SHIMADZU

FP 515

Quick Detection and Confirmation of Pigments in Cosmetics by MALDI-MS and High-Energy CID MALDI-MS/MS Analyses

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1. Introduction

Colour is a fundamental property for the success of a cosmetic product, as it determines the attractiveness for consumers and boosts confidence in the body image. Pigments are typically used as colourants in decorative make-up and are highly regulated for their safety for human use. Besides safety, the choice of product by customers is also influenced by the origin of ingredients based on the lifestyle or dietary practices. Here, we propose a simple and fast analytical workflow consisting of the extraction of the pigments from the lipstick material, whose identities were confirmed through negative mode high-energy CID MALDI-MS/MS analyses, based on precursors detected in MS profiles previously obtained on a dual polarity benchtop linear MALDI-TOF MS (Figure 1).

2. Methods

Samples of commercial branded lipsticks were purchased in the UK: two non-vegan/non-organic, one organic (non-vegan), one vegan/halal (non-organic). Pigment standards were purchased from Merck Life Science. The sample preparation involved placing an amount of lipstick material in 50 µL of water/methanol (1:1) or dichloromethane, depending on the pigment solubility. Pigment extraction was carried out by sonication for 30 min, followed by centrifugation. The extracted pigments were spotted with 9-Aminoacridine (9-AA, 10 mg/mL in methanol). MALDI-MS analyses were conducted in negative ion mode on a dual polarity benchtop linear MALDI-TOF MS to measure the isotopic masses. High-energy CID MALDI-MS/MS analyses were conducted in negative ion mode on a MALDI-TOF/TOF mass spectrometer (MALDI-7090, Shimadzu) to confirm the identity of the pigment species.

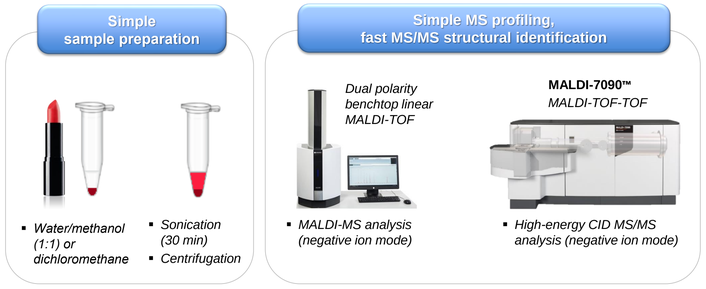

Figure 1. Sample preparation and analysis workflow for the detection and identification of pigments in cosmetics.

3. Results

3-1. MALDI-MS analyses

In Europe, pigments are regulated by the European Regulation of Cosmetic Products (EC 1223/2009), which imposes that they must be reported in product labelling with their unique Colour Index (CI) number (Table 1). Cultural and dietary practices also determine the choice of product by customers. For example, the vegan/halal market forbids the use of animal-derived pigments, e.g. Carmine, which is a strong red-coloured pigment that is extracted from the body of Cochineal insects (Figure 2). The four samples of lipsticks, which are representative of the different markets e.g. vegan/halal, organic, non-vegan/non-organic, were first screened on a dual polarity benchtop linear MALDI-TOF mass spectrometer for the presence/absence of the pigments according to the product labelling.

Figure 2. Carmine pigment.

Table 1. List of common pigments which are approved for use in cosmetics in Europe.

Common name	Colour Index (CI)	Colour
YELLOW 5 LAKE	19140	
YELLOW 6 LAKE	15985	
RED 6	15850	
RED 7	15850:1	
RED 22 LAKE	45380	
RED 27	45410:1	
RED 28 LAKE	45410:2	
RED 36	12085	
CARMINE	75470	
BLUE 1 LAKE	42090	

Table 2. Pigments reported in the ingredient list of the four commercial lipsticks.
* Depending on the shade, some pigments may/may not be present.
a confirmed by isotope distribution.
b confirmed by MSMS.

non-vegan/non-organic lipstick 1		
+/- May contain *	**Detected**	**ID confirmed**
CI 45380 / RED 22 LAKE	YES	*a*
CI 15850 / RED 7	YES	*b*
CI 15985 / YELLOW 6 LAKE	YES	*b*
CI 45410 / RED 28 LAKE	NO	–
CI 19140 / YELLOW 5 LAKE	NO	–
CI 42090 / BLUE 1 LAKE	NO	–
CI 75470 / CARMINE	NO	–

non-vegan/non-organic lipstick 2		
+/- May contain *	**Detected**	**ID confirmed**
CI 45410 / RED 28 LAKE	YES	*a*
CI 15850 / RED 7	YES	*b*
CI 15985 / YELLOW 6 LAKE	YES	*b*
CI 19140 / YELLOW 5 LAKE	YES	*b*
CI 45380 / RED 22 LAKE	NO	–
CI 42090 / BLUE 1 LAKE	NO	–
CI 75470 / CARMINE	NO	–

Organic (non-vegan) lipstick 3		
Contains	**Detected**	**ID confirmed**
CI 75470 / CARMINE	YES	*b*

Vegan/Halal (non-organic) lipstick 4		
Contains	**Detected**	**ID confirmed**
CI 15850:1	YES	*b*
CI 12085	YES	*a*

The instrument was able to generate pigment fingerprints for all lipstick samples. Table 2 reports a summary of the pigments listed in the labels of the four commercial lipsticks, those which were/were not found and how their identity was confirmed. Cosmetic manufacturers often produce their product lines in different colours or shades. The same ingredients/pigments may be listed for the whole product line whereas, in fact, depending on the colour, some of the pigments may not actually be present in the formulation.
The pigment identity was tentatively confirmed using the monoisotopic mass. For Red 22 and Red 28 pigments, whose bromine and chlorine elements provide a very distinctive isotopic distribution, a comparison between the isotopic signatures of the computed and detected species was used to confirm the pigment identity. Figure 3 shows the negative mode MALDI spectrum of one of the non-vegan/non-organic lipsticks (lipstick 2).

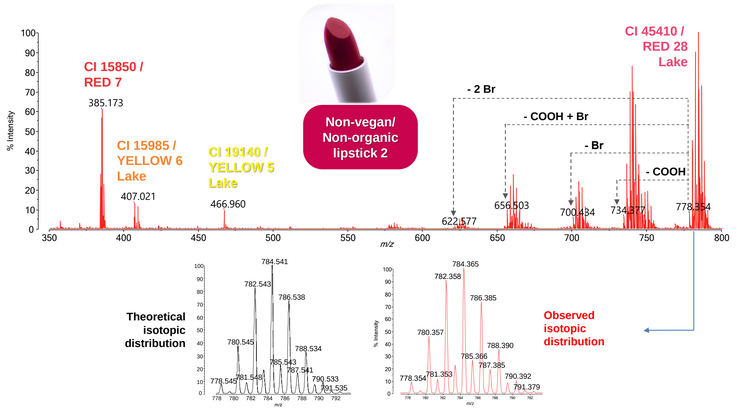

Figure 3. Negative mode MALDI spectrum of the pigments in the non-vegan/non-organic lipstick 2.

3. Results

3-2. High-energy CID MALDI-MS/MS analyses

Pigment's identity was confirmed through comparison between the MS/MS fingerprints of the pigment standard and the sample obtained through negative mode high-energy CID MALDI-MS/MS analyses on the MALDI-7090. Axial Spatial Distribution Focussing (ASDF) technology [1] resulted in isotopically resolved MS/MS fragments with good mass accuracy, allowing confirmation of the pigment identity with high confidence. Figure 4 shows the negative mode high-energy CID MS/MS spectrum of CI 75470/Carmine pigment (*m/z* 491.083), expected in lipstick 3 (organic (non-vegan)). The fragmentation pattern of Carmine in the sample matches that of the corresponding standard.

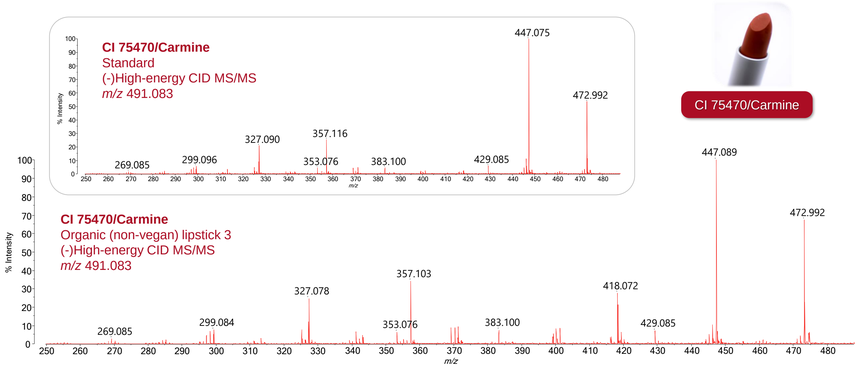

Figure 4. Negative mode high-energy CID MS/MS spectrum of CI 75470/Carmine (*m/z* 491.083) in lipstick 3 (organic (non-vegan)). The inset shows the negative mode MS/MS spectrum of the corresponding pigment standard.

Conclusions

This work demonstrates the powerful combination of a dual polarity benchtop linear MALDI-TOF instrument and the MALDI-7090 to detect and confirm the identity of pigments in cosmetics. The simple extraction method proposed, combined with the negative ion mode detection, offer a quick and simple analytical solution to obtain qualitative information on the pigment content of decorative make-up products. Where a conclusive identification of the pigments was required, the high-resolution MS/MS capability of the MALDI-7090 enabled to confirm the identity with high confidence.

References

[1] Belgacem, O., Pittenauer, E., Openshaw, M.E., Hart, P.J., Bowdler, A., Allmaier, G., 2016. Rapid Communications in Mass Spectrometry, 30(3):343-51.