

# Inverse Supercritical Fluid Extraction and Miniaturized AF4 for the Analysis of Nanoparticles in Commercial Sunscreens

## General Information

ID0044

<b>Application</b>	Nano, Cosmetics
<b>Technology</b>	mAF4-UV-MALS, ICP-MS
<b>Info</b>	Postnova AF2000 MT, PN3211 UV-Vis, PN3621 MALS, Agilent 7900 ICP-MS
<b>Keywords</b>	Miniaturized Asymmetrical Flow Field-Flow Fractionation, Multi-Angle Light Scattering, Inverse Supercritical Fluid Extraction, Sunscreens, Titanium Dioxide Nanoparticles

## Introduction

Due to the complexity of commercial sunscreen formulations, the determination of their nanoparticle content is usually very challenging and requires a tedious sample preparation step including the application of potentially hazardous organic chemicals [1,2,3]. We report here a novel analytical methodology to overcome these drawbacks based on the combination of Inverse Supercritical Fluid Extraction (I-SFE) and Miniaturized Asymmetrical Flow Field-Flow Fractionation hyphenated with UV-Vis and Multi-Angle Light Scattering (mAF4-UV-MALS) [4,5]. This approach allows for the fast and reliable fractionation and sizing of titanium dioxide nanoparticles in commercial sunscreens, thus representing a promising tool for the verification of the nano-labelling of such products.

## Sample preparation using Inverse Supercritical Fluid Extraction

Supercritical Fluid Extraction is a well-known, mild and environmentally friendly tool applied in a multitude of industrial processes including, for example, the extraction of caffeine from coffee beans or essential oils from herbs. In the preparation of sunscreen samples it is used in its inverse form, thereby taking advantage of the high solubility of sunscreen matrix constituents in supercritical carbon dioxide. This leaves behind the insoluble titanium dioxide nanoparticles for analysis by mAF4-UV-MALS (Figure 1).

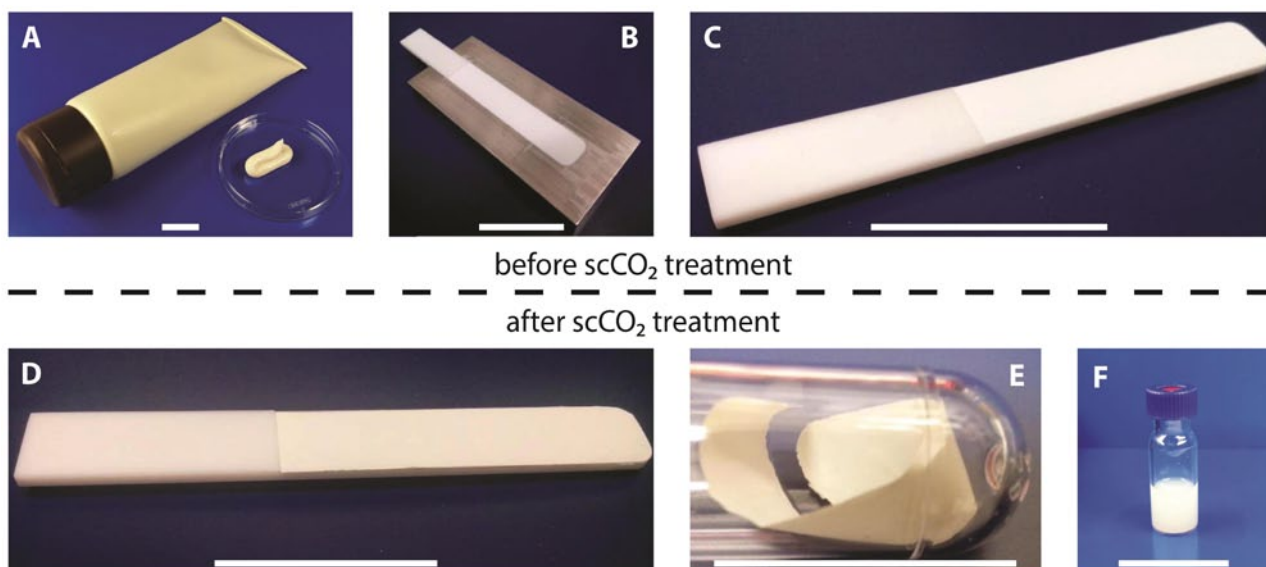


Figure 1: Different stages of the sample preparation process. A: Freshly dispensed sunscreen; B+C: Cream deposition onto Teflon cartridge; D+E: Dried sunscreen; F: Dispersed sunscreen ready for analysis. With permission from Elsevier from [4].

## Miniaturized AF4

AF4 in its miniaturized form is the fractionation cartridge of choice when it comes to short analysis times as well as low solvent and sample consumption [6,7]. In combination with I-SFE, it enables the rapid analysis of the nanoparticulate content in commercial sunscreens.

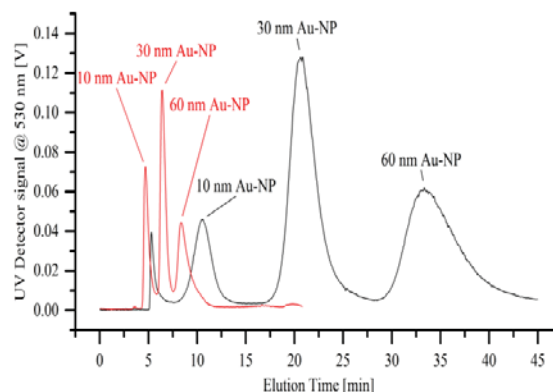
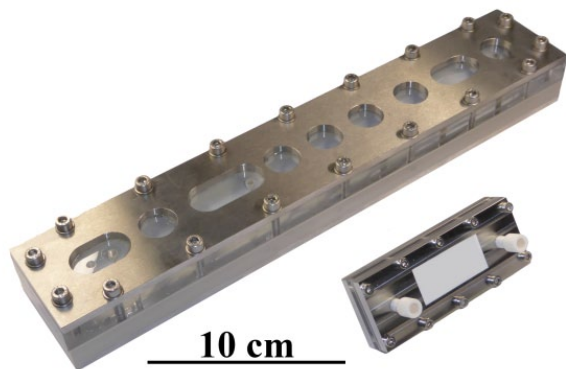


Figure 2: Photograph (left) shows the difference in dimensions of the mAF4 cartridge when compared with the conventional analytical AF4 cartridge. The graph (right) shows the respective particle size fractograms obtained using the two cartridges for a mixture of gold nanoparticles (10 nm, 30 nm, 60 nm). (With permission from [6]).

## Analysis of Commercial Sunscreen using mAF4-UV-MALS

Five different commercial sunscreens were investigated for their nanoparticle content using I-SFE followed by mAF4-UV-MALS analysis. Nanoparticulate titanium dioxide identified via ICP-MS was found in three sunscreens (NiveaCream15, NiveaCream30 and GarnierCream30), which was in agreement with the nano-labelling in the respective ingredients lists. The particle size distribution determined via MALS revealed particle sizes ranging from 50 nm to approximately 450 nm in diameter of gyration for all three samples. For both sunscreens that were not nano-labelled (CoopCream50 and SherpaSpray30), no nanoparticles were detectable (Figure 3).

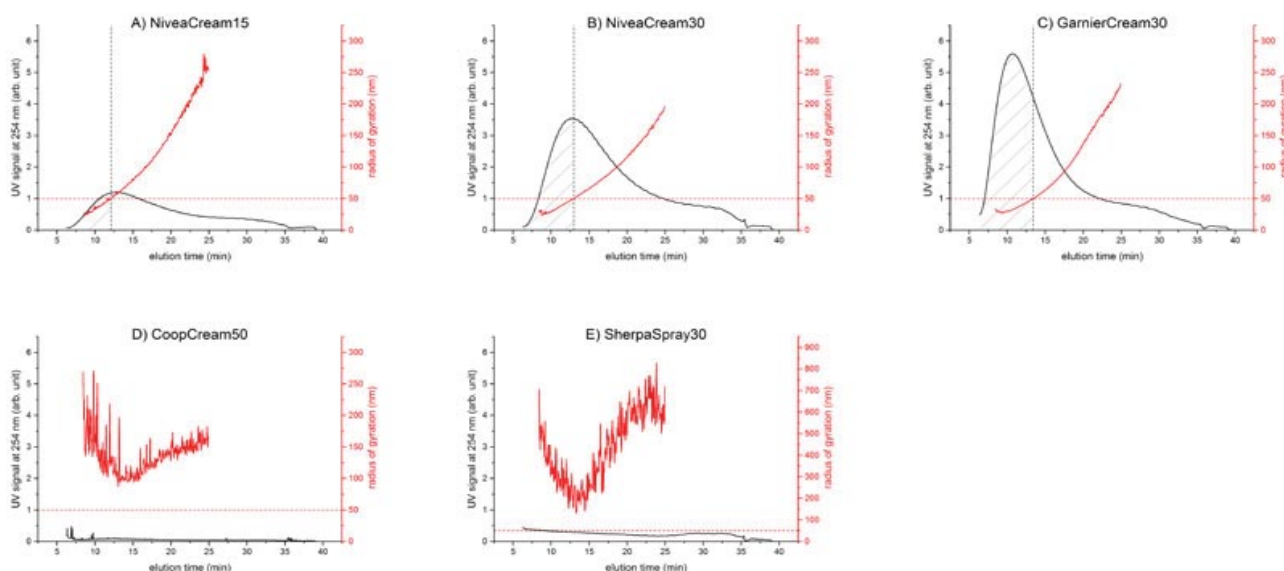


Figure 3: The mAF4-UV-MALS fractograms obtained for five different commercial sunscreens A-E (Adapted with permission from the American Chemical Society from [5]).

## Conclusion

The combination of Inverse Supercritical Fluid Extraction and Miniaturized Asymmetrical Flow Field-Flow Fractionation hyphenated with UV- and MALS-detection proved to be a highly powerful and efficient tool for the verification of the nanocontent of commercial sunscreens. Due to its robustness and wide applicability, this setup is not only limited to the analysis of sunscreens, but may also be a helpful tool for the investigation of nanoparticle-containing cosmetics in general.

## References

- [1] Contado, C. and Pagnoni A., *Analytical Chemistry*, 2008, 80(19), 7594-7608.
- [2] Nischwitz, V.; Goenaga-Infante, H., *Journal of Analytical Atomic Spectrometry*, 2012, 27, 1084-1092.
- [3] Sogne V., Meier F., Klein T., Contado C., *Journal of Chromatography A*, 2017, 1515, 196-208.
- [4] Müller D., Cattaneo S., Meier F. et al., *Journal of Chromatography A*, 2016, 1440, 31-36.
- [5] Müller D., Nogueira M., Cattaneo S., Meier F. et al., *Analytical Chemistry*, 2018, 90(5), 3189-3195.
- [6] Müller D., Cattaneo S., Meier F., Welz R., deMello A.J., *Frontiers in Chemistry*, 2015, 3.
- [7] You Z., Meier F., Weidner S., *Separations*, 2017, 4(1), 8-19.

## Acknowledgements

Funding by the European Union is gratefully acknowledged (Project SMARTNANO, FP7 Programme, contract no. 280779)