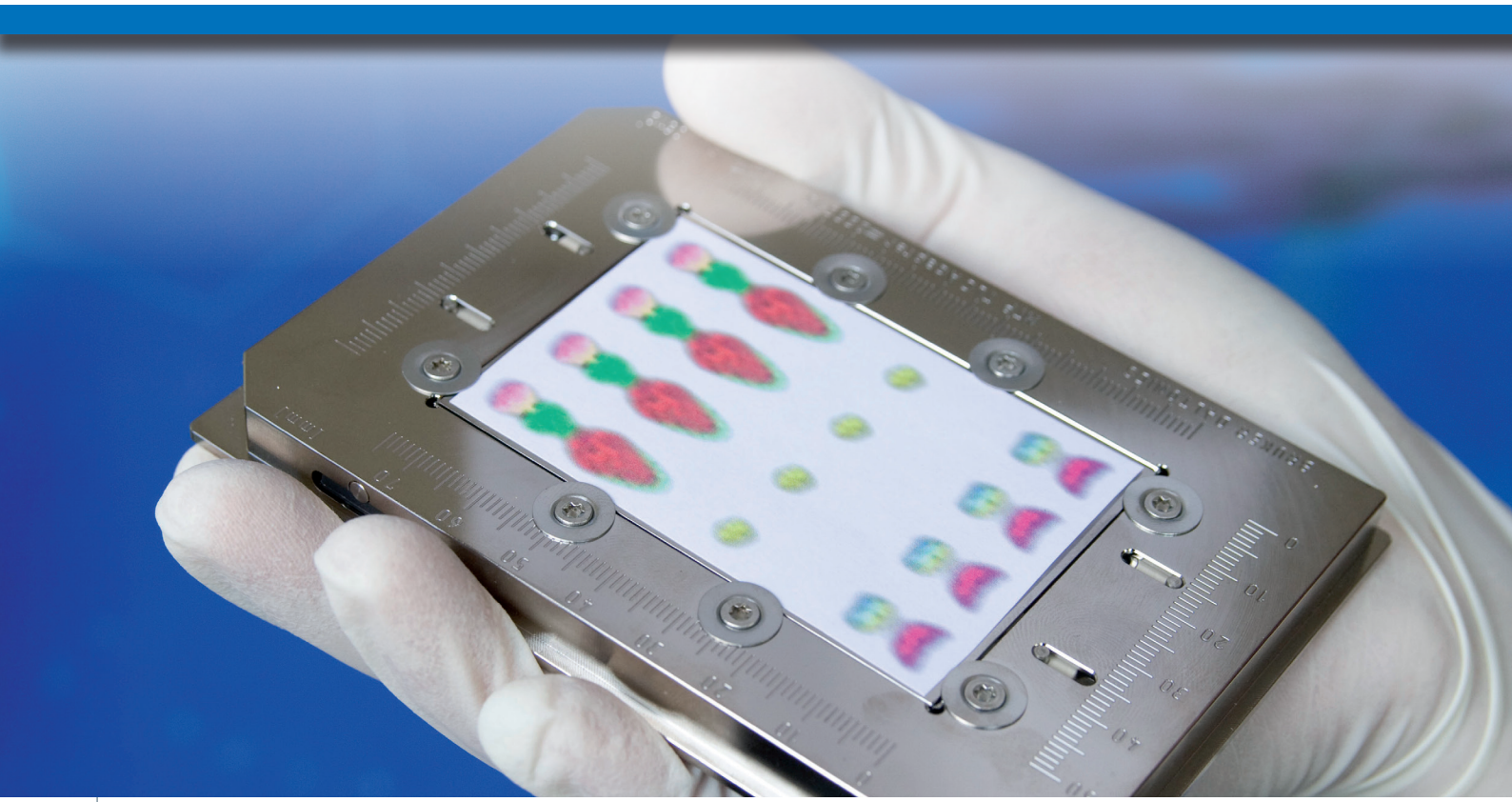

TLC-MALDI for analysis of industrial materials

Thin layer chromatography (TLC) is a widely used method for separation of mixture samples.

Introduction

In many cases, sample spots separated on TLC plates must be scraped, extracted, and then analyzed using a variety of techniques. Lately, TLC-MALDI has been already developed to enable direct MS measurement from TLC plates.

To date, most of the samples analyzed using TLC-MALDI are bio-related materials like lipids. Therefore, we explored the use of TLC-MALDI for analysis of industrial materials.

Methods

Charge Transport Materials (CTM) used in organic photo conductor (OPC) drums inside laser printers was employed as a model sample. A mixture consists of six CTMs (structures are shown in Figure 1) and titanyl phthalocyanine (TiOPC) also used

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in OPC, was diluted with THF. The diluted sample was applied on to a TLC plate and developed via one and two dimensional thin layer chromatography. MS measurements were performed on a MALDI-TOF MS (ultrafleXtreme, Bruker). For automated acquisition, dedicated TLC-MALDI software was used for 1D developed TLC plates and imaging MS software (flexImaging) was used for 2D TLC plates.

Further, engine oils before and after three months use were compared after analysis by 1D-TLC-MALDI. Afterwards, MALDI-MRMS (solariX, Bruker) was used for detailed analysis.

Results

Figure 2 is a MS image of the CTM-mix after 2D TLC, showing the separated CTMs. Figure 3A shows a mass spectrum of the CTM mixture before TLC separation. The signal of CTM-6 is interfering with the other components (broad signal at m/z 408, which is supposed to be a meta-stable fragment) in this spectrum. But with TLC separation, CTM-6 can be clearly detected (Figure 3B). Figure 4 shows the result from one dimensional MS measurement of CTM-mix after 1D TLC, displayed using the TLC-MALDI viewer. The X-axis represents m/z scale and Y-axis represents the number of spectra, which corresponds to the position or Rf value on TLC plate. MS intensity is expressed by color density.

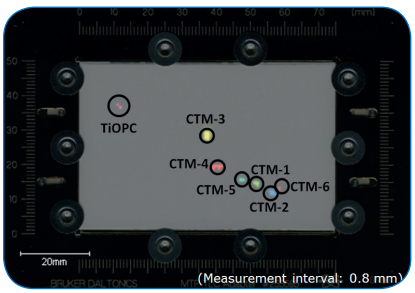

Figure 2: MS image of CTM-mix developed two dimensionally on TLC plate

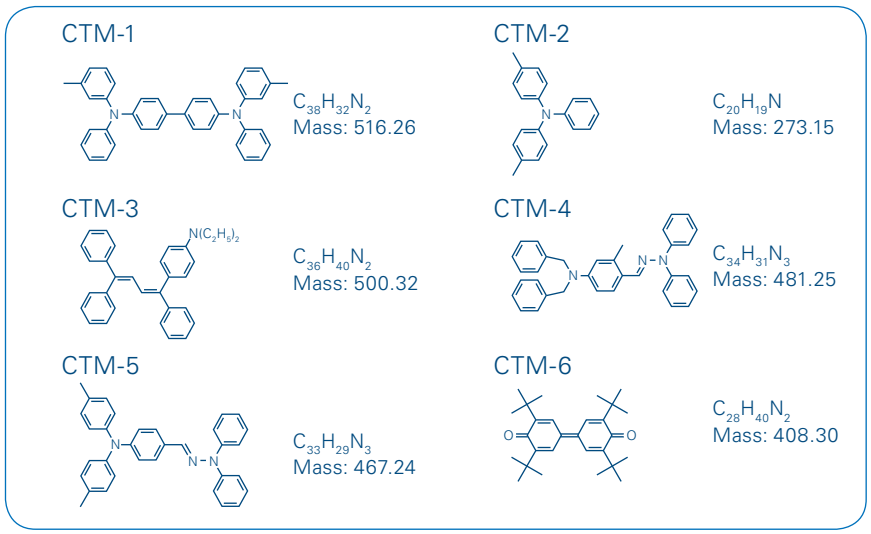

Figure 1: Molecular structures of components in CTM-mix

Every component including CTM-6 is clearly visible.

Generally, MS image is easy to understand but its acquisition takes time to cover the whole area of a TLC plate, e.g. a few hours depending on the conditions. On the other hand, a 1D experiment requires much shorter time and its unique data viewer simplifies data interpretation e.g. to find impurities or by-products.

Figure 5 shows a comparison between automotive engine oils using TLC-MALDI via 1D development

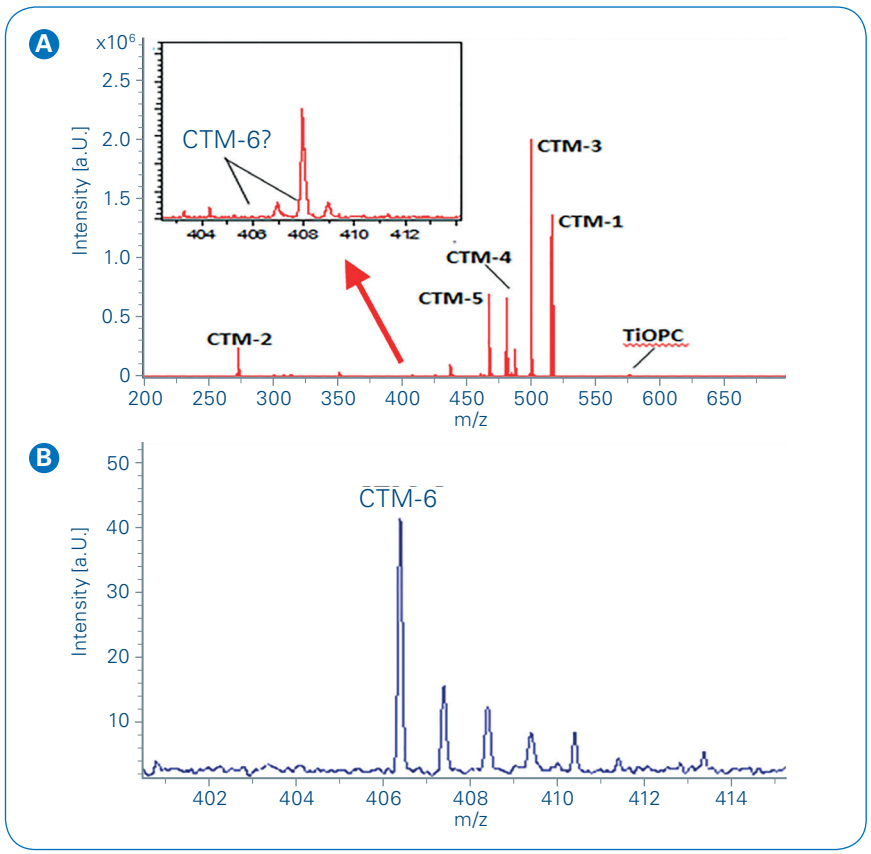

Figure 3: CTM-mix before separation (A) and CTM-6 spot on TLC plate (B)

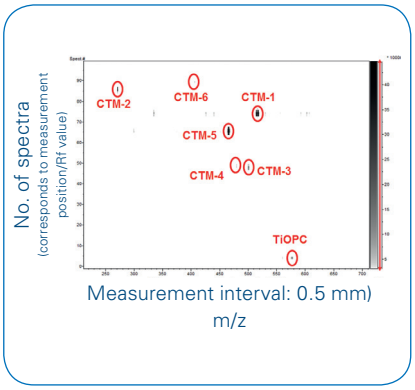

Figure 4: Result from one dimensional MS measurement of CTM-mix developed one dimensionally on TLC plate

and subsequent MS measurement. In this case 2,5-dihydroxy benzoic acid (DHB) was used as a matrix, unlike with CTM samples which could be ionized without the addition of a matrix. TLC plates were dipped into DHB solution and dried with hair dryer (Dip Coating Protocol) [1]. After TLC separation, differences between the two samples could be observed indicating many of the compounds are absent in the 'used' engine oil. Typically, engine oil consists of base oil and additives. Since the base oil is a non polar hydrocarbon and is considered to be difficult to ionize with MALDI, the components detected here should be considered additives. Various spots showing differences between used and non-used engine oil were subjected to MALDI-MRMS to elucidate their elemental composition or molecular structure using the extremely high mass resolution and accuracy the techniques provides. Among them, for example, Figure 6 shows a MS/ MS spectrum from a TLC spot shown in Figure 5 indicated by the yellow circle. Its elemental composition was determined using mass difference between precursor and fragment ion to be C13H26. This supports the structure as tritridecylamine.

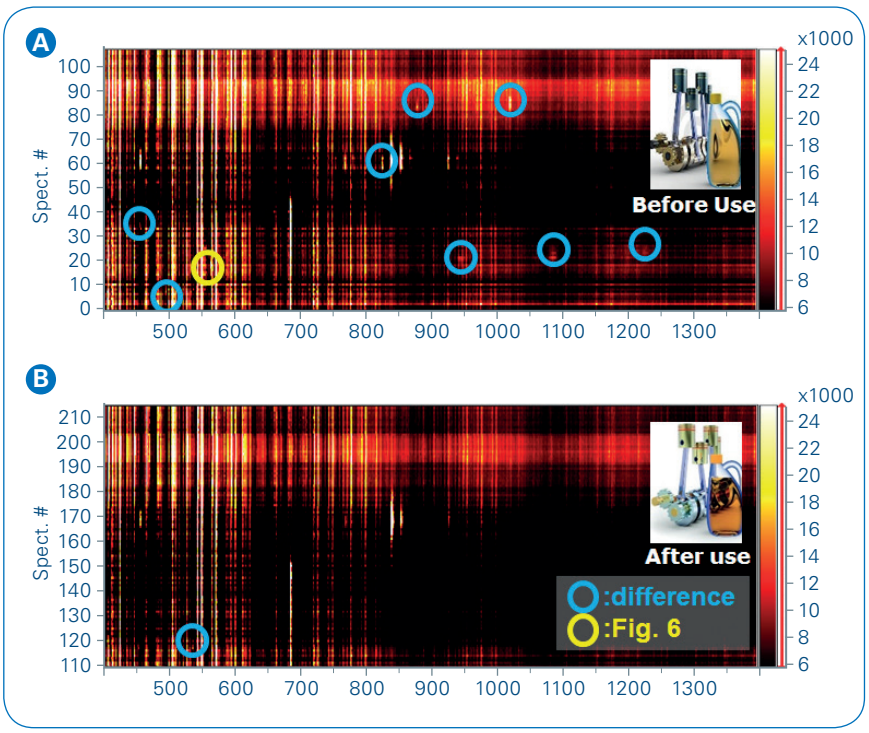

Figure 5: TLC-MALDI of engine oil before A and after B 3 months use

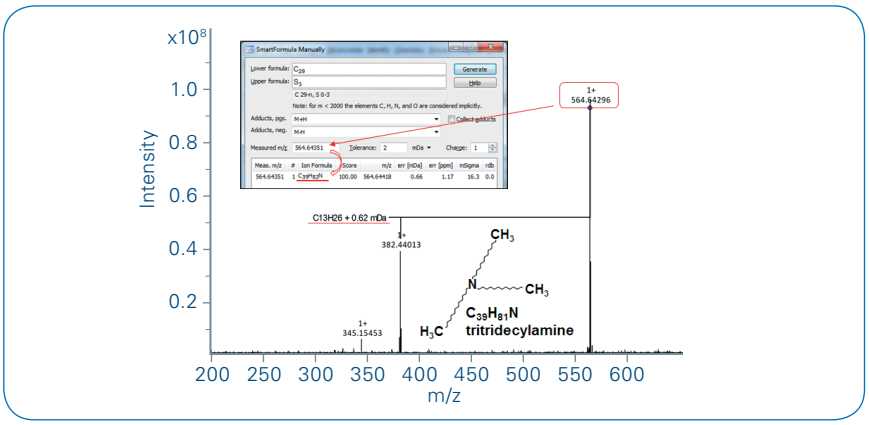

Figure 6: FT-ICR MS/MS from a TLC spot shown with yellow circle in Figure 5

Summary

1D and 2D TLC MALDI are valuable methods to get a fast inside into complexer samples. Applying TLC MALDI to industrial materials expands the range of samples which can be analysed. TLC MALDI can be used efficiently to monitor products or incoming goods.

MRMS is a powerful technique due to its inherent mass accuracy and mass resolving power. Here its use in context of TLC MALDI allows for the direct elucidation of compound structures.

Conclusions

- TLC-MALDI is effective also for the analysis of industrial materials
- Simple and easy; scraping and extraction of spot is not necessary
- MALDI-TOF MS is preferable for screening and MALDI-FT-ICR MS is preferable for detailed analysis

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Reference

[1] Please contact MALDI Application support at: Maldi.Appl.Support@Bruker.com

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