Supercritical CO_2 Treatment as a Novel Sample Preparation Method for the Analysis of Nanoparticle Content in Sunscreen Agents

D. Müller •, S. Cattaneo, F. Meier ••, R. Welz ••, T. de Vries •••, M. Portugal-Cohen **, D.C. Antonio **, C. Cascio **, L. Calzolai **, D.Gilliland **, A. de Mello •

Today, a growing number of consumer products make use of the unique physical and chemical properties of nanomaterials. As the number of such products increases, the ability to thoroughly characterize their properties and functionality becomes critical. In particular, the recent regulatory efforts concerning the labelling of nanoparticle-containing products call for the development of simple and robust sample preparation protocols enabling a reliable detection and quantification of nanoparticulate ingredients in complex matrices. In this work, we demonstrate the use of supercritical carbon dioxide (scCO$_2$) as a method of sample preparation for the analysis of complex nanoparticle-containing samples—in our case, a model sunscreen agent with titanium dioxide nanoparticles. This novel treatment can be executed in a single step using a lab scale supercritical fluid extraction system and has important ecological as well as economic advantages over currently used sample preparation techniques involving organic solvents.

Supercritical CO_2 is well-known for its application in extraction processes and is commonly used to extract small and/or non-polar molecules from natural materials under very mild conditions (e.g. essential oils from herbs or caffeine from coffee beans). In these prior applications, however, the scCO$_2$ was used to dissolve and extract the compounds of interest. In this work, it is used as a novel sample treatment to simplify the matrix of a model sunscreen by removing unwanted components, thus keeping the target nanomaterials (in our case titanium dioxide nanoparticles) in the residual sample.

The method was developed and tested on a model sunscreen spiked with TiO_2 nanoparticles (Figure 1a). The sunscreen was placed on a Teflon support surrounded by a stainless steel holder with a small recess (Figure 1b) and the excess sunscreen was removed using a spatula. The Teflon support was then removed from its holder (Figure 1c) and placed in the extraction vessel of a lab scale supercritical fluid extraction system, where it was subjected to a constant flow of scCO$_2$. The minimal surface tension of scCO$_2$ allows for thorough sample penetration whilst maintaining the structure of the residual material. After treatment, the remaining sample (Figure 1d) was removed from the support (Figure 1e) and easily re-dispersed in an aqueous solution (Figure 1f).

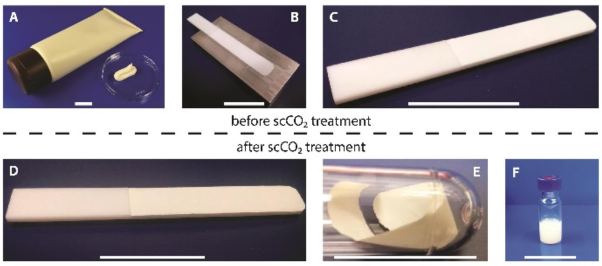

Figure 1: Model sunscreen at different stages before (A—C) and after (D—F) the novel supercritical CO_2 treatment. Scale bars are 25 mm.

After sonication, the re-dispersed sample was directly injected into an asymmetrical flow field-flow fractionation system (AF4) linked to UV and multi-angle light scattering (MALS) detectors.

As shown in Figure 2, the resulting UV curve allows a clear distinction between spiked and non-spiked sample. The black solid line is the signal obtained from the TiO_2 spiked sunscreen after scCO$_2$ treatment and resuspension in water. A wide peak, indicating particles with a broad size distribution and hence, eluting over an extended separation period, is evident. For the blank model cream (black dotted line, treated in the same way), no significant signal was detected over the whole separation cycle. The size distribution was measured by MALS (red line), and was found to be very similar to that of the original TiO_2 suspension used to spike the samples. The measurements were verified by a Scanning Transmission Electron Microscope (STEM) and energy-dispersive X-ray spectroscopy (EDX) analysis.

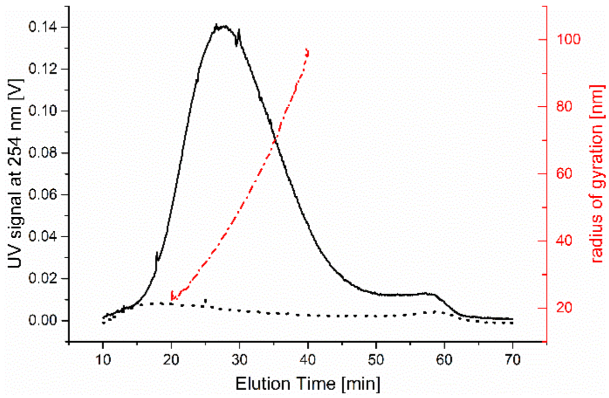

Figure 2: Elugrams of the TiO_2 spiked (solid line) and blank (dotted line) model sunscreens, after scCO$_2$ treatment and resuspension in water. The red line shows the radius of gyration measured by MALS.

The results demonstrated that the novel scCO$_2$ sample preparation method allows a precise determination of the nanoparticle content of sunscreens, while essentially maintaining the size distribution of the nanoparticles. Although the method is demonstrated using a model sunscreen matrix, we expect it to be applicable to a wide class of consumer products.

This work is supported by the European Commission 7th Framework Programme (project SMART-NANO NMP4-SE-2012-280779). CSEM thanks them for their support.

• CSEM/ETH Zurich, Biochemical Engineering

•• Postnova Analytics GmbH, Landsberg am Lech, Germany

••• Feyecon Carbon Tioxide Technologies, Weesp, The Netherlands

* AHAVA Dead Sea Laboratories, Lod, Israel

** Joint Research Center (JRC), Ispra, Italy