Molecularly imprinted polymers for the removal of Iprodione from wine: experimental design and synthesis optimization

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Introduction

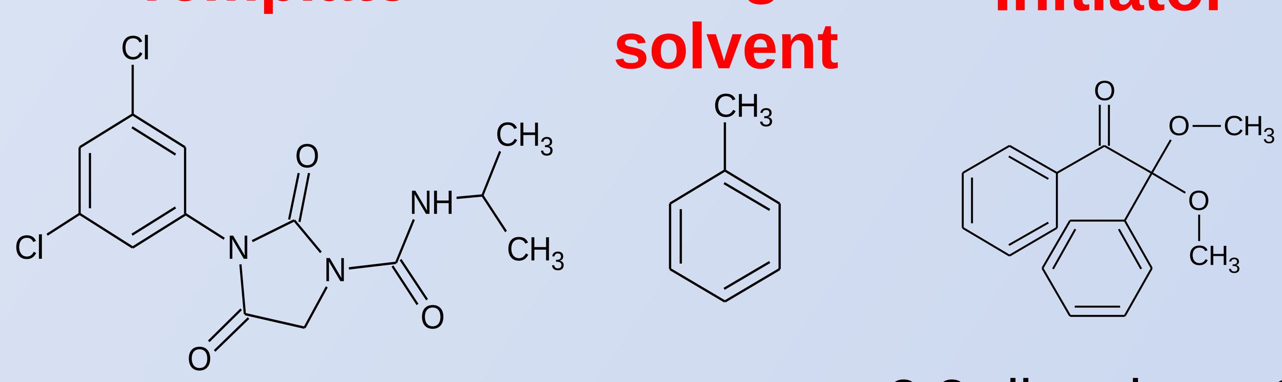
Substantial evidence demonstrates the potential for transfer of fungicides during the winemaking process. In order to remove these fungicides from wine samples, molecularly imprinted polymers (MIP) have been prepared and tested in a hydro-alcoholic solution containing Iprodione. Iprodione was chosen as fungicide because it was detected in more than 90 % of the French wine according to a survey done by the French ministry of agriculture [1].

Materials and methods

1- Synthesis

Iprodione-MIPs' non-covalent synthesis

Template | Porogen solvent | Initiator

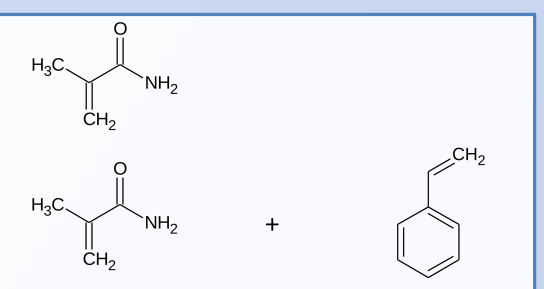


iprodione | toluene | 2,2-dimethoxy-2-phenyl acetophenone (DMPAP)

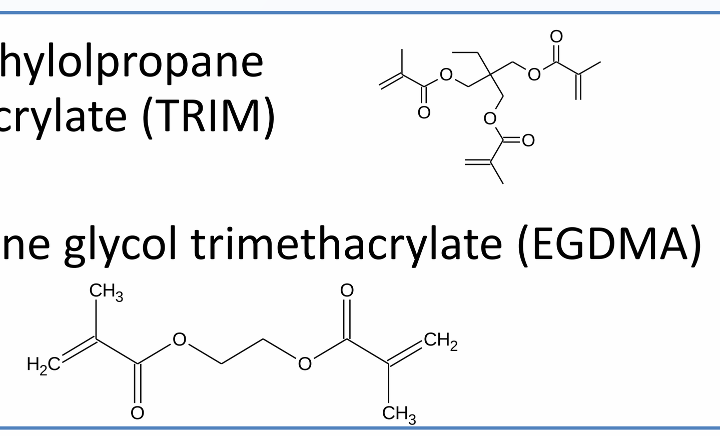
Under UV radiation

2^3 factorial experimental design

Factor 1 **Functional Monomer** (FM)
- -1 Methacrylamide
- +1 Methacrylamide + styrene



Factor 2 **Crosslinker** (C)
- -1 Trimethylolpropane trimethacrylate (TRIM)
- +1 Ethylene glycol trimethacrylate (EGDMA)



Factor 3 **Polymerization method** (PM)
- -1 Monolith
- +1 Precipitation

8 iprodione-MIPs

2- Template removal

acetic acid/ethanol
+ ultrasonication

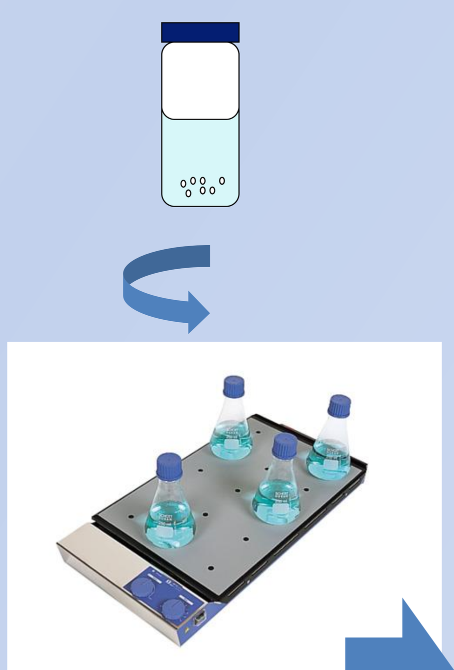
3- NIPs synthesis

8 NIPs were synthesized in a similar manner without template

4- Binding experiments

Iprodione solutions
- 20 mL ethanol/water
- 10^{-5} M < C(iprodione) < 10^{-3} M
- 10 mg polymer
- 25 ^{0}C

Extraction
- Batch extraction
- Magnetic stirring



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Freundlich isotherms

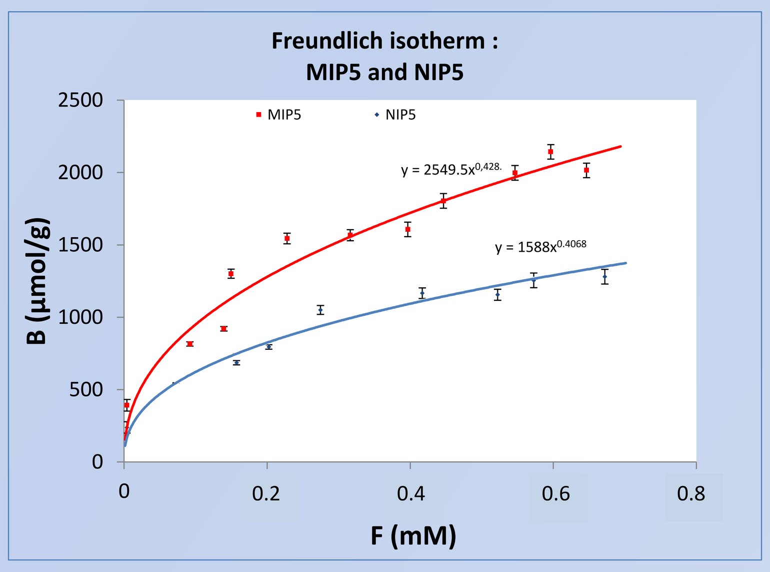


Fig. 2 : Freundlich isotherm exemple MIP5 and NIP5.

HPLC
- ❑ **C18** stationary phase
- ❑ **Acetonitrile/water (60/40)** Mobile phase
- ❑ **UV detection**

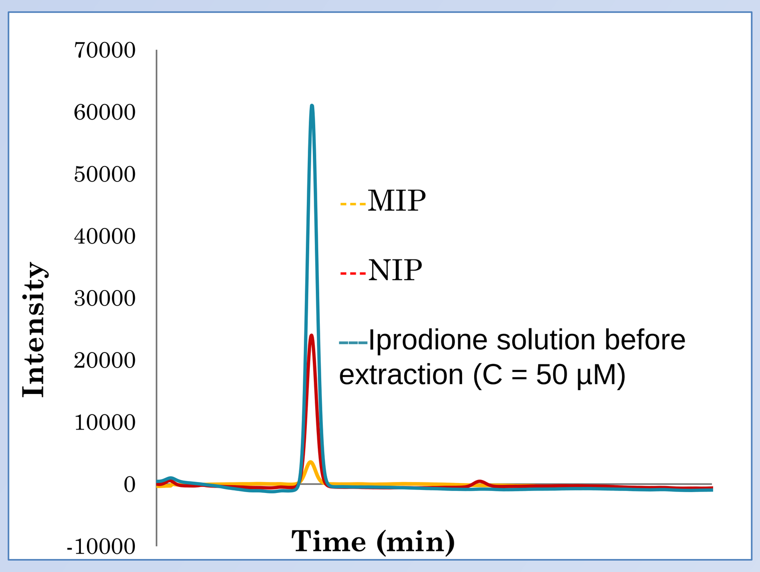


Fig. 1 : iprodione chromatograms supperpostition before and after extraction by MIP5 and NIP5 (methacrylamide, TRIM, precipitation).

$$B = a\,F^{m}$$

B : binded iprodione
F : free iprodione
a, m : ***Freundlich parameters***

5- Response variables

- ❑ **K** : apparent weighted average affinity
- ❑ **N** : apparent number of sites
- ❑ **K(MIP)/K(NIP)**

Results

Table 1 : full experimental design

MIP	PM	FM	C	K	N	K(MIP)/K(NIP)
1	-	-	-	8.78	702	1.76
2	-	-	+	5.32	538	1.39
3	-	+	-	8.81	667	1.60
4	-	+	+	10.27	726	4.50
5	+	-	-	3.38	1093	6.46
6	+	-	+	19.36	1172	1.17
7	+	+	-	7.36	623	1.01
8	+	+	+	7.49	685	1.01

The optimal MIP :
MIP5
- ❑ **F1 : precipitation**
- ❑ **F2 : TRIM**
- ❑ **F3 : methacrylamide**

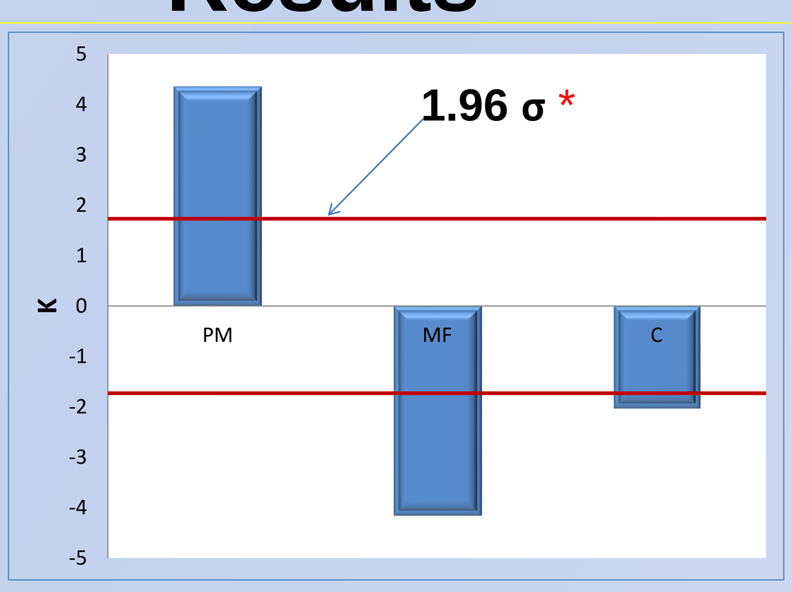


Fig. 3 : Factors significant influence on the apparent affinity.
*6 repetitions for MIP5 =>Degree of freedom = 5; 95% confidence interval

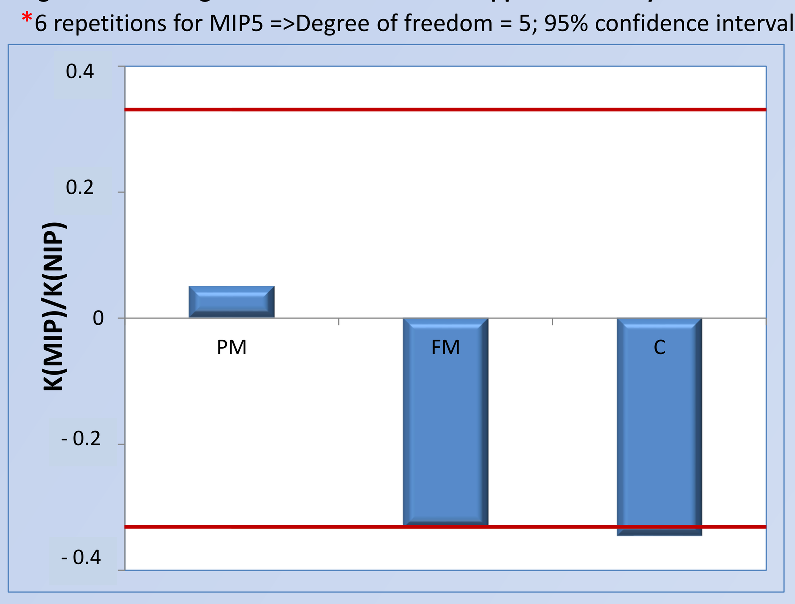


Fig. 4 : Factors significant influence on the ratio K(MIP)/K(NIP).

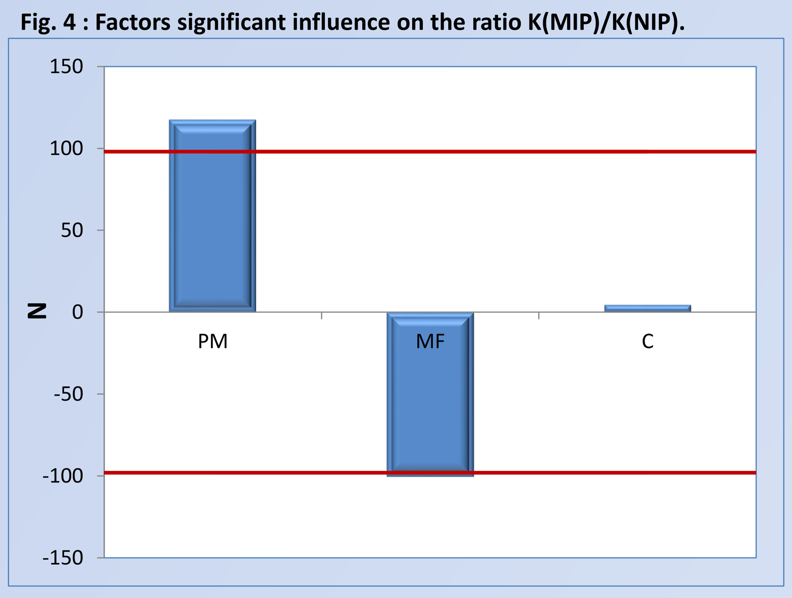
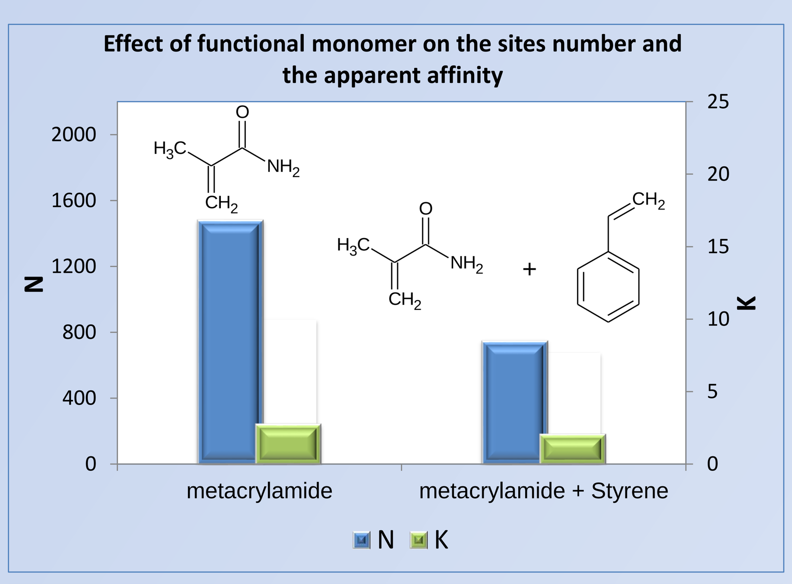
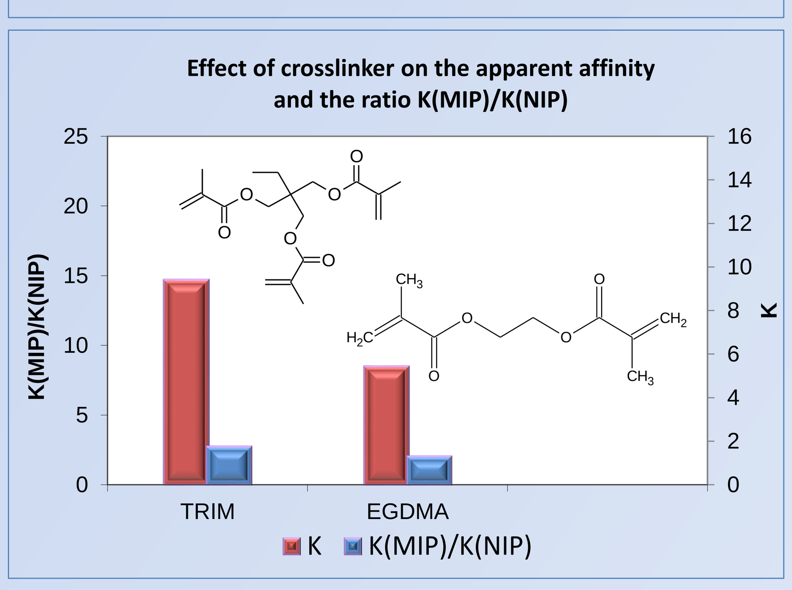
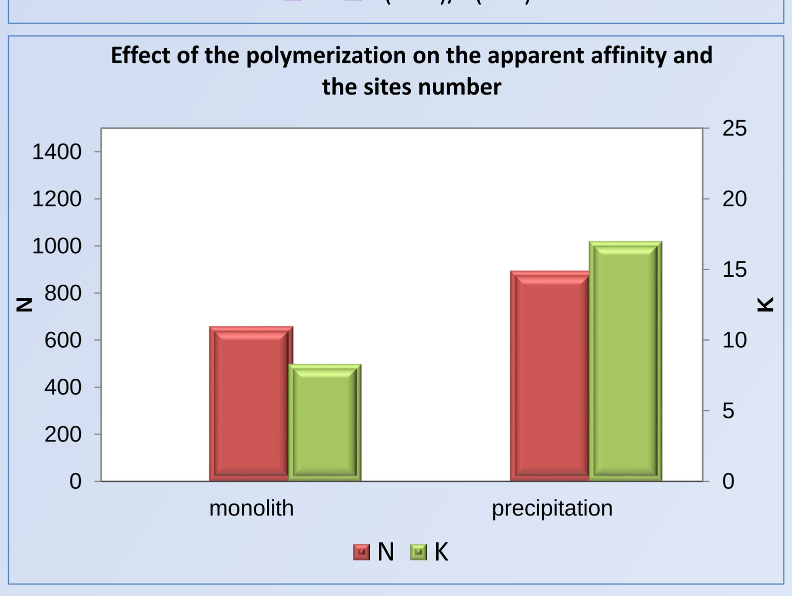


Fig. 5 : Factors significant influence on the sites number.







Conclusion

The addition of styrene decreases the apparent affinity and the sites number.

The use of TRIM increases the apparent affinity and K(MIP)/K(NIP).

The precipitation polymerization increases the apparent affinity and the sites number.

References
[1] Cugier, J.-P., & Bruchet, S.. Plan de surveillance résidus en Viticulture. Campagnes viticoles 1990-2003. Direction Générale de l'Alimentation. Sous Direction de la Qualité et de la Protection des Végétaux, 2005.

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