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High-speed characterization of candle waxes using SALDI-MS with etched silver foil as substrates

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Overview

- Etched silver foil was used as substrate for surface-assisted laser desorption/ionization mass spectrometry (SALDI-MS).
- High-speed method to analyze complex lipid mixtures.
- Large range of lipid classes can be detected: Free fatty acid (stearin), wax ester (beeswax), and actually alkanes without any functional group (paraffin).
- With eMSTAT unknown samples can be matched to lipid profiles of reference samples.

Introduction

The content of beeswax in candles is an important quality criterium often used in marketing. Due to the high price of beeswax, it is often replaced by cheaper alternatives like paraffin wax. Stearin is seen as renewable and therefore green alternative to paraffin, as it is made of plant material and not of petroleum. To check marketing slogans, these main components can be detected due to the characteristic profile of wax compounds produced by bees or plants. Here we present a fast method for the analysis: Wax can be stuck directly from the candle on the silver substrate and analyzed using SALDI-MS. No time-consuming dissolving step or chromatographic separation is necessary. Discriminant software like eMSTAT can determine main components, no deeper analytical knowledge is needed.

Compact – benchtop design
Affordable (low cost)
Robust
- Fewer components
- Solid-state laser

Fast
- 200 Hz laser
- Fast sample stage
- Rapid sample introduction

Low maintenance
- Wide bore optics
- UV laser-based source cleaning
- Quiet operation

Figure 1 MALDI-8020 benchtop mass spectrometer

Methods

For etched silver substrates, silver foil was cut, washed with pentane, acetone, methanol and water, flattened and etched in nitric acid (23 %) at 50 °C, until the surface appearance changes to grey. Finally, substrates were washed with water and stuck with conductive tape on a MALDI target.[1,2]

Wax was directly stuck from the candle on the silver substrate and analyzed with a benchtop linear MALDI-TOF mass spectrometer (MALDI-8020, Shimadzu, figure 1). To characterize the method, standards and dissolved candle samples were analyzed, too.

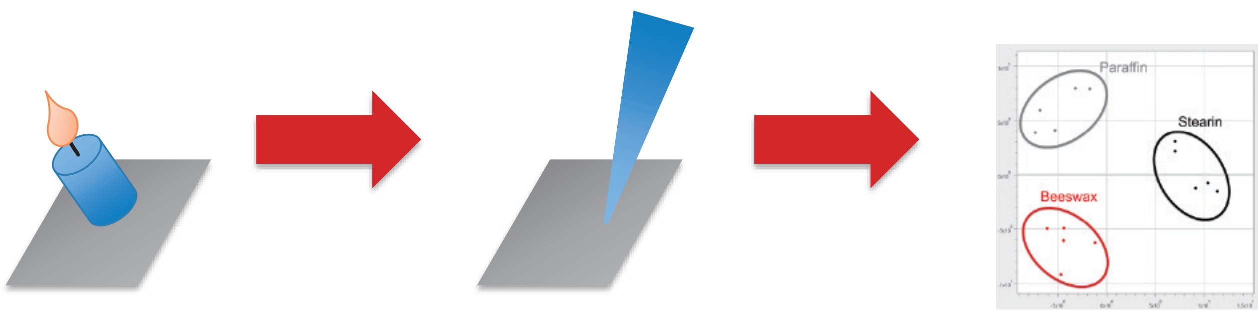

Figure 2 Workflow: Stuck wax directly from candle → Analyze in MALDI mass spectrometer → Match in statistical software

Results

Mass spectra of different lipid classes

The compounds of candles are detected as Ag+-adducts. The range of lipid classes that can be observed by this method cover even alkanes although these fully saturated hydrocarbons do not possess any functional group. Their detection is only limited by the vapor pressure of these volatile compounds that alkanes with 23 or more carbon atoms can be analyzed. Even shorter chain-lengths can be seen in some spectra, if the sample is analyzed directly after introduction into the mass spectrometer (figure 3).

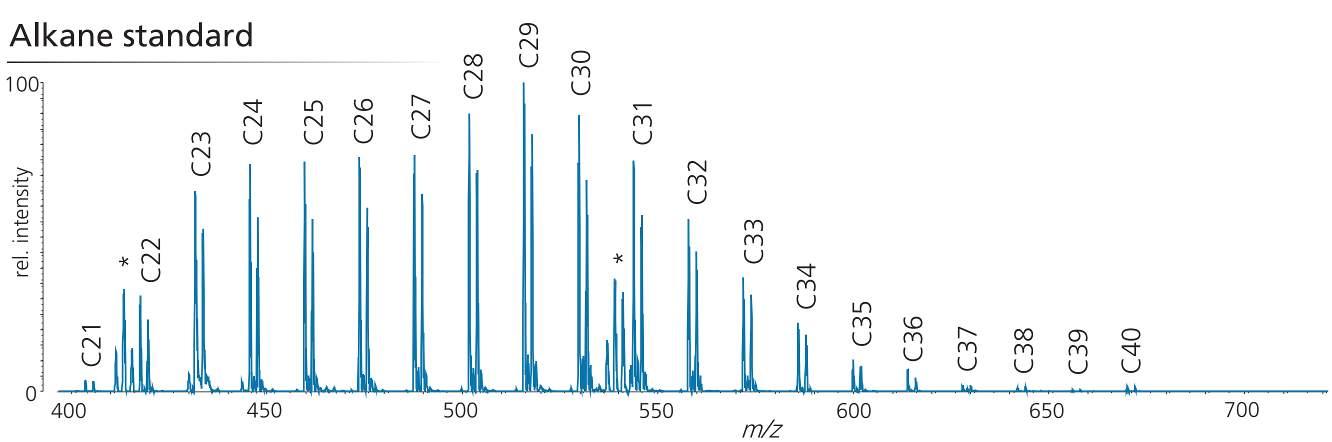

Figure 3 Alkane mixture (GC-standard, same mass of each component).

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The natural origin of beeswax can be verified by the characteristic profile that are exclusively produced by these insects (figure 4). It consists essentially of wax esters with an overall even amount of carbon[1,3] and of saturated or monounsaturated hydrocarbons with odd amount of carbon.[1,4]

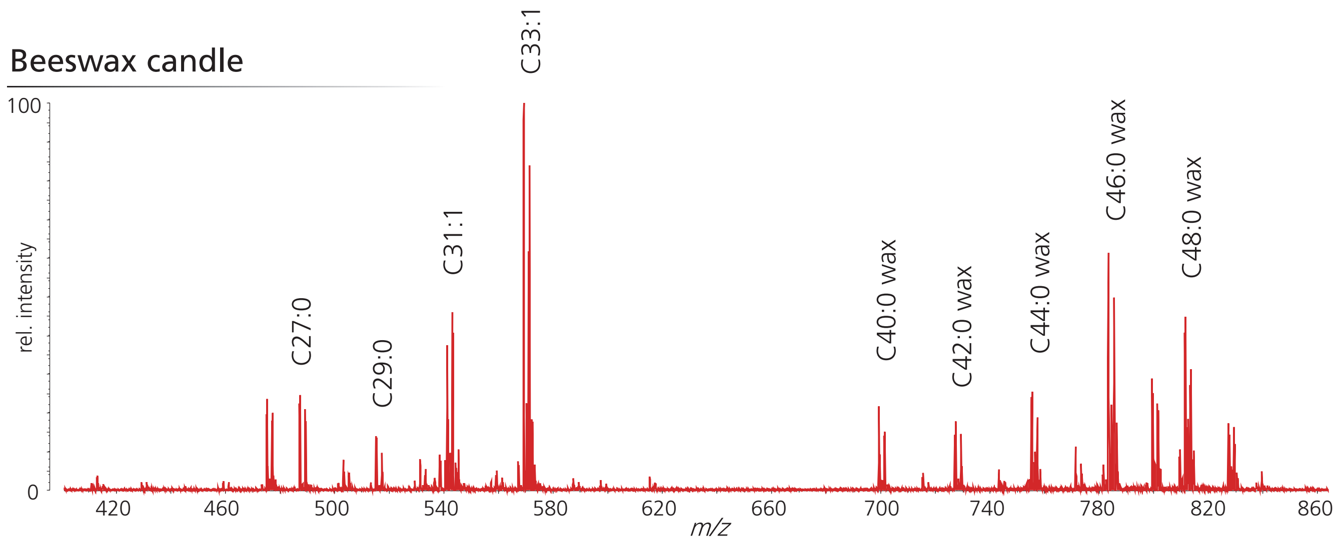

Figure 4 Beeswax candle (already described[1,3,4] components annotated).

Stearin candles are made from vegetable or animal fat after saponification. Therefore they are seen as renewable – green alternative to petroleum. Stearin candles show a characteristic profile dominated by two free fatty acids (FFA): Palmitic and Stearic acid.

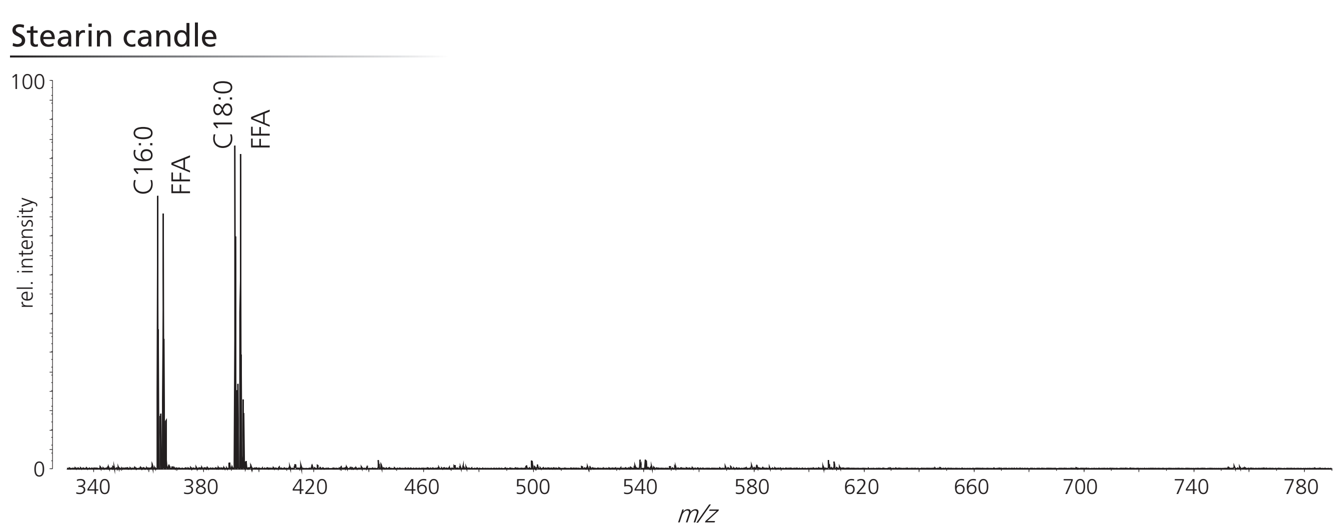

Figure 5 Stearin candle (Palmitic acid (C16) and Stearic acid (C18)).

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Paraffin is the cheapest and therefore most common resource to produce candles. Due to their origin in petroleum, alkanes with all different chain lengths of the used fraction are present in the mass spectrum.

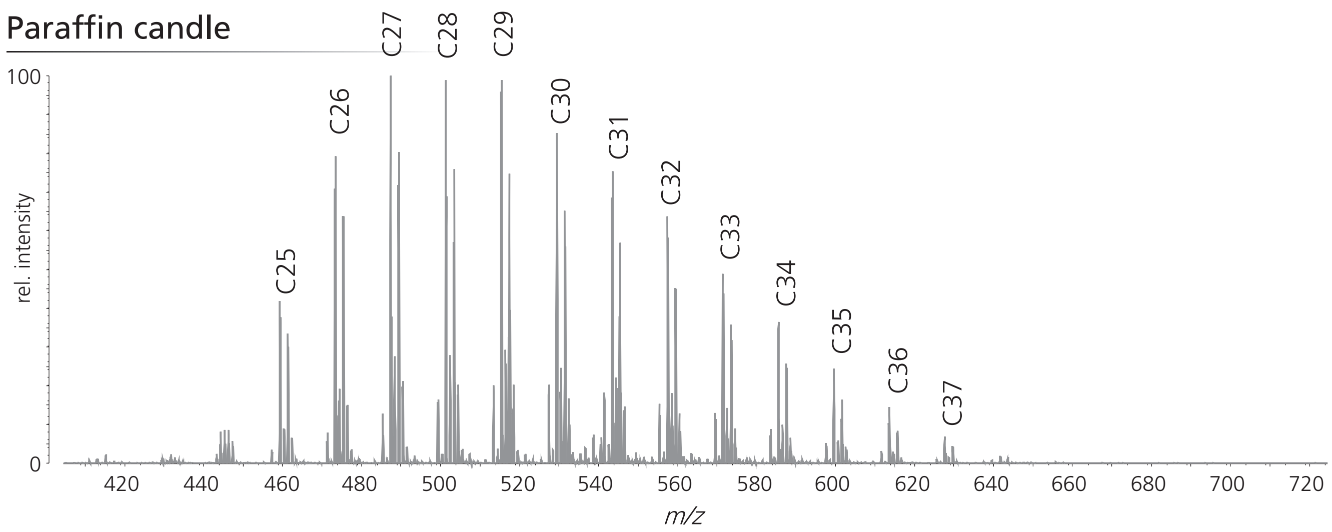

Figure 6 Paraffin candle (alkanes from C25-C37).

These three examples show the large range of different lipid classes that can be analyzed with SALDI-MS using etched silver foil as substrates: Alkanes without any functional group which are classically analyzed via GC and more polar and less volatile lipids like FFA and wax esters that therefore are commonly not suggested to be analyzed via GC without derivatization. As no chromatographic separation is necessary, this method is much faster.

Main component determination with statistical software

With a statistical software like eMSTAT, the main components can be determined. With multivariate analysis, the different raw materials in the candles can be separated (figure 7). Discriminate analysis give the main component and rate the similarity with a score.

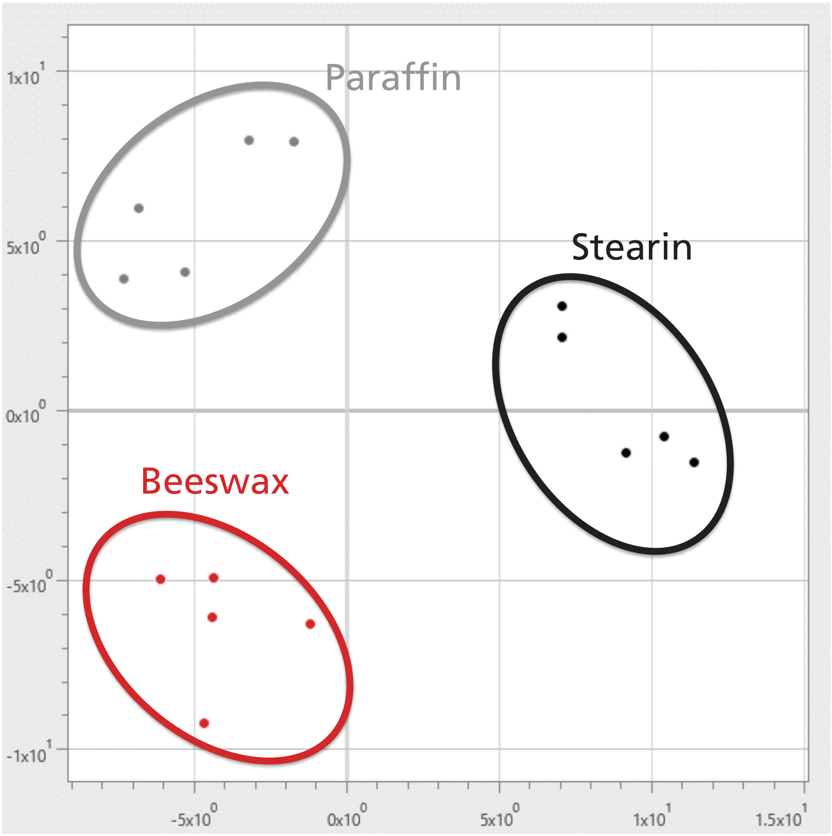

Figure 7 Score plot in statistical software eMSTAT.

Conclusions

- This application shows the potential of the method to analyze complex lipid mixtures that contain both: hydrocarbons and less volatile compounds that are challenging to be detected with GC-MS.
- Fast method: No chromatographic separation, sample preparation or derivatization is needed.
- Easy to use method: Statistical software can help to correlate sample spectra to reference spectra.

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References

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