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Profiling of epoxidized soybean oil in PVC using a linear benchtop MALDI-TOF MS.

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AMS2021
FP-623

Overview

- ESBO is a complicated mixture of epoxidized triacylglycerols (TAGs) consisted of various fatty acids.
- Profiling of ESBO in medical PVC tubes using a benchtop linear MALDI-TOFMS is conducted successfully with minimum preparation.
- MALDI-TOFMS can distinguish three ESBOs by detecting the molecular weight distribution of epoxidized TAG.

1: Introduction

Techniques for the analysis of polymer additives have been quite significant not only to develop chemical/physical properties of polymer materials but also to examine whether hazardous chemicals exist in the polymers. Recently, as high functionality of polymer materials have been required, various additives have been applied to develop the polymers. These additives often have higher molecular weights than previously developed additives and are sometime difficult to analyze with GC/GCMS due to their non-volatile property. Epoxidized soybean oil (ESBO), which is a plasticizer and a stabilizer for PVC, is regarded as a typical non-volatile compound. Moreover, analysis of the ESBO is challenging due to a wide molecular weight distribution derived from a variety of epoxidized triacylglycerols (TAGs). We will report results obtained by profiling of the ESBO in PVC tubes using a linear benchtop MALDI-TOF MS.

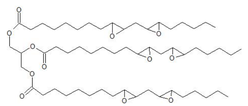
2: Methods

- PVC tubes and preparation

A DEHP-free PVC tube for a drip infusion and a PVC tube for suctioning sputum were purchased from online web-shop. Extraction of additives in PVC was performed with the following procedures. The tubes were shredded and dissolved in THF, which is a good solvent for PVC, then a certain volume of the polymer solution was mixed with 10-fold methanol, which is a poor solvent for the polymer. After removal of precipitated PVC by a syringe filter, the filtered solutions were subjected to MS analysis.

- Standard Epoxidized Soybean oil (ESBO)

A standard ESBO (European Pharmacopoeia Reference Standard) was purchased from Sigma-Aldrich. 10mg/mL of ESBO in THF was prepared and subjected to MS analysis.
Chemical structure of epoxidized-Linolein is shown in a right figure as one of the major component of ESBO.



Epoxidized-Linolein
C57H98O12; Exact mass: 974.71

- MALDI-TOFMS

Analysis of additives by MALDI-TOF MS was performed with a benchtop linear mode MALDI-TOF MS (MALDI-8020, Shimadzu Corp., Japan) in positive mode. 20 mg/mL of dithranol and 10 mg/mL of NaI in THF were applied to all experiments as MALDI matrix. Four wells of each samples were prepared on MALDI plate and analyzed to perform a statistical analysis.

MALDI-8020

- GC-MS

The extracted additives were also analyzed with GCMS (GCMS-QP2020 NX, Shimadzu Corp., Japan) to identify diethylhexyl phthalate (DEHP) and tris 2-ethylhexyl trimellitate (TOTM).

- Calculation of theoretical mass and Statistical data analysis

"Polymer software" (Shimadzu/Kratos) was applied to calculate molecular weight of epoxidized TAGs ([M+Na]$^+$), assuming epoxidized-palmitic, -stearic, -oleic, -linoleic and -linolenic acid as constituents. eMSTAT Solution™ (Shimadzu Corp., Japan) was applied to perform classification/differentiation of the extracted ESBO and the standard one.

3: Results

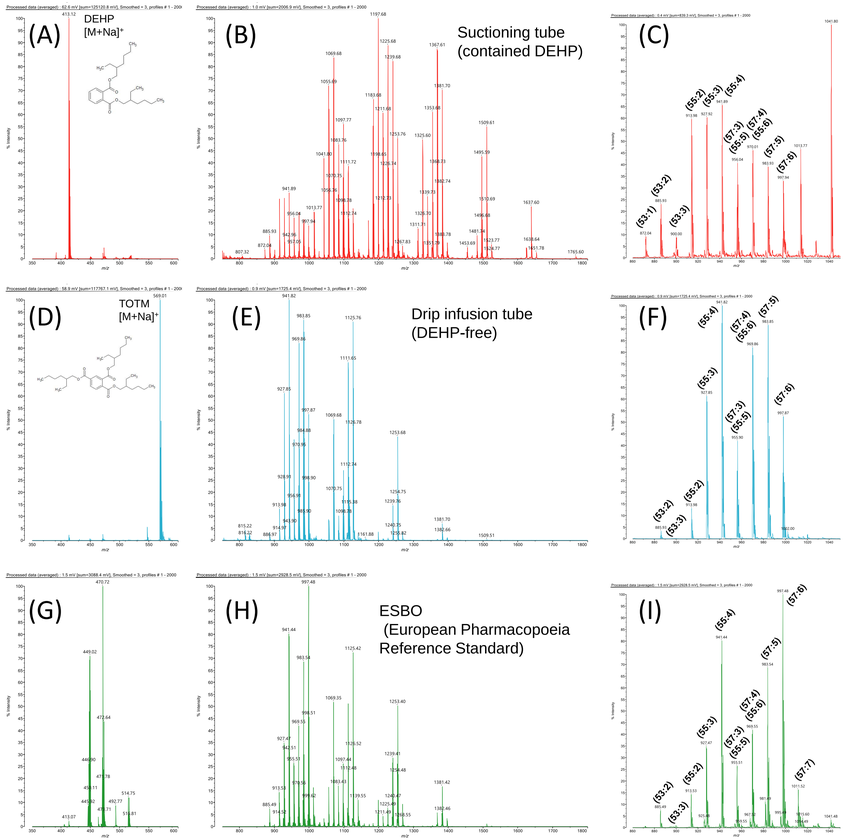


Fig.1 MALDI TOF-MS of the extracted solution and the standard ESBO
(A), (D), (G): low mass region, (B), (E), (H): (extracted) ESBO, (C), (F), (I): m/z 860-1050 with a conceivable assignment. (m:n) indicates number of the carbon atoms and epoxide groups.

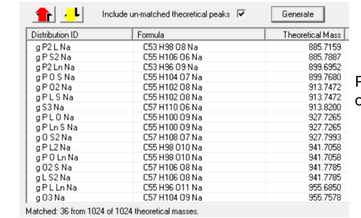


Fig.2 Theoretical mass of epoxidized TAGs obtained with "Polymer software".

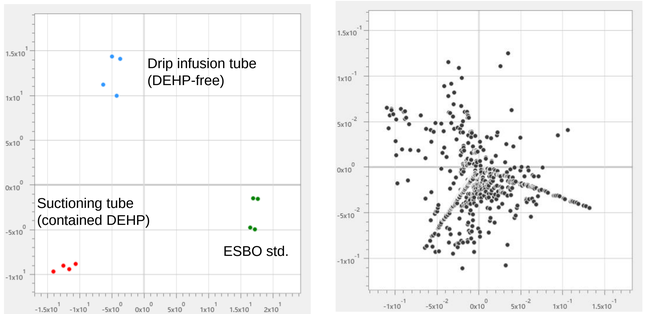


Fig.3 Score plot in PCA analysis of the two extracted solution and the standard ESBO. Signals at *m/z* 750-1800 were subjected to the analysis.

4: Conclusions

- ✓ Non-volatile additives in medical PVC tubes were profiled successfully using a benchtop linear MALDI-TOFMS with minimum preparation.
- ✓ In the *m/z* range of ESBO-related signals, MS of the infusion tube was similar with the standard ESBO, whereas MS of the suctioning tube had a wider distribution than them.
- ✓ A statistical analysis with eMSTAT Solution enabled a differentiation of three ESBOs, which could be applicable to QA/QC.

Reference:

1. Supporting information of "Synthesis of High-Molecular Weight Biobased Epoxy Resins: Determination of the Course of the Process by MALDI-TOF Mass Spectrometry; ACS Sustainable Chem. Eng. 2018, 6, 5, 6084–6093".
2. "Mass Spectrometric Characterization of Epoxidized Vegetable Oils"
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