Potential of polymer-based MALDI matrices for the detection of food-relevant low molecular weight compounds: Application to crucial authenticity issues

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Introduction

Matrix-assisted Laser-Desorption Ionization- High-Resolution Mass Spectrometry (MALDI-HRMS), among other Mass Spectrometry (MS) techniques, has become an omnipresent analytical technique in a wide range of research fields for the identification of large molecules (proteins, glycans, polymers). Although MALDI-MS is being used for the analysis of large molecules, its application to Low-Molecular-Weight Compounds (LMWCs) has been regarded, for a long time, to be not appropriate due to the large background from matrix-related signals. This study focuses on the investigation of polymers as potential MALDI matrices for food-related compounds and their application to food studies. To evaluate their efficiency, different compounds were exploited as analytes and polymers were used as MALDI matrices in dairy products authenticity investigation as a case study.

Methods

Polymer-based MALDI matrices were exploited for their efficiency in the ionization of selected groups of analytes (natural products, amino acids, LMW lipids, veterinary drugs etc.). Selected polymers are commercially available and have been studied about their physicochemical properties by Horatz et. al and their application to selected analytes (1). In our study, two polymers were investigated about the specific requirements they should meet in order to allow high-quality measurements for reliable detection of LMWCs, relevant to food authenticity studies (e.g., detection of contamination, discrimination of origin/variety, detection of adulteration). Specifically, polymers are being evaluated about their efficiency as MALDI matrices according to their presence of high absorption at the laser wavelength, high vacuum stability which is obligate for this technique, sufficient solubility in common solvents, chemically inert towards the analyte, and being MALDI silent (no matrix-related signals) in the LMW area. MALDI matrices were also tested for their dual-mode utilization, permitting measurements in both positive and negative ionization mode. For MALDI-TOF analysis, a microflex LRF (Bruker Daltonics, Bremen, Germany) was used, operated in reflector mode. The selected mass range was set up to 1500 Da, as LMW food-related metabolites, lipids and residues are detected within this mass window.

Results

Potential of polymers as MALDI matrices

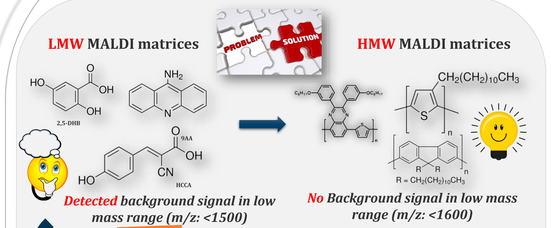

Figure 1. Reflector positive mode MALDI MS spectra of (a) Reserpine (RP) as analyte (1 μg/mL in Acetone) and 2,3-DHB (10 mg/mL) as matrix (b) detection and identification of RP in laser intensity 30%

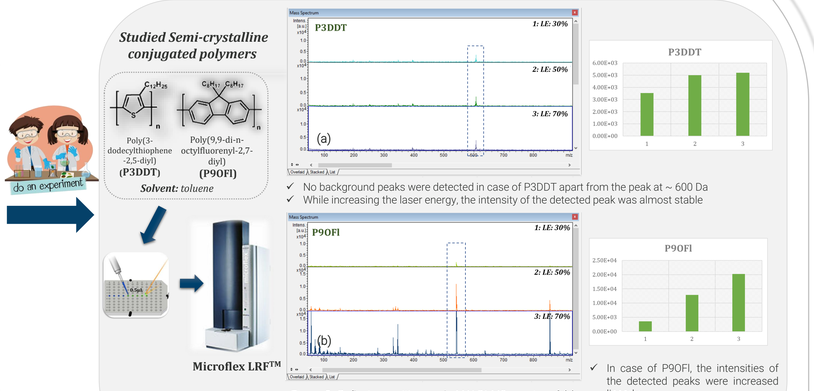

Figure 2. Reflector positive mode MALDI MS spectra of (a) only the pure matrix P3DDT in toluene (100μg/mL) in laser intensities 1: 30%, 2: 50%, 3: 70% (b) only the pure matrix P9OFI in toluene (100μg/mL)) in laser intensities 1: 30%, 2: 50%, 3: 70%

Ionization efficiency & application to real samples

A straightforward approach was applied to study their effectiveness with selected analytes.

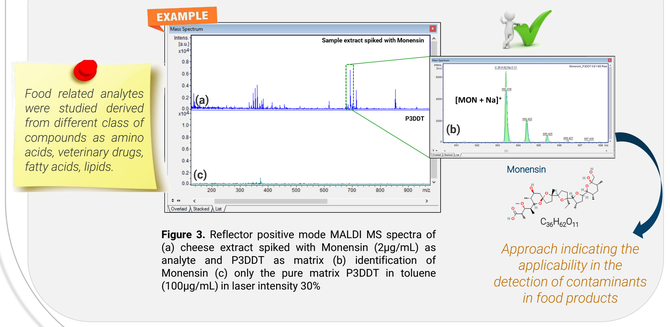

Figure 3. Reflector positive mode MALDI MS spectra of (a) cheese extract spiked with Monensin (2μg/mL) as analyte and P3DDT as matrix (b) identification of Monensin (c) only the pure matrix P3DDT in toluene (100μg/mL) in laser intensity 30%

Application to dairy product authenticity study

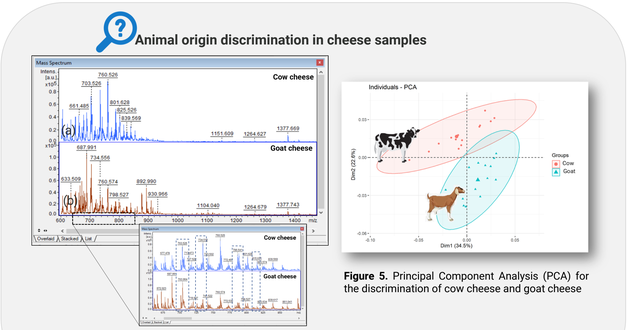

Figure 4. Reflector positive mode MALDI MS spectra of (a) goat cheese extract using P3DDT as matrix (b) cow cheese extract using P3DDT as matrix indicating characteristic detected lipids

Figure 5. Principal Component Analysis (PCA) for the discrimination of cow cheese and goat cheese

Summary

Tracing the occurrence and composition of LMWCs (including metabolites, lipids, as well as xenobiotics/contaminants) is crucial in the research of the formation and progression of the detection of LMW authenticity markers, detection of migration, and other contaminations in food authenticity matrices. Exploiting the potential of polymer-based MALDI matrices, existing MALDI-HRMS screening approaches were expanded, allowing a more general overview of food-relevant LMWCs.

References

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Conclusion

- Polymer- based matrices presented to be efficient in the detection of LMWCs
- P3DDT showed sufficient performance with a range of laser intensities, while P9OFI can be efficiently used at lower laser energies
- P3DDT was further studied for a wide range of food relevant compounds and successfully applied as a matrix for the majority of the analytes
- For the applicability study, P3DDT was used as matrix and adequate discrimination was accomplished in the cheese authenticity challenge.
- Universal analytical strategies can be developed that will provide high-throughput detection of a wide range of LMWCs, investigating crucial authenticity challenges as cheese discrimination.

MALDI-HRMS