the QCM) may play a major / combined role. Figure 7 presents further results for different monomer types synthesized with the three solvents. In the case of PMAAM-MIPs the best TNT adsorption capacity was achieved using acetonitrile, the solvent having the medium boiling point and nearly the same polarity respectively solubility as DMF.

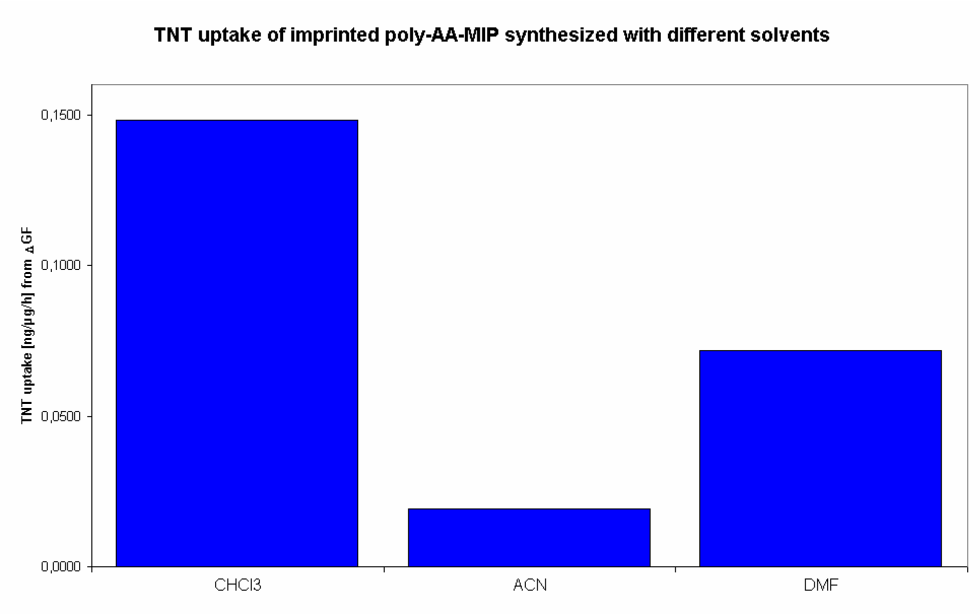


Figure 6: Comparison of TNT-uptake (normalized to ng TNT per µg polymer per hour) of different imprinted poly-AA MIPs synthesized with different solvents

Until now the monomers hydroxypropylmethacrylate (HPMA) and butandiolmonoacrylate (BDMA) have only been tested using DMF whereas the latter showed a considerable TNT adsorption tendency (figure 7). In further synthesis these monomers should also be tested in combination with chloroform and acetonitrile.

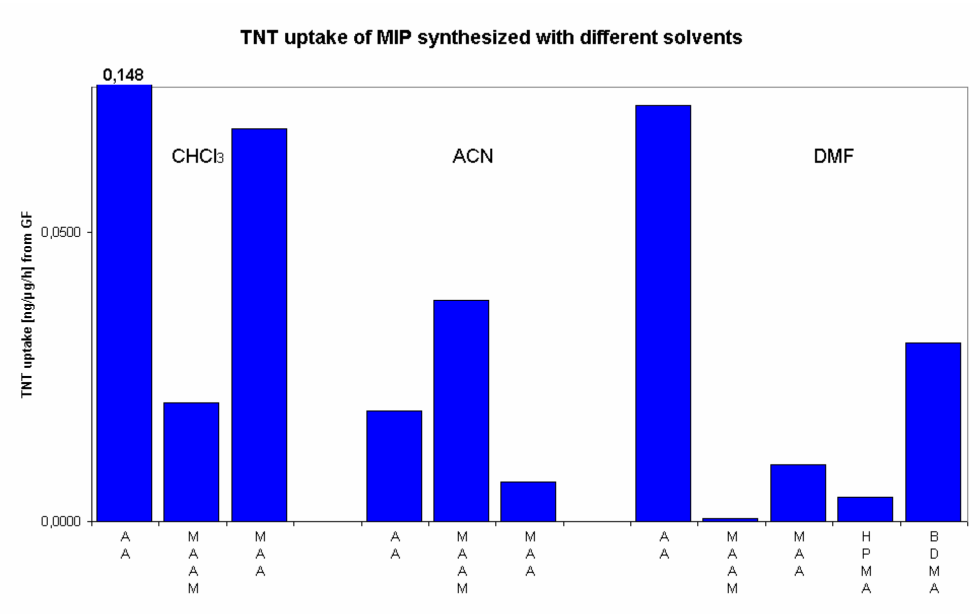


Figure 7: Comparison of TNT-uptake (normalized to ng TNT per µg polymer per hour) of different imprinted polymer types synthesized with different solvents

5 Summary and outlook

Results so far demonstrated that the used gaslab21 QCM module is suitable for a fast screening of MIP-coatings so that an improvement of the synthesis conditions could be started. Preliminary results show that TNT specific MIPs could as well be synthesised as thin films. The produced coatings have thicknesses in the range of some to about 500 nm matching the requirements of common mass-sensitive sensors. In order to improve the coating process currently we are working out an automatic spray-apparatus with a gun in the mid of a circle able to semi-continuously coat lots of QCMs at the outer circle. To get a better understanding of the underlying physical phenomena of the coating further measurements will address the wettability of the QCMs by the synthesis solutions. Best TNT sensitivity until now showed a PAA-MIP synthesized with chloroform. Due to modification of the synthesis conditions in comparison to first attempts the TNT absorption was increased by a factor of about 100. The response time reached with the quartz crystal microbalances, QCMs, is in the pg per minute range. Further improvement of MIP capacity will lead to shorter detection times (ca. one second).

6 References

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