COMPARISON OF DERIVATIZATION METHODS FOR THE QUANTITATIVE GAS CHROMATOGRAPHIC ANALYSIS OF OILS

Eliise Tammekivi[(1)], Signe Vahur[(1)], Ott Kekišev[(1)], Inez D. Van der Werf[(2)], Lauri Toom[(1)], Koit Herodes[(1)] and Ivo Leito[(1)]

[1]Institute of Chemistry, University of Tartu, Ravila 14a, 50411 Tartu, Estonia

[2]Ministry of Education, Culture and Science, Cultural Heritage Agency, Amsterdam, The Netherlands

E-mail of presenting author: eliise.tammekivi@ut.ee

Introduction

A wide variety of derivatization methods have been developed to enable the GC analysis of non-volatile oil components in cultural heritage samples.

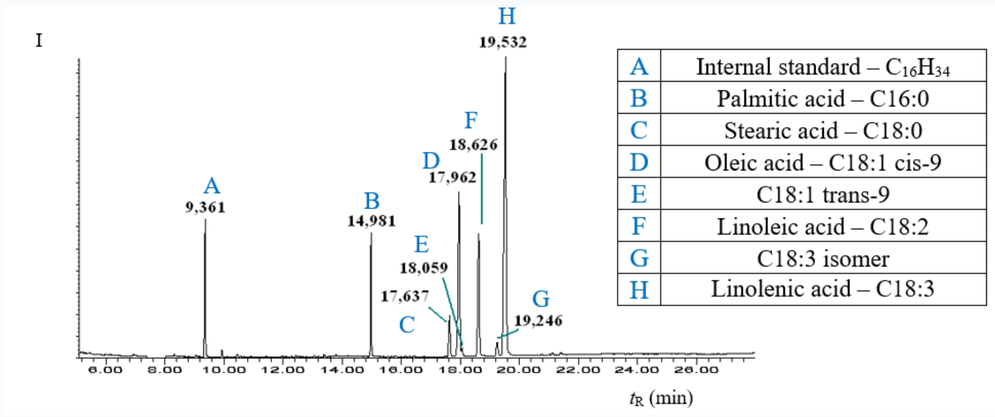
However, there has been no wide-scale and systematic comparison of these derivatization procedures in truly quantitative terms, i. e. with absolute amounts of the fatty acids, not just ratios.

Experimental

- A comprehensive **quantitative comparison** of four derivatization methods: 1) TMTFTH, 2) acid-catalyzed methylation, 3) NaOEt with BSTFA ethylation and 4) KOH with BSTFA trimethylsilylation.
- GC-MS/FID analysis combined with internal standard method for the determination of **absolute quantities of fatty acids**.
- Synthesis of trimethylsilylester standards for KOH-BSTFA method.
- Study of **derivatization efficiency** and **within-lab reproducibility** of the procedures.

Principle of analysis

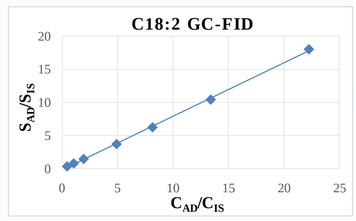
Derivatization and GC analysis



A	Internal standard – $C_{16}H_{34}$
B	Palmitic acid – C16:0
C	Stearic acid – C18:0
D	Oleic acid – C18:1 cis-9
E	C18:1 trans-9
F	Linoleic acid – C18:2
G	C18:3 isomer
H	Linolenic acid – C18:3

Mass chromatogram of clarified linseed oil (Lefranc & Bourgeois) derivatized with TMTFTH. Peaks correspond to methylated fatty acids.

Quantitative analysis

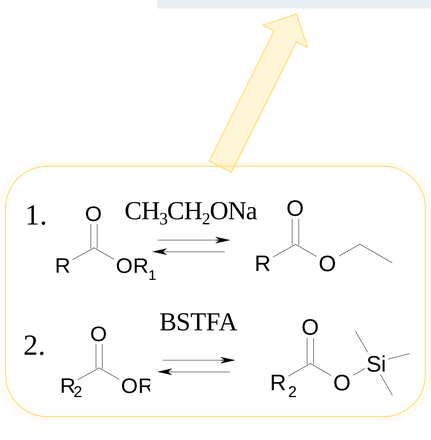


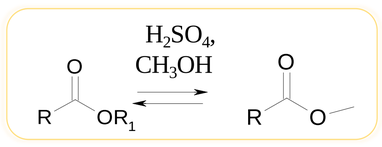
C18:2 – methylated linoleic acid, S – signal, C – concentration, AD – derivatized analyte, IS – internal standard

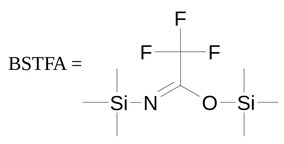
Absolute quantities of fatty acids

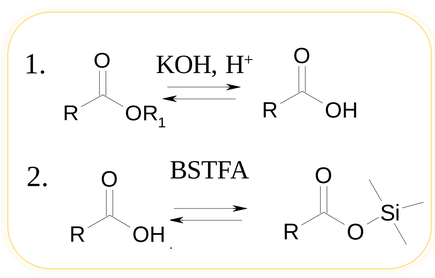
Comparison of derivatization procedures

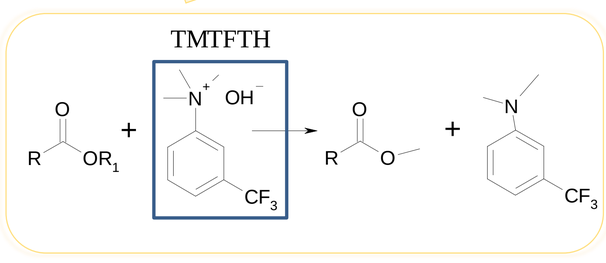
Sodium ethoxide + BSTFA	Acid-catalyzed methylation	KOH + BSTFA	TMTFTH
✓ Operator time: 4h ✓ Differentiating between free and bound fatty acids ✓ Stable results	✓ One-step derivatization ✓ Determination of degradation products ✓ Stable results	✓ Operator time: 4h ✓ Quantitative analysis ✓ Determination of degradation products	✓ Operator time: 1h ✓ One-step derivatization ✓ No sample transfer ✓ Easy procedure ✓ Quantitative analysis ✓ Determination of degradation products ✓ Stable results
○ Two-step derivatization ○ Multiple derivates complicate the interpretation	○ Operator time: 7h ○ Labor-intensive	○ Two-step derivatization ○ Unstable results ○ Labor-intesive ○ No commercial standards	○ The most expensive chemicals
Efficiency: **64 ± 2 %**	Efficiency: **83 ± 3 %**	Efficiency: **95 ± 7 %**	Efficiency: **96 ± 2 %**











Conclusions

- **TMTFTH** derivatization exhibited **the highest reproducibility and derivatization efficiency**.
- **KOH+BSTFA** derivatization exhibited also **high derivatization efficiency**, however, with unstable results.
- TMTFTH, KOH+BSTFA and acid-catalyzed methylation enabled the determination of degradation products.
- GC-MS and GC-FID methods are **equivalent** in the analysis of absolute quantities of fatty acids.
- **Overall, TMTFTH derivatization is the preferred procedure.**

ACKNOWLEDGEMENTS

This work was supported by the Personal Research Funding PUT1521 and the Institutional Fundings IUT20-14 and IUT20-15 from the Estonian Research council and by Graduate School of Functional Materials and Technologies receiving funding from the European Regional Development Fund in University of Tartu, Estonia. This work was carried out using the instrumentation at the Estonian Center of Analytical Chemistry (AKKI, www.akki.ee).

UNIVERSITY OF TARTU 1632

European Union
European Regional Development Fund
Investing in your future