MIPS (MOLECULARY IMPRINTED POLYMERS) AS SELECTIVE ULTRATHIN LAYERS FOR THE DETECTION OF TNT

J. Hürttlen, G. Bunte, D. Röseling, M. Heil, H. Pontius, K. Hartlieb, H. Krause
Fraunhofer Institut Chemische Technologie (ICT)
Joseph-von-Fraunhofer-Str. 7, 76327 Pfinztal, Germany

1 Introduction

Recent terrorist attacks such as 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, NQR,) are inadequate and have to be improved as well as new counter-action / detection concepts have to be developed. Common ingredients in improvised explosives like 2,4,6-TNT, 2,4-DNT, NGl, EGDN, tagging substances like DMNB or the self-made explosive most frequently used by terrorists, TATP, exhibit vapour pressures in the ppb to percentage range which in principle enable a possible detection of these substances via vapour trace detection methods [1]. In concerns with national security there are needs for inexpensive, rapid, high sensitive and selective sensors. In this respect, we decided to use QCMs (quartz crystal microbalances) as a mass sensitive device that can be coated with a sensitive layer. For this study we decided to use 2,4,6-TNT and 2,4-DNT as templates to examine the selectivity and the sensitivity of the MIPs against similar substances. Preliminary results for 2,4,6-TNT and possible concepts for MIP-based low-cost sensors are presented.

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 subsequent 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 [2] or via non-covalent interactions [3, 4, 5] such as hydrogen bonds.

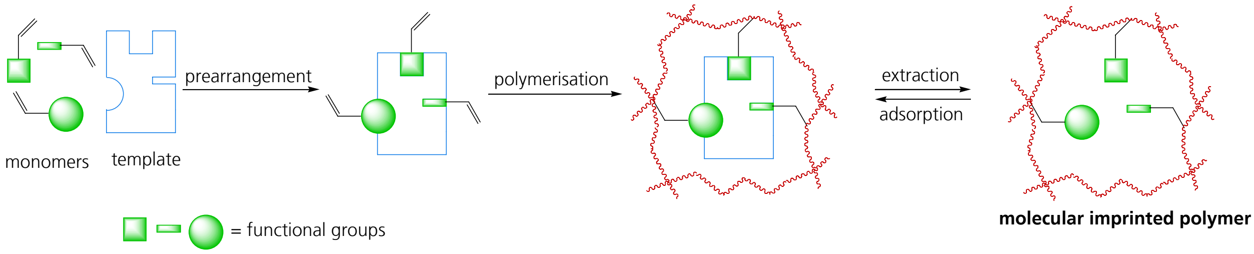

Figure 1: principle of molecular imprinting

For TNT or DNT 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 [6], for the synthesis of the MIPs we used several acrylates with different functional groups as monomers (Figure 2) and ethylene glycol dimethacrylate (EGDMA) as cross linking agent.

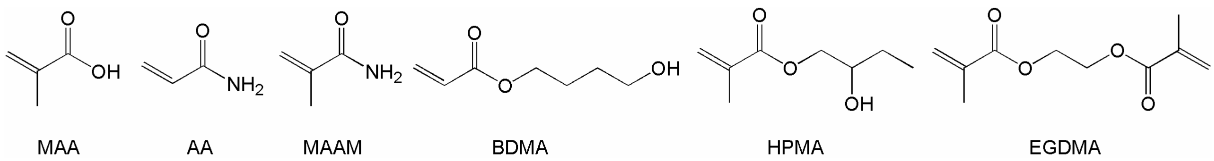

Figure 2: used functional monomers and crosslinker

3 Synthesis

3.1 Layer polymerisation

Direct synthesis of TNT-imprinted MIPs as thin film coatings on so called quartz crystal micro balances, QCMs was performed via manual spray-coating with an art air-brush gun. In later experiments we used a nanoplotter for applying the MIP solution onto the sensor surface followed by UV polymerisation (UV starter Irgacure type) with a point lamp (Dymax) as for the spray coated ones. As porogenic solvents acetonitrile (ACN), chloroform ($CHCl_3$) or dimethylformamide (DMF) were tested. To verify the enhanced uptake of TNT from the vapour stream, the imprinted polymer type was always tested against the non-imprinted correspondent using a special TNT gas generator [8]. The TNT uptake was directly measured via the decreasing QCM frequency of the treated MIP layers. As empirically found by Sauerbrey [9] the frequency of a QCM decreases linearly up to about 2 per cent of the quartz mass as a mass attachment occurs. For QCM measurements a commercial gaslab (ifak, Magdeburg) with quartzes having a ground frequency of 10 MHz were used. 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 polymerisation with a point UV-lamp (Dymax, BW50) under nitrogen atmosphere (30 to 120 sec). In case of the nanoplotter we used different plot programs (single spot or multiple spots dispensed over the electrodes). 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 or DNT. As solvent acetonitrile (ACN), chloroform ($CHCl_3$) or dimethylformamide (DMF) were used.

3.1 Performance tests of MIPs

To test the performance of the synthesized polymer beads imprinted by 2,4,6-TNT or 2,4-DNT, the MIPs were exposed to a constant flow of these explosives accomplished in a special vapour generator [8]. To verify the enhanced uptake of the templates from the vapour stream, the imprinted polymer type was always tested against the non-imprinted correspondent.
Performance tests of the produced TNT- or DNT-imprinted and non-imprinted MIP coatings on the QCMs were realised using a commercial gaslab (ifak, figure 4), 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.

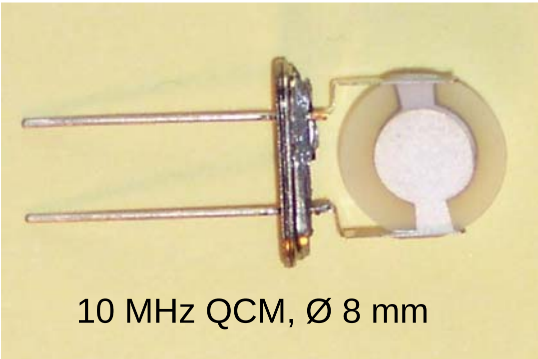

Figure 3: QCM measurement equipment (Gaslab 21) and used 10 MHz quartz crystals

4 Results and discussion

4.1 Performance of spray-coated MIP layers on QCMs

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 such as SAWs (surface acoustic wave) or micro cantilevers or workfunction-specific

FETs (field effect transducers), 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 initially we tested manual spray-coating with a commercial artist spray gun.

After some adjustments of the synthesis conditions (N_2-atmosphere, distance of spray gun and UV-point-lamp to the QCM) typically treatment times under TNT vapour of one to two hours are sufficient to examine the performance of coated QCMs. The production of porous MIP materials with selective binding sites for the template depends amongst others 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.

As detected for the particulate MIPs [10] independent of the used monomers the non-imprinted MIP coated QCMs show minor tendencies to adsorb TNT from loading vapour exemplarily shown in figure 4 for PAA, PMAA and PBDMA MIPs synthesized with DMF.

The different TNT-uptake of QCMs coated with imprinted MIPs synthesized with the three different solvents respectively is shown in figure 5. The highest sensitivity for TNT was regarded for the PAA-MIP which was synthesized in the presence of chloroform followed by that of DMF. Probably due to the lower boiling point of acetonitrile in comparison to DMF the ACN-based PAA resulted to the lowest TNT sensitivity with an acrylamide polymer. Therefore not only the polarity of the solvent is a driving force for producing higher MIP capacities but also other parameters (e.g. solubility, wettability of the surface) may play a major / combined role.

Figure 5 also 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. Until now the monomers 2-hydroxypropyl-methacrylate (HPMA) and butandiolmonoacrylate (BDMA) have only been tested using DMF whereas the latter showed a considerable TNT adsorption tendency. In further synthesis these monomers should also be tested in combination with chloroform and acetonitrile.

As calculated via the decrease of the frequency of the coated QCMs, improved handling of the manual spray-coating technique led to reproducible film thicknesses in the range of some to about 500 nanometers and enhanced TNT-adsorption characteristics, nevertheless a “person factor” remained.

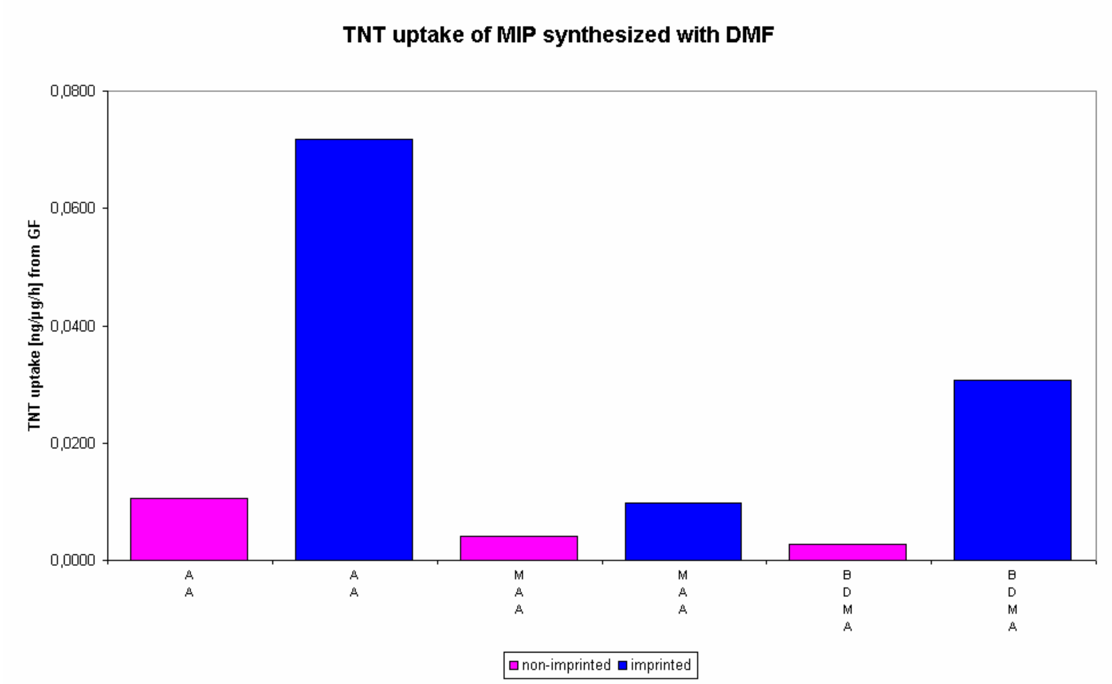

Figure 4: Comparison of TNT-uptake {ng/µg polymer/h] of different QCMs coated with imprinted or non-imprinted polymers (PAA, PMAA and PBDMA) using DMF

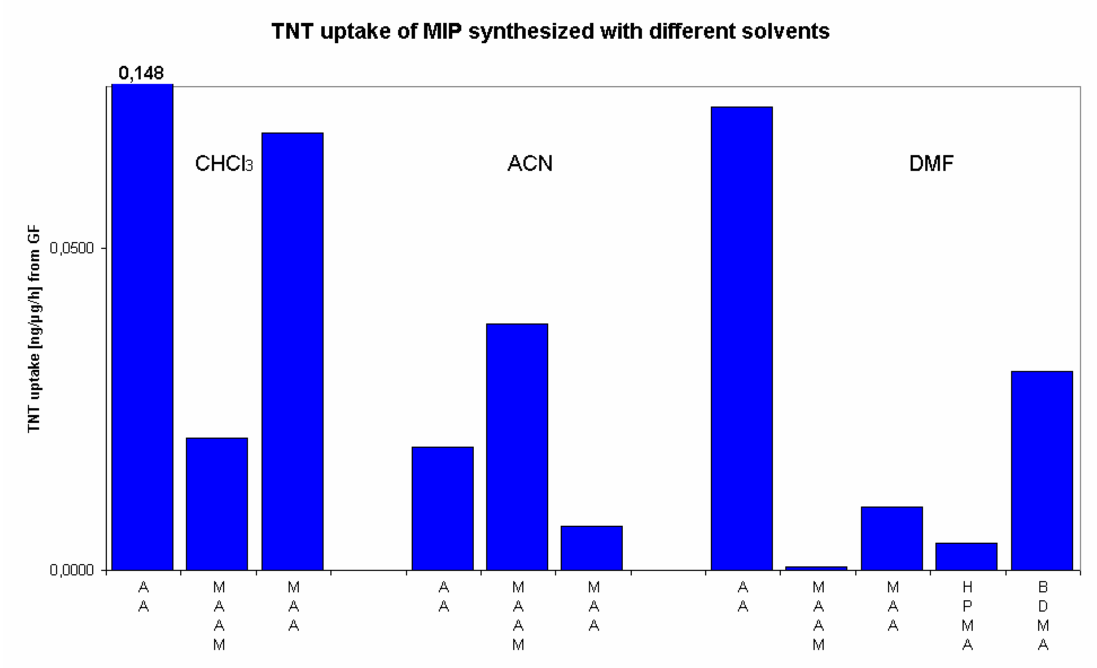

Figure 5: Comparison of TNT-uptake (normalized to ng TNT per µg polymer per hour) of different imprinted polymer types synthesized with different solvents

4.2 Layered MIPs after nanoplotting

In order to improve the coating process currently we are working with a computer controlled so called nanoplotter (GeSiM, Großerkmannsdorf) that can produce very accurately small drops in the size of 300 pl and put them onto surfaces (figure 6).

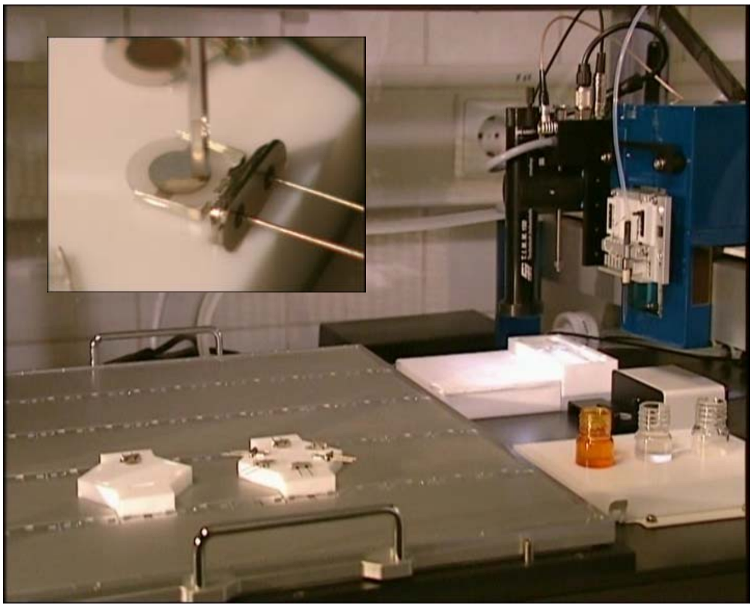

Figure 6: Coating of QCMs with a nanoplotter (Fa. GESIM)

We wrote and tested several print programs including different point raster applications with single or multiple drop applications to apply the MIP synthesis solution onto the circular QCM sensor electrode. Exemplarily figure 7 shows some raster electron microscopic pictures of different plotted and polymerised MIP film as well as an image of a cut into the MIP layer using a so called FIB technique (focused ion beam) for measuring the film thickness.

As shown in figure 7, nanoplotting yielded to very regular and closed films. At the edge of the circular film always a small so called "coffee drop" effect can be recognized. Via the FIB cutting technique the film thickness of a single drop was estimated to be 3,2 µm. The film thicknesses measured via the decrease of the QCM frequencies of uncoated to coated sensors were estimated to be in the range of 1 to 4 µm which is consistent with the FIB measurement. This is the ideal film thickness e.g. for field effect transistor sensors (FETs). In order to be able to coat sensors such as SAWs, which need very thin film thicknesses currently we are working on a concept for a spin-coater to further improve our MIP coating capabilities.

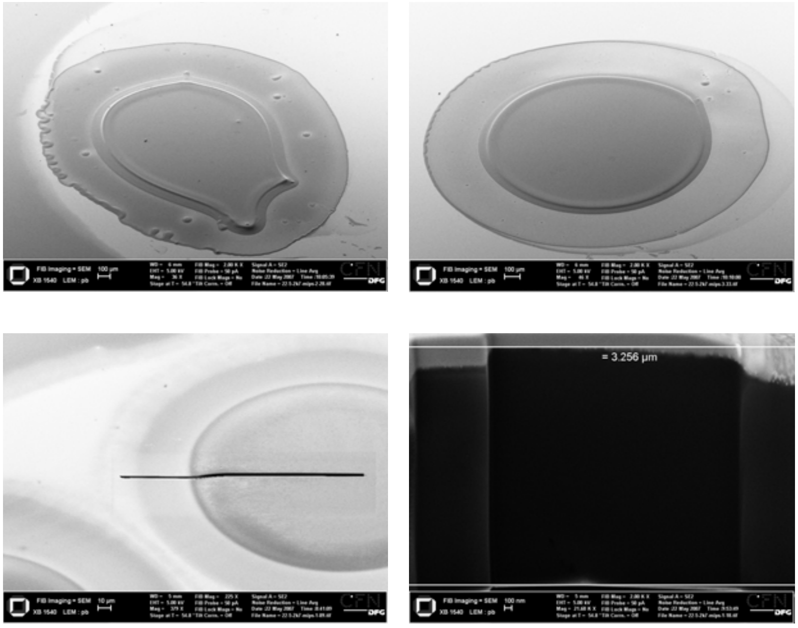

Figure 7: SEM pictures of MIP films nanoplotted on QCM electrodes using single-drop programs followed by UV polymerisation (above) and an image of a cut into a single MIP drop layer using a focused ion beam , FIB (bottom: left side view onto the drop and right side perspective of the produced cut)

5 Summary and outlook

Results received for the MIP layers on QCMs 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. The MIP layers produced via manual spray-coating have thicknesses in the range of some to about 500 nm matching the requirements of common mass-sensitive sensors. Nevertheless the reproducibility of the films should be improved. Best TNT sensitivity until now showed a PAA-MIP synthesized with chloroform. The response time reached with the quartz crystal microbalances, QCMs, is actually in the pg per minute range. Further improvement of MIP capacity will lead to shorter detection times (ca. one second).

Nanoplotting of MIPs leads to layers with very regular and closed films. Due to the basic operating parameters of the used nanoplotter as well as the viscosity of the applied MIP synthesis solutions the nanoplotter will be ideal e.g. for the coating of FET sensor surfaces. Future experiments will address e.g. DNT as template and the cross-sensitivity of these MIP layers against TNT and vice versa. Also environmental conditions such as humidity and cross sensitivity / affinity to solvent vapours or other explosive components will be tested. In order to be able to achieve very thin MIP films we are working on a concept for a suitable spin-coating technology.

6 References

[1] J.W. Gardner and J. Yinon (Eds.), Proc. of NATO Advanced Research Workshop on Electronic noses and Sensors for the detection of explosives, Warwick, UK, 2003

[2] G. Wulff, A. Sarhan, Angew. Chem., 84, 364 (1972)

[3] B. Sellergren, Molecularly Imprinted Polymers – Man-Made Mimics of Antibodies and their Applications in Analytical Chemistry, Elsevier Science B.V., Amsterdam, 2001

[4] M. Komiyama, T. Takeuchi, T. Mukawa, H. Asanuma, Molecular Imprinting, Wiley-VCH, 2003, ISBN: 3-527-30569-6

[5] K. Mosbach, K. Haupt, J. of Molecular Recognition, Vol 11: 62-68 (1998)

[6] W. F. Baitinger, P. R. Schleyer, T. Murty, L. Robinson, Tetrahedron, 1964, 20,1635-1637

[7] J.-P. Lai, X.-Y. Lu, C.-Y. Lu, H.-F. Ju, X.-W. He, Anal. Chim. Acta, 2001, 442, 105-111.

[8] G. Bunte, J. Hürttlen, G. Unkelbach, K. Niedergall, H. Krause, Imprinted polymers for gas phase detection of TNT, MIP2004 – Third International Workshop on Molecularly Imprinted Polymers, Cardiff, UK, September 12-15th, 2004

[9] Sauerbrey, Verwendung von Schwingquarzen zur Wägung dünner Schichten und zur Mikrowägung, Zeitschrift für Physik 155, (1959), 206–222

[10] G. Bunte, J. Hürttlen, H. Pontius, K. Hartlieb, H. Krause, "Gas phase detection of explosives such as 2,4,6-trinitrotoluene by molecularly imprinted polymers", Anal. Chim. Acta 591 (2007) 49-56