Migration solvents for free isocyanates in food contact materials using experimental design

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Introduction

Agglomerated cork stoppers are currently used for still wines, semi-sparkle and gaseous wines, beer and cider. Methylene diphenyl diisocyanate (MDI) is presently the adhesive in use due to its lowest toxicity comparing with toluene diisocyanate (TDI) previously employed. However, free monomeric MDI can migrate from agglomerated cork stoppers to food stuff and this is worrying subject according to food contact materials.

The objective of this study is to determine which solvent is better to extract isocyanates from agglomerated cork stoppers, essentially MDI to quantify its free monomer. A long term migration study was performed in order to compare with soxhlet extraction.

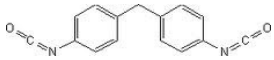


Fig 1 – 4,4'-MDI

Internal standards

$OCN-(CH_2)_6-NCO$

Fig 2 – Hexamethylene diisocyanate (HDI)

Fig 3 – 1-Naphtylisocyanate (Naphtyl)

Materials and Methods

Firstly a global migration test was performed in order to select the best solvents for soxhlet extraction. A Design of Experiments (DOE) with two factors, solvent and wax (to spike adhesive film), at six and two levels, respectively, was done. Six different solvents were put in contact with adhesive film during ten days at a temperature of forty degrees (table 1). Experiments were replicated and repeated three times. Through a TWO-WAY ANOVA the significance of solvents was evaluated and the three better solvents selected.

Experimental design

Table 1 – Solvent names and design conditions

Solvent	Name
1	Water
2	Ethanol
3	Acetonitrile
4	Diclorometane
5	Methanol
6	n-Heptane

Global migration	
S: Solvent	6 levels
W: Wax	2 levels
Replication	3
Repetition	3
Time	10 days
Temperature	40 ºC
Sample type	Adhesive film

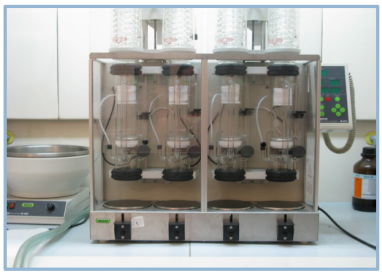
Table 2 – Design conditions

		Levels		
Factors		1	2	3
A	Number of cycles	20	55	90
B	Solvent	ethanol	acetonitrile	n-heptane
C	Sample	Natural cork	Agglomerated cork	Adhesive film

Table 3 – Experimental design 3 3-1

Experiment	A	B	C=AB
1	1	1	1
2	1	2	2
3	1	3	3
4	2	1	2
5	2	2	3
6	2	3	1
7	3	1	3
8	3	2	1
9	3	3	2

Soxhlet extraction



Afterwards, soxhlet extraction was performed with the three better solvents, ethanol, acetonitrile and n-heptane, regarding ANOVA results. The other control factors were cycles' number (20, 55 and 90) and sample type (natural, agglomerated cork stopper and adhesive film) (Table 2). In a fractional factorial DOE (table 3), with three factors at three levels, nine experiments with three replicates were performed.

All experiments were performed using an UPLC system with conditions described in table 4.

UPLC Conditions

Table 4 - Operating Conditions	
Solvent	AcN:H_2O 60:40 (v/v)
% TEA	3%
Column	UPLC BEH C18
Flow	0,3 mL/min
Temperature	30 ºC
Injection Volume	10µL
Detector	Fluorescence λ_{exc}: 254nm; λ_{em}: 412nm

Results and Discussion

The results obtained with a TWO-WAY ANOVA for isocyanates were consistent. The solvent reveals to be a significant factor whereas wax and correspondent interaction do not influence the response. As an example table 5 shows MDI results.

Table 5 – TWO-WAY ANOVA results

Fonte	SS	g.d.l	MS	F0	Fcrit 5%	%
S	2,71E+11	5	5,42E+10	4,213	2,485	58,83%
W	7,59E+09	1	7,59E+09	0,590	4,121	8,24%
SW	8,73E+10	5	1,75E+10	1,358	2,485	18,96%
e	3,09E+11	24	1,29E+10			13,96%
T	6,74E+11	35	9,21E+10			100,00%

Soxlhet method with conditions described in table 2 were performed according experimental design presented in table 3 and repeated for isocyanates. However, ANOVA tables were inconclusive for all studies.

Conclusions

The Design of Experiments reveals to be a suitable statistical tool to determine the best conditions to measure the migration of free isocyanates from agglomerated cork stoppers to real foodstuff. The best solvent to monitor the migration from cork to wine by long term migration was acetonitrile, although for soxhlet extraction the results were inconclusive.

References

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