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Bio vs. Mimetics in Bioanalysis: An Editorial

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Editorial

Natural evolution has created biopolymers on the basis of amino acids and nucleotides showing high chemical selectivity and catalytic power. Molecular recognition by antibodies and catalytic conversion of the substrate molecules by enzymes take place in so called paratopes or catalytic centres of the macromolecule which comprise typically 10-15 amino acids. The concerted interaction between the reaction partners result in affinities down to nanomolar concentrations for the antigen binding and approaches one million turnovers per second in enzyme-catalyzed reactions.

Nucleic acids bind complimentary single stranded nucleic acids by base pairing (hybridisation) with nanomolar affinities but also interact highly specific with proteins, e.g. transcription factors, and low-molecular weight molecules and even with ions.

Biomimetic binders and catalysts have been generated using "evolution in the test tube" of non-natural nucleotides or total chemical synthesis of (molecularly imprinted) polymers in order to substitute the biological pendants in bioanalysis.

Molecularly imprinted polymers (MIPs)

To mimic the active sites of proteins synthetic polymers are imprinted by the analyte during the formation of a polymeric network. In the pre-polymerisation mixture, the target interacts by covalent (pre-organised approach) [1] or non-covalent (self-assembly approach) [2] binding with the chemically active moieties of the functional monomers. This arrangement is fixed in the following polymerization of the functional monomers or the reaction with a cross-linker. After polymerisation the template molecules are removed, providing binding sites ideally complementary in size, shape and functionality to the template thus the template preferential rebinds to the cavity.

Whilst nature has a spectrum of 20 amino acids as building elements of proteins in MIPs only one up to three different functional monomers have been applied. This is a limitation as compared with protein based reagents [3,4]. The most common functional monomers applied in thermal or photo polymerisation are methacrylic acid, vinylimidazole, vinylpyridine and their derivatives. In contrast to the three dimensional networks obtained by bulk polymerisation electropolymerisation of pyrrole, phenylenediamine, thiophene, p-aminophenylboronic acid and their derivates in the presence of the target molecule allow the one-step preparation of MIPs for a broad spectrum of analytes [5,6].

Molecularly imprinted polymers have been successfully developed for low molecular weight substances [7]. The application of the simple concept of MIP preparation for complex macromolecular templates like proteins is however still a challenge [8-11]. For effective removal of the target molecule from the polymer and accessibility for rebinding, the binding sites should be located on the surface of the polymers. Therefore, so-called surface imprinting techniques have been developed, where the template is imprinted in ultra-thin polymer films [9,12-14]. Uniform orientation of the templates during polymerization is a prerequisite for homogeneous binding sites [12,15]. For this reason the template should be bound during the polymer formation via a site-specific affinity ligand.

MIPs have still found routine application in affinity chromatography and it has been expected that they will substitute antibodies in bioanalysis [3,8]. They are especially attractive for toxic targets and for the measurement in organic solvents, i.e. in extracts of environmental samples or foods. In spite of big efforts, the performance of MIPs is still behind that of antibodies. In addition to binding MIPs, catalytically active MIPs have been developed for the application in sensors and syntheses [16-18]. So far, however, the catalytic activity of MIPs have in general been between one percent and one per mill of their biological counterparts. On the other hand MIPs have been prepared as catalysts for reactions where no enzymes are available.

Molecularly imprinted polymers have the potential to replace in future biological recognition elements, especially in affinity chromatography but also biosensors and biochips for the measurement of low molecular weight substances, proteins, viruses and living cells.

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