DETERMINATION OF LILIAL, LYRAL AND METHYL-N-METHYLANTHRANILATE IN COSMETICS BY STIR BAR SORPTIVE DISPERSIVE MICROEXTRACTION AND GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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INTRODUCTION

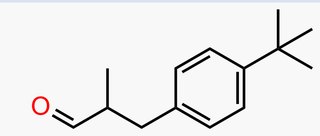
Lilial, Lyral and **methyl-N-methyanthranilate** are fragrance ingredients that have been used for several years in many cosmetic and non-cosmetic products. However, due to their high allergenic incidence, Lilial and Lyral have recently been **prohibited**, whereas methyl-N-methylanthranilate has been **restricted** in terms of concentration [1]. Hence, sensitive analytical methods for the determination of these analytes at trace levels are needed to ensure the safety of consumers.

The **aim** of this work is to develop an **environmentally friendly**, **rapid** and **sensitive method** for the simultaneous determination of Lilial, Lyral and methyl-N-methylanthranilate in cosmetics.

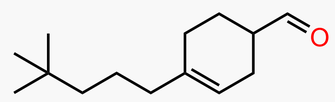
The presented method is based on **stir bar sorptive dispersive microextraction** (SBSDME) [2] followed by gas chromatography coupled to mass spectrometry (GC-MS). In this work, the **magnetic $CoFe_2O_4$@p(DVB-co-NVP) copolymer** was used as sorbent and 3,5-di-tert-butylsalicylaldehyde as surrogate [3].

ANALYTES

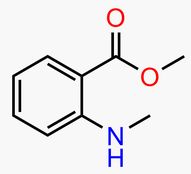
Lilial
LIL



Lyral
LYR

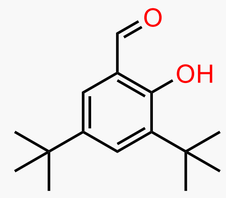


Methyl-N-methylanthranilate
MNMA



SURROGATE

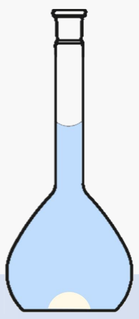
3,5-di-tert-butylsalicylaldehyde
DTBSA



As **DTBSA** is **not present in cosmetics**, it could be used as surrogate during the analysis

EXPERIMENTAL

Lixiviation



0.025 – 0.25 g sample

25 mL EtOH:H_2O 20:80 (10% w/v NaCl)

Extraction

Filtration

10 mL sample solution

200 µL surrogate (1 µg mL^{-1})

11.5 mg of $CoFe_2O_4$@p(DVB-co-NVP)

High stirring

5 min

Stirring stopped

Desorption

Filtration

250 µL ACN:acetone 40:60 v/v

7.5 min

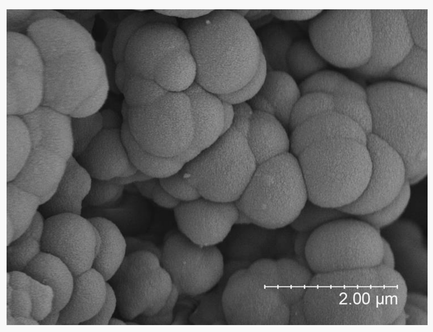
Analysis

GC-MS

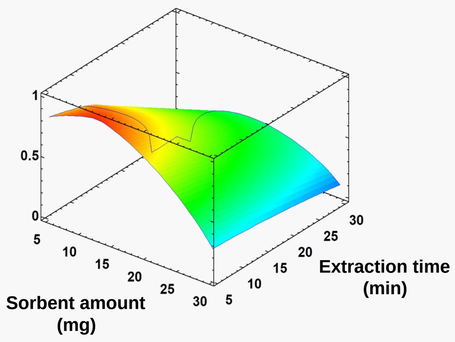
- **Column:** VF-WAXms (30 m x 0.25 mm, 0.25 µm)
- **Injection volume:** 1 µL
- **Inlet temperature:** 230 ºC
- **Transfer line temperature:** 230 ºC
- **Ion source temperature:** 230 ºC
- **Helium flow rate:** 1 mL min^{-1}

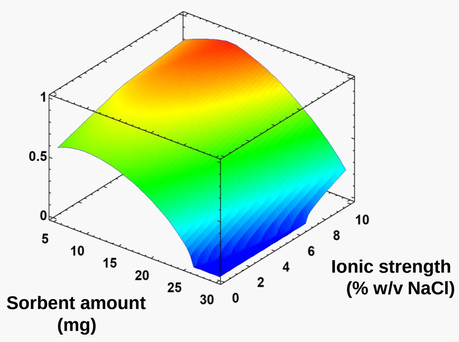
RESULTS AND DISCUSSION

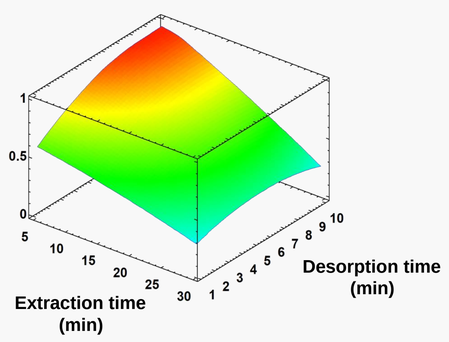
Characterization



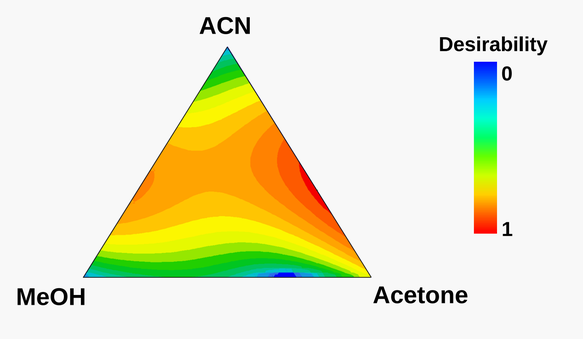
Optimization of quantitative variables



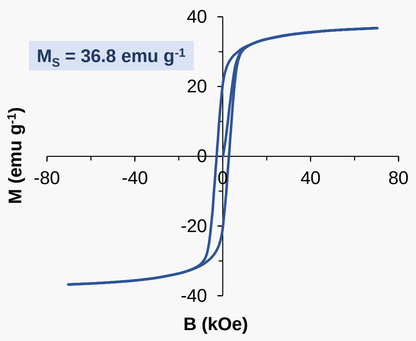




Optimization of desorption solvent



SEM image

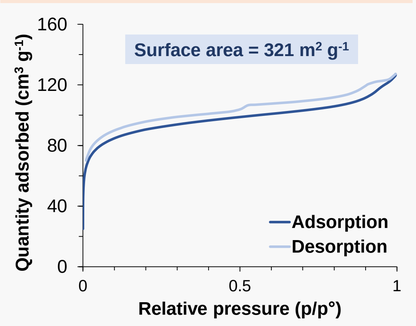


Figures of merit

Analyte	R^2	EF	EE (%)	MLOD (µg g^{-1})		MLOQ (µg g^{-1})		Repeatability (% RSD)						Relative recovery (%)
								Intra-day			Inter-day			
				FS[a] samples	WS[a] samples	FS[a] samples	WS[a] samples	2.5 ng mL^{-1}	20 ng mL^{-1}	40 ng mL^{-1}	2.5 ng mL^{-1}	20 ng mL^{-1}	40 ng mL^{-1}	
LIL	0.998	26	66	0.04	0.01	0.1	0.05	2.2	1.5	1.3	8.4	5.3	1.1	86 – 107
LYR	0.9996	18	45	0.1	0.04	0.3	0.1	3.2	1.3	1.9	6.5	9.4	5.7	76 – 95
MNMA	0.9990	23	58	0.07	0.03	0.2	0.1	1.6	1.4	1.1	3.1	7.8	1.8	85 – 108

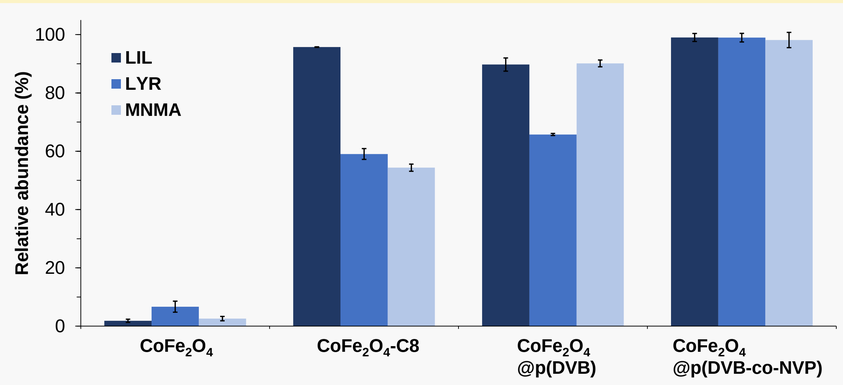
[a] FS: Fat-soluble; WS: Water-soluble

Magnetization curve



Adsorption properties

Selection of sorbent

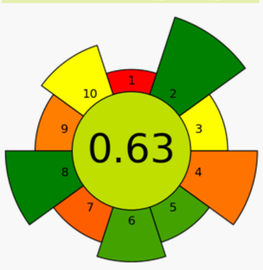


Found concentration (µg g^{-1}) of the analytes

Analyte	Sample A[a]	Sample B[b]	Sample C[c]
LIL	18.1 ± 0.6	19.5 ± 0.4	25.1 ± 0.6
LYR	n.d.[d]	n.d.[d]	n.d.[d]
MNMA	n.d.[d]	n.d.[d]	n.d.[d]

[a] Sample A: Body milk
[b] Sample B: Moisturizing body cream
[c] Sample C: Shooting gel
[d] n.d.: Not detected

AGREEprep



Green sample preparation

CONCLUSIONS

- A rapid, simple, and environmentally friendly SBSDME-GC-MS method that contributes to the development of sensitive methods for the determination of prohibited and restricted substances in cosmetic samples has been presented.
- The use of $CoFe_2O_4$@p(DVB-co-NVP) copolymer as sorbent provides good extraction of the LIL, LYR, and MNMA, through hydrophobic, π-π and dipole-dipole interactions.
- The proposed method was applied to three real samples, all of them containing the word 'parfum (fragrance)' on their label. All the samples contained LIL, whereas LYR and MNMA were not found in any sample.

REFERENCES

ONLINE VERSION

[1] Regulation (EC) No 1223/2009 of the European Parliament and of the Council of 30 november 2009 on cosmetic products. Available on: https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=celex%3A32009R1223

[2] V. Vállez-Gomis, J. Grau, J.L. Benedé, D.L. Giokas, A. Chisvert, A. Salvador, Anal. Chim. Acta 1153 (2021) 338271

[3] V. Vállez-Gomis, S. Carchano-Olcina, J.L. Benedé, A. Chisvert, A. Salvador, Microchem. J. 183 (2022) 108044

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