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Application News

MALDI-TOF Mass Spectrometry Analysis MALDI-8030

# Negative Mode Detection of Pigments in Cosmetics using the MALDI-8030 Dual Polarity Benchtop MALDI-TOF Mass Spectrometer

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## User Benefits

- Simple easy analysis of pigments in lipsticks on an affordable benchtop MALDI-TOF
- Quality spectra with good resolution and accuracy in negative ion mode is useful in the field of cosmetics safety
- Workflow useful for identifying cosmetic product compatibility for organic, vegan and halal practitioners

## ■ Introduction

Cosmetics is a huge industry that is still growing, with an estimated value of around USD 863 billion in 2024 [1]. The three major sectors include skin care, hair care and make-up. 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. They can be present in the free form, which is partially hydro-soluble and miscible; or as 'lakes', which are water-insoluble, more stable derivatives, imparting long-lasting properties to the make-up product. The lakes of the pigments are produced through incorporation of a salt (e.g., aluminium, barium, calcium, zirconium) to the pigment core.

In Europe, the use and safety of pigments in cosmetics are regulated by the European Regulation of Cosmetic Products (EC 1223/2009). Pigments which are permitted for use in cosmetics must be reported in product labelling with their unique Colour Index (CI) number alongside their common names. Table 1 lists some of the most common pigments that can be found in lip products.

Besides safety, the choice of product by customers is also influenced by the origin of ingredients based on the lifestyle or dietary practices, so this is analytically important to ascertain.

For example, the vegan/halal market forbids the use of animal-derived pigments. Among these is Carmine, a strong red-coloured pigment which is extracted from the body of Cochineal insects (Fig 1). Besides cultural barriers to the use of this pigment, Carmine is also an allergen. In contrast with the vegan/halal market, there is also the organic market, which doesn't restrict the use of natural (and animal)-based pigments, such as Carmine, but requires the organic source of pigments is certified.

Here, we demonstrate the capability of the dual polarity MALDI-8030 benchtop linear MALDI-TOF mass spectrometer to detect the presence of pigments in lipsticks. Examples of vegan/non-vegan as well as organic lip products have been selected to represent the various markets. We propose a simple and fast method consisting of the extraction of the pigments from the lipstick medium and analysis in negative ion mode (Fig 2).

Fig. 1 Carmine pigment

## ■ Measurement Conditions and Samples

Samples of commercial branded lipsticks were purchased in the UK: two non-vegan/non-organic, one organic (non-vegan), one vegan/halal (non-organic). The following pigment standards were purchased from Merck Life Science: Yellow 6, Yellow 5, and

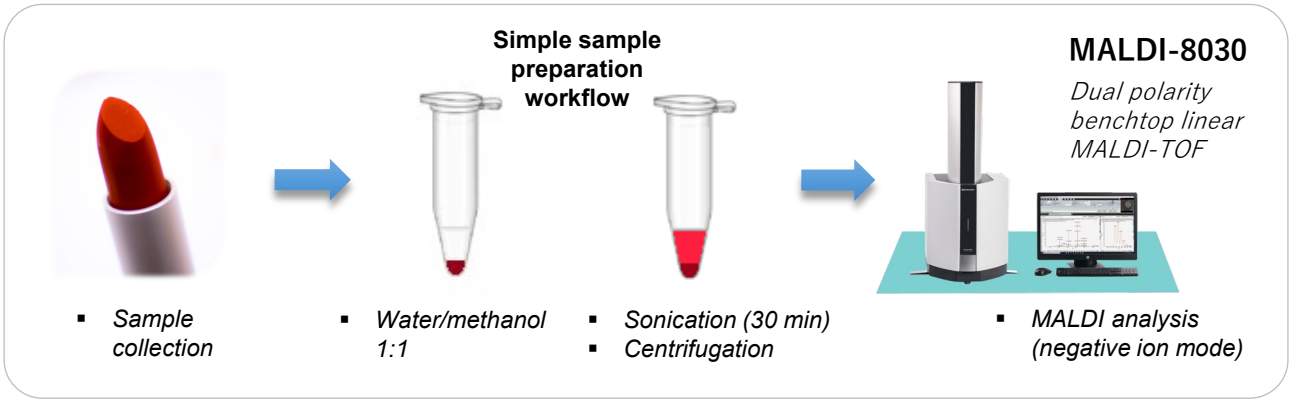


Fig. 2 Sample preparation and analysis workflow for the detection of pigments in cosmetics

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 | |

Carmine. Red 7 and Red 36 were purchased from Tokyo Chemical Industry (TCI). Individual stock solutions of the pigment standards were prepared as 1 mg/mL in water/methanol (1:1).

The sample preparation workflow is illustrated in Fig 2. An amount of lipstick material was placed in a microcentrifuge tube, to which 50 µL of water/methanol (1:1) were added. The pigment extraction was carried out by sonication for at least 30 min, until the solvent solution became coloured and cloudy. This process facilitates the transfer of the pigments from the wax/oil medium into suspension. After centrifugation, the solution containing the extracted pigments was recovered for analysis.

For the MALDI analyses, samples were spotted with 9-Aminoacridine (9-AA, 10 mg/mL in methanol). All analyses were conducted in negative ion mode on the MALDI-8030 to measure the isotopic masses. To confirm the identity of the pigment species in the samples, MALDI-MSMS data were acquired on the MALDI-7090 for the standards and samples, but will not be required in routine analysis (data not shown).

## ■ Results of non-vegan/non-organic lipsticks

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.

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. For purposes of completion, the other pigments were confirmed by MSMS data (data not shown).

Fig 3 shows the negative mode MALDI spectra of the two non-vegan/non-organic lipsticks (lipstick 1 and lipstick 2). For lipstick 1, the following pigments were found: CI 15850/Red 7 (m/z 385.049 exact, m/z 385.078 detected); CI 15985/Yellow 6 Lake (m/z 407.001 exact, m/z 407.007 detected); CI 45380/Red 22 Lake (m/z 642.702 exact, m/z 642.552 detected). For lipstick 2, the following pigments were found: CI 15850/Red 7 (m/z 385.049 exact, m/z 385.173 detected); CI 15985/Yellow 6 Lake (m/z 407.001 exact, m/z 407.021 detected); CI 19140/Yellow 5 Lake (m/z 466.997 exact, m/z 466.960 detected); CI 45410/Red 28 Lake (m/z 778.547 exact, m/z 778.354 detected).

The exact m/z values are calculated for the monoisotopic species, excluding the salt(s).

Table 2 Pigments reported in the ingredient list of the four commercial lipsticks and detection on MALDI-8030.

| 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* |

* Depending on the shade, some pigments may/may not be present.
*a* confirmed by isotope distribution.
*b* confirmed by MSMS (MALDI-7090).

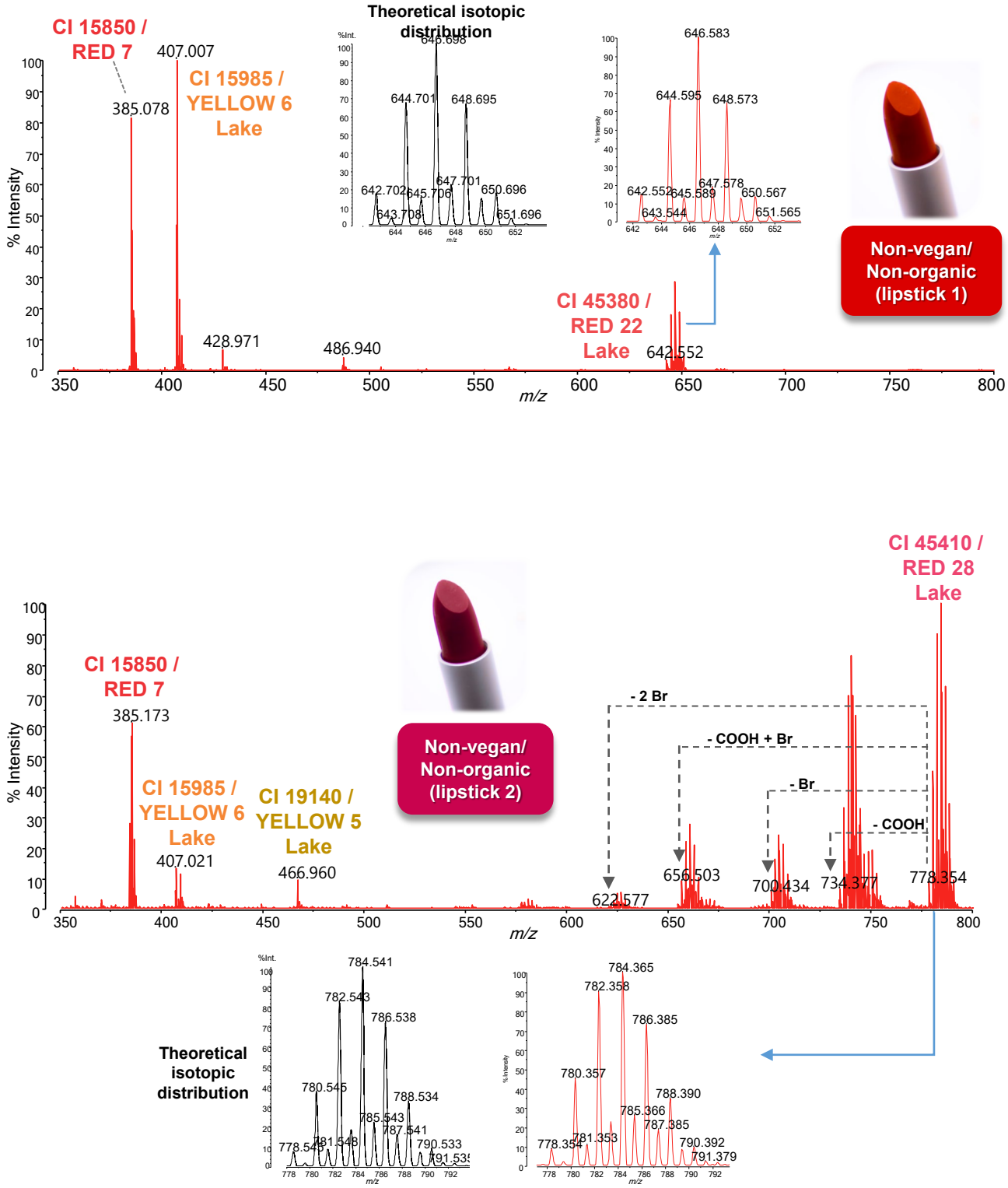


Fig 3. Negative mode MALDI spectra of the pigments in two non-vegan/non-organic lipsticks

## ■ Results of organic (non-vegan) lipstick

Fig 4 shows the negative mode MALDI spectrum of the organic (non-vegan) lipstick (lipstick 3). The expected CI 75470/Carmine pigment was successfully detected (m/z 491.083 exact, m/z 491.060 detected). Note that Carmine is considered to be 'haram' or not permissible in Islamic religion [2].

## ■ Results of vegan/halal (non-organic) lipstick

Fig 5 shows the negative mode MALDI spectrum of the vegan/halal (non-organic) lipstick (lipstick 4). The following expected pigments were found: CI 12085 (m/z 326.033 exact, m/z 325.996 detected); CI 15850:1 (m/z 385.049 exact, m/z 385.002 detected).

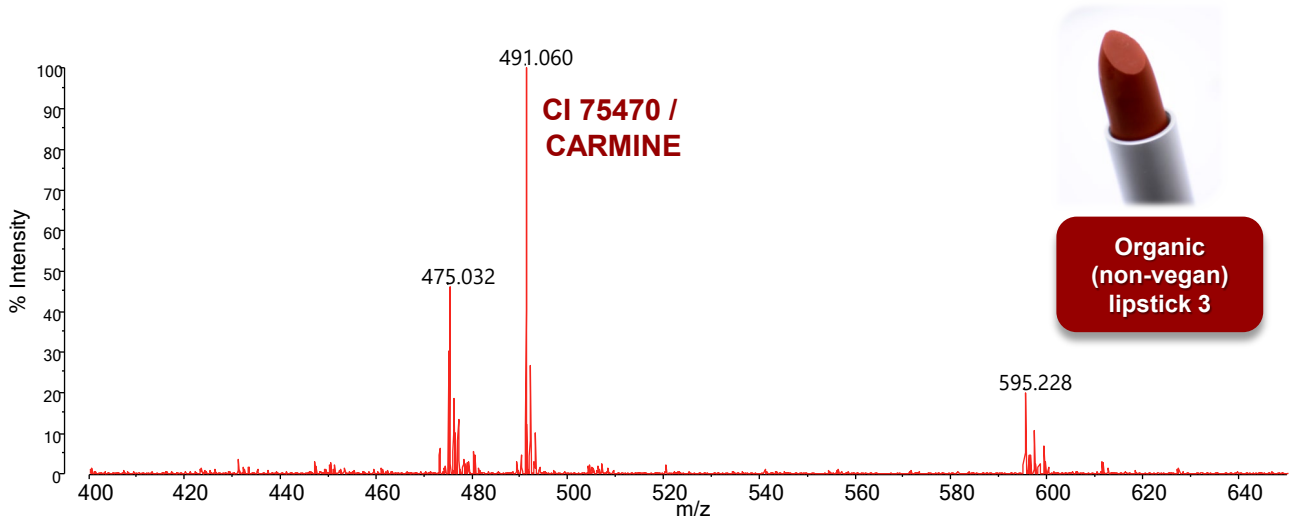


Fig 4. Negative mode MALDI spectrum of pigments in the non-vegan/organic lipstick. The only expected CI 75470/Carmine pigment was successfully detected.

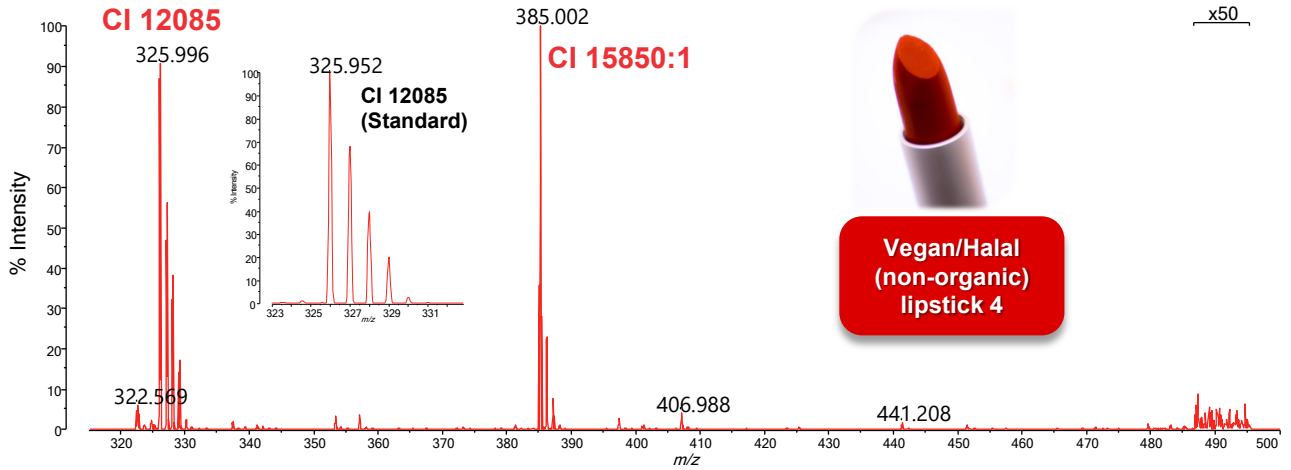


Fig 5. Negative mode MALDI spectrum of pigments in the vegan/non-organic lipstick. Both CI 12085 and CI 15850:1 expected pigments were successfully detected. Carmine was not listed as an ingredient in this lipstick and therefore no peak is detected at m/z 491.

## ■ Conclusion

This application demonstrates the capability of the MALDI-8030 to detect pigments in cosmetics. The examples shown are representative of the different markets e.g., vegan/halal, organic, non-vegan/non-organic.

The simple extraction method proposed, combined with the negative ion mode detection, offers a quick and simple analytical solution to obtain qualitative information on the pigment content of decorative make-up products. This can then be used to confirm their suitability according to the cultural demands of users such as vegans, organic and halal practitioners.

## ■ References

[1] Zion Market Research. 2018. 'A Global Cosmetic Products Market Size, Share 2017: Industry Trends, Growth Analysis and Forecast, 2024." [online]. [Accessed 20 December 2020]. Available from: http://www.globenewswire.com/news-release/2018/06/22/1528369.

[2] Riaz, M.N. and Chaudry, M.M., 2018. 30 Halal Food Model. Handbook of Halal Food Production, p.30.

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