DEVELOPMENT OF AN ANALYTICAL METHOD FOR THE DETERMINATION OF PROHIBITED ACRYLAMIDE IN COSMETIC PRODUCTS BASED ON VORTEX-ASSISTED REVERSED-PHASE DISPERSIVE LIQUID-LIQUID MICROEXTRACTION

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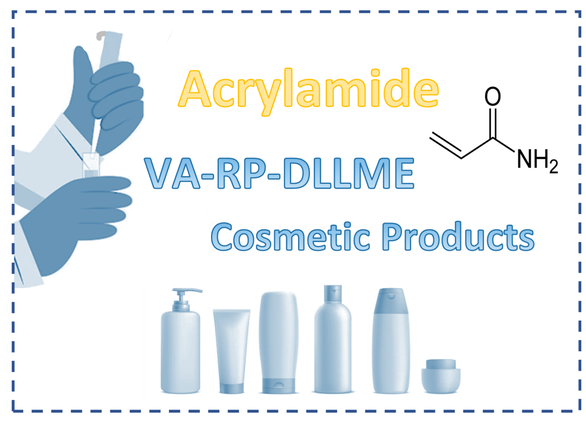
INTRODUCTION

Acrylamide presents mutagenic and potentially carcinogenic effects. It belongs to the group of compounds 2A, defined as probably carcinogenic to humans, according to the classification of the International Agency for Research on Cancer (IARC) [1]. The use of **acrylamide-based polymers** as ingredient in cosmetic products correlates with the presence of traces of **acrylamide** in the finished products, exposing the consumer to risk [2].

The determination of compounds at trace levels in complex matrices such as cosmetics needs sensitive and selective methods, usually including a **sample preparation** step where the analytes are extracted and preconcentrated.

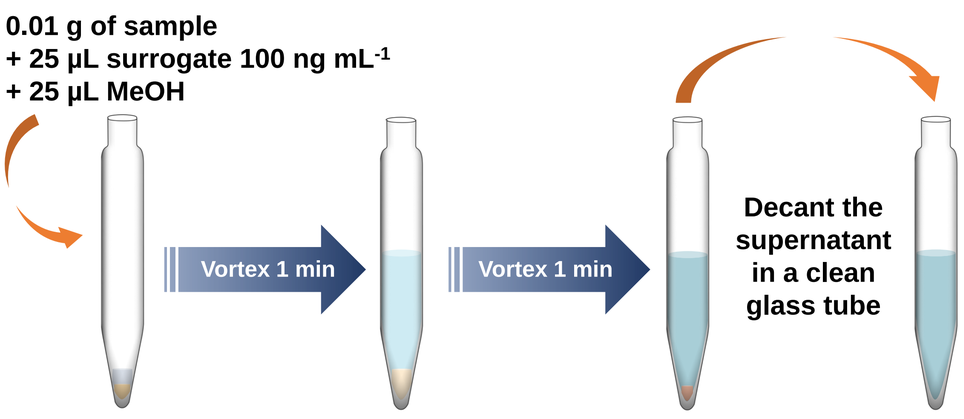
The **aim** of this work is to develop an analytical method to determine traces of acrylamide in cosmetic products.

The presented method is based on **vortex-assisted reversed-phase dispersive liquid-liquid microextraction (VA-RP-DLLME**) by using water as extraction solvent, taking advantage of the highly polar behaviour of this analyte, followed by **liquid chromatography-tandem mass spectrometry** (**LC-MS/MS**) for its determination. Acrylamide-D3 was used as surrogate.

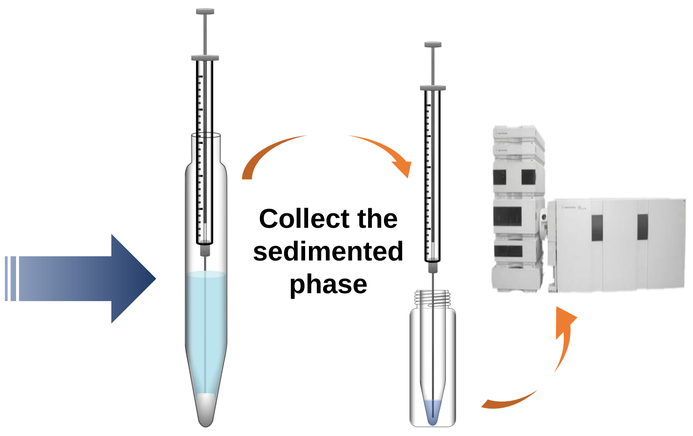


EXPERIMENTAL

PRETREATMENT OF THE SAMPLE



MICROEXTRACTION



ANALYSIS

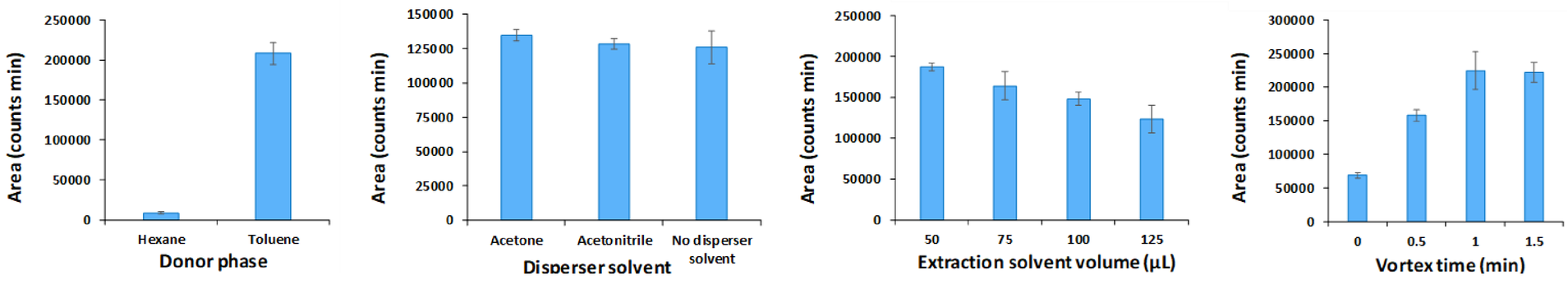
		Instrumental variable					
LC	Injection volume	5 µL					
	Column temperature	40 ºC					
	Flow rate	0.2 mL min^{-1}					
	Mode	Isocratic					
	Mobile phase	40% MeOH : 60% H_2O (with 0.5 mM of NH_4F)					
		Precursor ion: 72			**Precursor ion: 75**		
		(Acrylamide)			**(Acrylamide-D3)**		
		m/z = 55 [a]	**m/z = 44**	**m/z = 27**	**m/z = 58** [a]	**m/z = 44**	**m/z = 30**
MS/MS	Fragmentor	40 V	40 V	40 V	45 V	45 V	45 V
	Collision energy	10 V	26 V	18 V	10 V	22 V	34 V
	Capillary voltage (ESI+)	5 kV					
	Gas temperature	340 °C					
	Gas flow	13 L min^{-1}					
	Nebulizer	40 psi					

[a] Used as quantification transitions

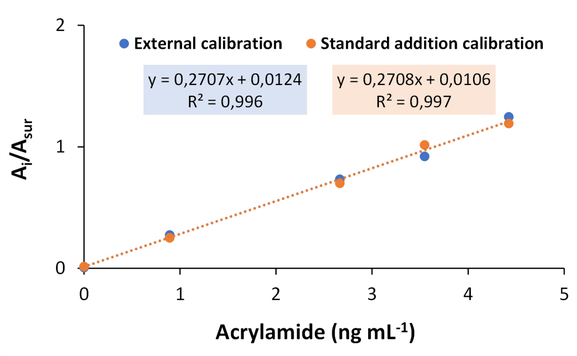
Sample solution preparation → + 5 mL toluene → Centrifuge 6000 rpm – 5 min → + 50 µL water → Centrifuge 6000 rpm – 5 min → LC-MS/MS

RESULTS AND DISCUSSION

STUDY OF THE EXPERIMENTAL VARIABLES INVOLVED IN THE VA-RP-DLLME



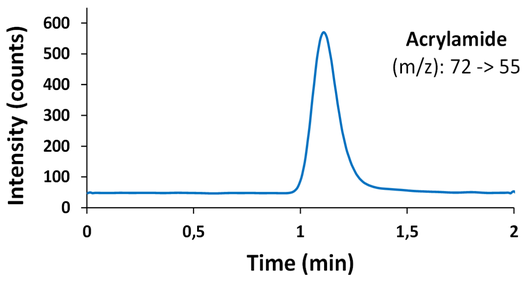
STUDY OF THE MATRIX EFFECT



FIGURES OF MERIT OF THE PROPOSED METHOD

R^2	EF	LOD (ng mL^{-1})	LOQ (ng mL^{-1})	MLOD (µg kg^{-1})	MLOQ (µg kg^{-1})	Repeatability (%RSD)			
						Intra-day (N = 5)		Inter-day (N = 5)	
						0.5 ng mL^{-1}	1 ng mL^{-1}	0.5 ng mL^{-1}	1 ng mL^{-1}
0.998	52	0.001	0.003	0.51	1.69	2.5	2.6	4.0	4.1

CHROMATOGRAM



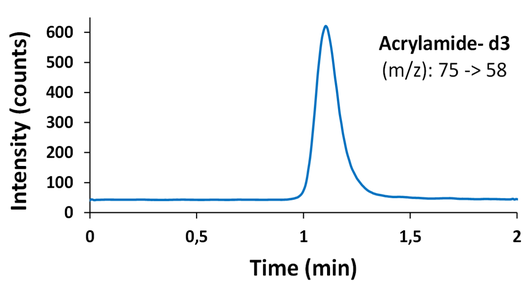
ANALYSIS OF COSMETIC SAMPLES

❖ **Three different commercially available cosmetic samples** containing acrylamide-based polymers in their formulation were analyzed by the proposed VA-RP-DLLME method:

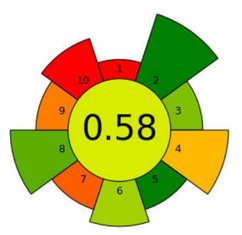
- Revitalizing gel for legs (A)
- Make-up remover milk (B)
- Liquid hand soap (C)

❖ Acrylamide was quantitatively determined in two of the three samples analyzed. In one of the samples, the acrylamide content was above 0.1 mg kg^{-1}, the maximum concentration for leave-on body products that contain polyacrylamides as an ingredient. Therefore, this product does not comply with European Regulation [3]

Sample	Spiked amount (µg g^{-1})	Found amount (µg g^{-1})	Relative recovery (%)
A	-	0.38 ± 0.04	-
	0.23 ± 0.04	0.62 ± 0.05	101 ± 3
	0.55 ± 0.19	0.97 ± 0.16	108 ± 8
B	-	< LOD	-
	0.26 ± 0.02	0.23 ± 0.03	88 ± 4
	0.48 ± 0.10	0.47 ± 0.06	94 ± 9
C	-	0.020 ± 0.003	-
	0.19 ± 0.05	0.19 ± 0.05	90 ± 1
	0.41 ± 0.12	0.45 ± 0.11	106 ± 6



AGREEprep



Green sample preparation

CONCLUSIONS

❖ The proposed analytical method is fast, simple and highly sensitive, allowing the determination of acrylamide in different types of cosmetic matrices well below the threshold values established by the European Regulation on cosmetic products [3]

❖ The proposed methodology overcomes some of the drawbacks of the previous work [4] with the same purpose, such as the need for a derivatization process and time-consuming procedures

REFERENCES

[1] Monographs on the Evaluation of Carcinogenic Risks to Humans, International Agency for Research on Cancer, IARC (1994) 60-389.
[2] Opinion of the Scientific Committee on Cosmetic Products and No-Food Products for consumers concerning acrylamide residues in cosmetics adopted by the plenary session of the SCCNFP of 30 September 1999.
[3] Regulation (EC) No 1223/2009 of the European Parliament and of the Council of 30 November 2009 on Cosmetic Products, and its Successive Amendments.
[4] L. Schettino, J.L. Benedé, A. Chisvert, A. Salvador, Development of a sensitive method for determining traces of prohibited acrylamide in cosmetic products based on dispersive liquid-liquid microextraction followed by liquid chromatography-ultraviolet detection, Microchem. J. 159 (2020) 105402.

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ONLINE VERSION