STIR BAR SORPTIVE-DISPERSIVE MICROEXTRACTION MEDIATED BY MAGNETIC NANOPARTICLES-METAL ORGANIC FRAMEWORK COMPOSITE FOR THE DETERMINATION OF N-NITROSAMINES IN COSMETIC PRODUCTS

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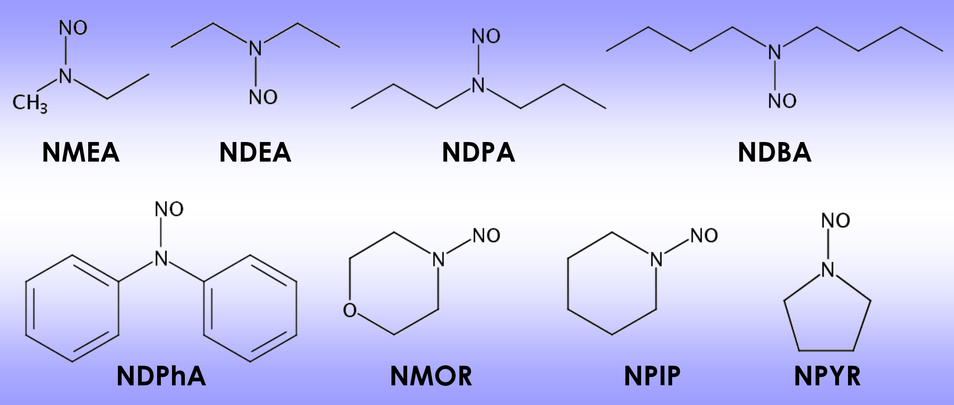
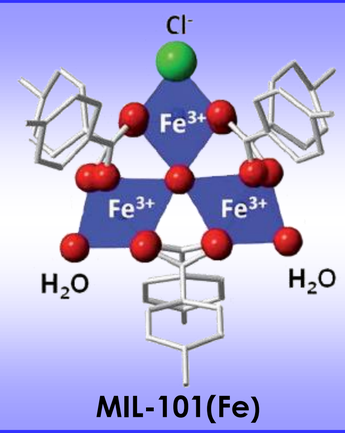
INTRODUCTION

N-nitrosamines are a family of organic compounds to which mutagenic, carcinogenic, and teratogenic effects have been attributed:

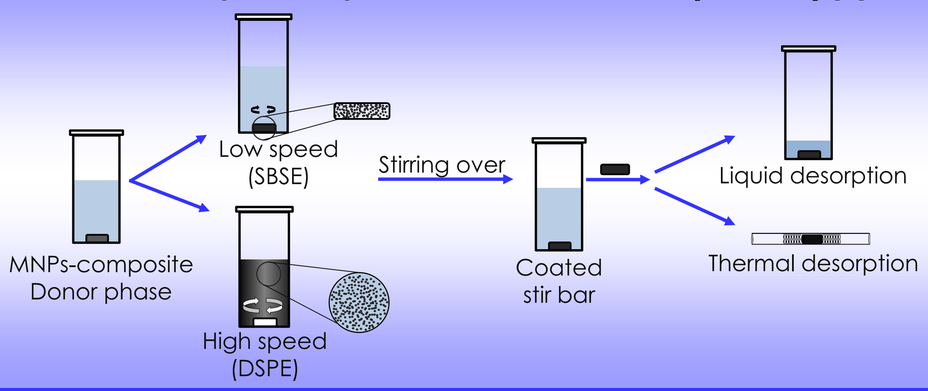
- They can be present in cosmetics containing nitrosating and amine ingredients
- Prohibited by the European Regulation on Cosmetic Products (Annex II)
- Scientific Committee on Consumer Safety stablished a limit of 50 µg/kg for all N-nitrosamines contained in both raw materials and finished cosmetic products in order to ensure the safety

The **aim** of this work is to develop and validate a new analytical method to determine trace levels of eight hazardous N-nitrosamines in cosmetic products employing SBSDME mediated by a novel magnetic nanoparticles-metal organic framework composite, $CoFe_2O_4$/MIL-101(Fe)

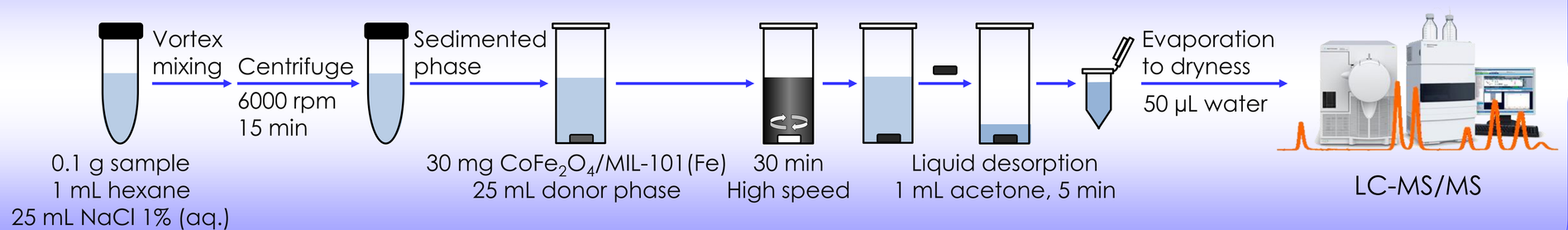




Stir bar sorptive-dispersive microextraction (SBSDME) [1]



EXPERIMENTAL

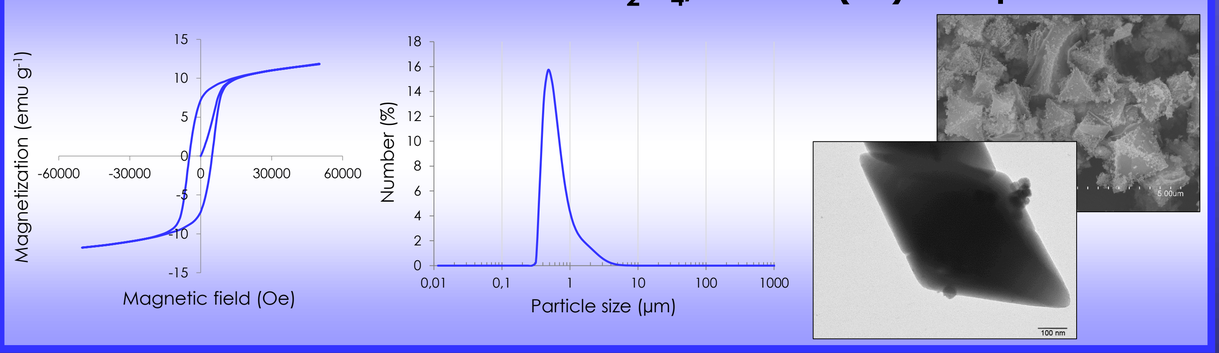


LC-MS/MS Conditions

- Injection volume: 10 µL
- Column: Zorbax SB-C18 (50x2.1 mm, 1.8 µm)
- Column temperature: 35 °C
- Mobile phase: gradient MeOH: H_2O (0.1 % formic acid)
- Flow rate: 0.3 mL min^{-1}
- Acquisition mode: ESI^+-MRM

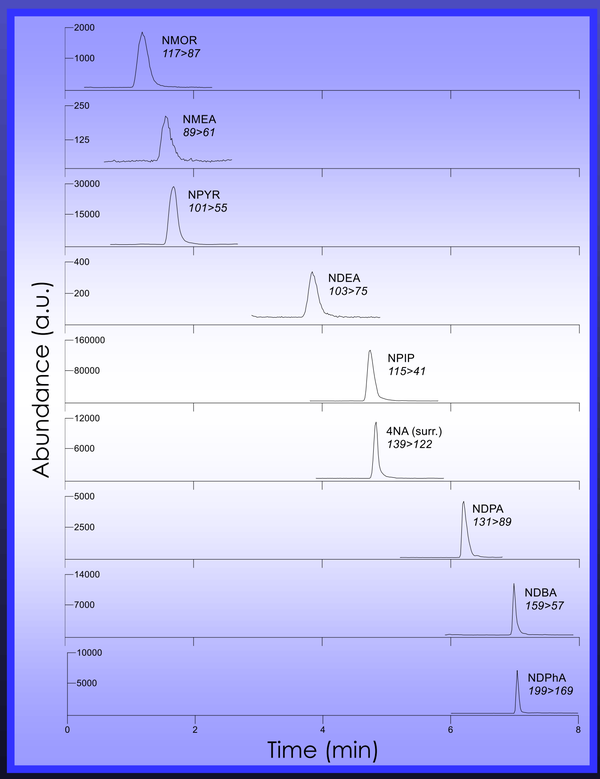
RESULTS AND DISCUSSION

Characterization of the $CoFe_2O_4$/MIL-101(Fe) composite



Analysis of cosmetic samples

- ✓ The proposed method was satisfactorily applied to **3 cosmetic samples** with different matrices:
  - 1 shower gel (sample A)
  - 2 body creams (samples B,C)
- ✓ Several **N-nitrosamines** were detected in the samples, and even significant concentrations of some of them were found:
  - **NDBA**: sample A, <LOQ
    sample B, 160 ± 30 µg kg^{-1}
  - **NDEA**: sample A, 440 ± 20 µg kg^{-1}
    sample B, 240 ± 50 µg kg^{-1}
  - **NDPhA**: sample A, <LOQ
  - **NPIP**: sample B, <LOQ



MRM cromatograms obtained by applying the proposed method to a body cream (sample B) spiked with the target analytes at 100 µg L^{-1}

Analytical features of the proposed method

- ✓ High level of **linearity** (R^2 > 0.990) at least to 100 µg L^{-1}
- ✓ **Limits of detection** (*3 S/N*): 0.06 – 0.3 µg L^{-1} (3 – 13 µg kg^{-1} in sample)
- ✓ **Limits of quantification** (*10 S/N*): 0.2 – 0.8 µg L^{-1} (10 – 40 µg kg^{-1} in sample)
- ✓ **Enrichment factors**: 4 – 62
- ✓ **Intra-day** and **inter-day repeatability**, expressed as RSD (%):
  - 5.6 – 13.9 % and 8.8 – 17.0 % at 10 µg L^{-1}
  - 5.9 – 8.7 % and 6.2 – 10.8 % at 100 µg L^{-1}

✓ **PRECISION**

- ✓ Quantitative **recovery values**, 96 – 109 %, using standard addition calibration

✓ **ACCURACY**

Conclusions

The proposed method expands the analytical applicability of SBSDME to the analysis of cosmetic products with new magnetic materials. Moreover, its good analytical features make it useful to perform the quality control of cosmetic products. The method is in accordance with the principles of the so-called Green Analytical Chemistry, as it is harmless to the operator and the environment.

[1] J.L. Benedé, A. Chisvert, D.L. Giokas, A. Salvador, *J. Chromatogr. A* 1362 (2014) 25-33.

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Consulta otras comunicaciones presentadas por el GICAPC en la **XXII Reunión de la Sociedad Española de Química Analítica:**

Determination of nitro musks in environmental waters by stir bar sorptive dispersive microextraction followed by thermal desorption-gas chromatography-mass spectrometry. J.L. Benedé, A. Chisvert, A. Salvador. Flash Communication. Ver comunicación.

Stir bar sorptive-dispersive microextraction mediated by a magnetic nanoparticles-metal organic framework composite for the determination of n-nitrosamines in cosmetic products. P. Miralles, I. Van Gemert, A. Chisvert, A. Salvador. Flash Communication. Ver comunicación.

Development of an analytical method for the determination of acrylamide in cosmetic products based on dispersive liquid-liquid microextraction. L. Schettino, J.L. Benedé, A. Chisvert, A. Salvador. Flash Communication. Ver comunicación.

Determination of hydroxylated ingredients with preservative activity in cosmetic products by gas chromatography-mass spectrometry. C. Azorín, J.L. Benedé, A. Chisvert, A. Salvador. Ver comunicación.

A green analytical method for the determination of hydroxyethoxyphenyl butanone in cosmetic products. P. Miralles, J.L. Benedé, A. Mata-Martín, A. Chisvert, A. Salvador. Ver comunicación.

Determination of polycyclic aromatic hydrocarbons in cosmetics by stir bar sorptive dispersive microextraction and gas chromatography-mass spectrometry. Vállez-Gomis, J. Grau, J.L. Benedé, A. Chisvert, A. Salvador. Ver comunicación.

Reversed-phase dispersive liquid-liquid microextraction prior to liquid chromatography-tandem mass spectrometry for the determination of acrylamide in cosmetic products. L. Fernández, J.L. Benedé, A. Chisvert, A. Salvador. Ver comunicación.

Development of dispersive liquid-solid microextraction: application to the determination of cortisone and cortisol in human saliva. J. Grau, J.L. Benedé, A. Chisvert, A. Salvador. Ver comunicación.