Characterization of Metal-Containing Nanoparticles in Tattoo Ink Using Asymmetrical Flow Field-Flow Fractination Coupled with Multi Angle Light Scattering and ICP-MS

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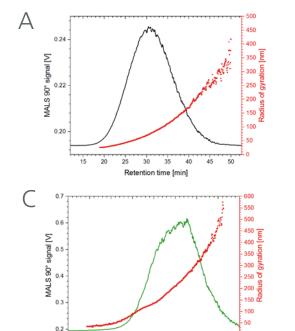
Introduction

Nowadays, tattoos have become increasingly popular with both men and women, particularly with younger people. However, with gaining popularity, more and more adverse effects have been reported including infections as well as allergies. This is due to the fact that tattoo inks can be complex in their formulation, containing several of a range of more than 100 pigments and additives, but also a significant quantity of impurities. The pigments are normally of particularly low purity and a majority of the ingredients are not even approved for an application in cosmetic products in the European Union. Despite these well-known facts, harmonized and well-established analytical methods for the comprehensive characterization of tattoo ink ingredients are still lacking [1].

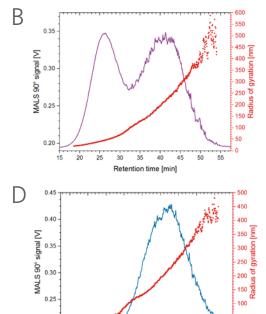
A powerful technology for the investigation of the particulate content in tattoo inks is Asymmetrical Flow Field-Flow Fractionation (AF4) coupled with Multi Angle Light Scattering (MALS) and Inductively-coupled Plasma Mass Spectrometry (ICP-MS) [2]. In this study, AF4-MALS-ICP-MS was applied to characterize four commercial tattoo inks - Outlining Black, Purple Deep Violet, Green Grasshopper and Blue Ice.

Sizing of Particulate Tattoo Ink Ingredients Using AF4-MALS

Using AF4-MALS, the particle size distribution in all four investigated tattoo inks could be assessed and it shows that all have a significant nanoparticulate content. While Outlining Black, Green Grasshopper and Blue Ice revealed monomodal particle size distributions ranging from 30 - 350 nm, 35 - 550 nm and 25 - 450 nm radii of gyration (Rg), respectively, Deep Purple Violet showed a bimodal distribution with particle sizes ranging from 20 - 550 nm Rg (Fig. 1).



Retention time [min]



30 35 40 45

Retention time [min]

Figure 1: AF4-MALS fractograms with overlaid size (Rg) in red of Outlining Black (A), Purple Deep Violet (B), Green Grasshopper (C) and Blue Ice (D).



Chemical Identification of Particulate Tattoo Ink Ingredients Using AF4-ICP-MS

Coupling to ICP-MS, AF4 enabled size-resolved chemical identification of particulate tattoo ink ingredients. By this means, it could be demonstrated that Outlining Black contains particulate titanium (Ti) and copper (Cu), but no aluminium (Al), while Green Grasshopper and Blue Ice contain all three elements in particulate form. Purple Deep Violet, however, contains particulate Ti and Al, but no Cu (Fig. 2). All investigated metals were most likely present as pigments in their oxidic state as TiO₂, Al₂O₃ and CuO.

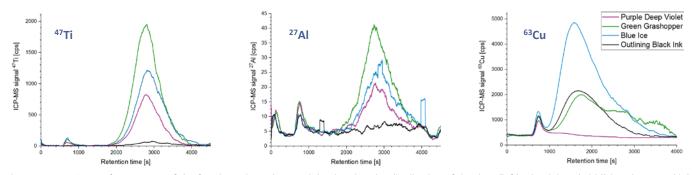


Figure 2: AF4-ICP-MS-fractograms of the four investigated tattoo inks showing the distribution of titanium (left), aluminium (middle) and copper (right).

Comparison of AF4-ICP-MS with Batch ICP-MS Results

By comparing the results obtained from AF4-ICP-MS with batch ICP-MS measurements, a quantitative differentiation between particulate and dissolved metals in the investigated tattoo inks could be achieved. While Al was predominantly dissolved, most of the Ti and Cu was present in particulate form (Table 1).

Sample	²⁷ Al [mg/mL] (AF4)	²⁷ Al [mg/mL] (Batch)	⁴⁷ Ti [mg/mL] (AF4)	⁴⁷ Ti [mg/mL] (Batch)	⁶³ Cu [mg/mL] (AF4)	⁶³ Cu [mg/mL] (Batch)
Outlining Ink Black	< LOD	< LOD	7.28	< LOD	0.18	0.18
Purple Deep Violet	0.3	2.7	65.2	114.0	< LOD	0.001
Green Grasshopper	0.8	5.9	160.2	195.3	2.2	2.0
Blue Ice	0.4	5.9	109.6	196.9	4.6	4.2

Table 1: Summary of the obtained results from AF4-ICP-MS and batch ICP-MS.

Conclusion

This study demonstrates the excellent suitability of AF4-MALS-ICP-MS for the comprehensive characterization of tattoo inks. Besides the particle size distributions obtained from the MALS data, ICP-MS additionally allows statements on the elemental distributions of various metals as a function of the respective particle sizes, providing valuable insight into the composition of the inks. This can not only facilitate the reliable identification and quantification of possible allergenic ingredients (and thus a better risk assessment) but may also help tattoo ink manufacturers to improve their formulations, eventually leading to safer products.

References

[1] Piccinini P., Pakalin S., Contor L., Bianchi I., Senaldi C., Safety of tattoos and permanent make-up. Final report, EUR 27947 EN; doi: 10.2788/011817.

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